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New Pressure Swing Adsorption Cycles for Carbon Dioxide Sequestration

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Abstract. A rigorous pressure swing adsorption (PSA) process simulator was used to study a new, high temperature PSA cycle, based on the use of a K-promoted HTlc adsorbent and a simple, 4-step, Skarstrom-type, vacuum swing cycle designed to process a typical stack gas effluent at 575 K containing (in vol%) 15% CO_2, 75% N_2 and 10% H_2O. The effects of the purge-to-feed ratio (γ), cycle step time (t_s) (with all four steps of equal time), and pressure ratio (π_T) on the process performance was studied in terms of the CO_2 recovery (R) and enrichment (E) at a constant throughput θ of 14.4 L STP/hr/ kg. R increased with increasing γ and π_T and decreasing t_s, while E increased with increasing t_s and π_T and decreasing γ. The highest E of 3.9 was obtained at $R = 87\%$ and $\pi_T = 12$, whereas at $R = 100\%$ the highest E of 2.6 was obtained at $\pi_T = 12$. These results are very encouraging and show the potential of a high temperature PSA cycle for CO_2 capture.

Keywords: pressure swing adsorption, hydrotalcite, carbon dioxide, sequestration, mathematical modeling

Introduction

It is now generally accepted by most climate scientists that increasing global temperatures over the last 50 years are the result of increased atmospheric concentrations of greenhouse gases such as methane (CH_4), nitrous oxide (N_2O) and, most especially, carbon dioxide (CO_2). Since the beginning of the industrial revolution, atmospheric concentrations of CO_2 have increased nearly 30%, CH_4 concentrations have more than doubled, and N_2O concentrations have risen by about 15%. These increases have enhanced the heat-trapping capability of the earth's atmosphere via the greenhouse effect. Predictions of global energy use in the next century suggest a continued increase in carbon emissions and rising concentrations of CO_2 in the atmosphere unless major changes are made in the way humans produce and use energy, in particular how humans manage carbon (Reichle et al., 1999).

There are three courses of action that can be taken to stabilize the CO_2 concentration in the atmosphere. The first approach is increased efficiency of primary energy conversion. This will decrease the amount of fossil fuels needed to provide the same energy service. The second approach is to use lower-carbon or carbon-free energy sources, with the obvious outcomes of less or no CO_2 production. The final approach is carbon sequestration, which involves the capture and storage of carbon. This last approach is probably the newest means being studied to manage CO_2 in the environment (White et al., 2003).

The most likely options for CO_2 separation and capture include (1) chemical and physical absorption, (2) physical and chemical adsorption, (3) low-temperature distillation, and (4) gas separation membranes. Among these, physical absorption using amines is currently the most widely deployed commercial technology; however, there is a significant energy penalty associated with this technology from the heat required to regenerate the solvent. Cryogenic distillation is certainly feasible and widely practiced for CO_2 recovery; but, it is only viable for CO_2 concentrations higher that 90 vol%, which is outside the range for flue gas streams. Polymeric, ceramic and metallic membranes are all viable for CO_2 recovery from flue gas streams; however, they each have their own issues involving low fluxes,

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degradation, fouling, cost, etc. Various adsorption processes for concentrating CO_2 from flue gas streams have also been proposed and explored, with many of the results being controversial (IEA, 1994; White et al., 2003).

An International Energy Agency (IEA, 1994) study evaluated CO_2 separation and capture using 13X zeolite in both pressure swing adsorption (PSA) and temperature swing adsorption (TSA) processes. They concluded that PSA and TSA are too energy intensive for use with gas- and coal-fired power systems. But little information was offered in the IEA study on the type of cycle employed. Nevertheless, this conclusion has led others to extrapolate these findings and further conclude that adsorption systems, in general, are not applicable for CO_2 separation and capture. It is strongly suggested that this may not be the case. It is true that the commonly studied adsorbents (e.g., zeolites and activated carbons), which have a very high capacity for CO_2 at ambient temperatures, suffer from low CO_2 capacity at elevated temperatures (Yong et al., 2002). It is also true that it may be too costly to pre-dry, cool and/or pressurize the feed and/or purge streams, which appears to be the basis for the pessimistic conclusions made in the IEA study about adsorption technology. This has not stopped research on ambient temperature CO_2 capture by PSA, however, as evidenced by some recent studies (Gomes and Yee, 2002; Ko et al., 2003). Moreover, there are some new adsorbents, generally referred to as hydrotalcite-like compounds (HTlcs), that are selective to CO_2 at elevated temperatures, even in the presence of H_2O; and they release CO_2 simply by decreasing the pressure (Yong et al., 2002). Hence, an HTlc may be a viable adsorbent for use in a high temperature PSA process for CO_2 capture.

HTlcs are anionic clays consisting of positively charged layers of metal oxides (or metal hydroxides) with inter-layers of anions, such as carbonate (Yong et al., 2002). Exchange of the metal cations, as well as intercalation of the anionic layer, allow the hydrotalcites to have stability under wet conditions and high temperatures (Ding and Alpay, 2000). Experimental results show that hydrotalcites have a reversible capacity of about 0.83 mol/kg at 575 K and 1 atm under dry or wet conditions (Yong et al., 2002). In comparison, zeolites and activated carbons have a relatively high adsorption capacity for CO_2 of 4 mol/kg and 1.5–2.5 mol/kg, respectively, at 300 K and 1 atm; however, at 575 K and 1 atm their capacities decrease substantially to about 0.10–0.25 mol/kg (Yong et al., 2002). Although, basic alumina has a CO_2 capacity ranging from 0.39 to 0.62 mol/kg under the same conditions (Yong et al., 2000), HTlcs not only exhibit a higher CO_2 capacity at elevated temperatures, but they also tend to be H_2O insensitive, which is not necessarily true for zeolites, activated carbons, and basic aluminas.

As a first step in capturing CO_2 from stack gases, the objective of this study is to introduce a new high temperature PSA cycle, based on the use of a K-promoted HTlc adsorbent and a simple, 4-step, Skarstrom-type, vacuum swing adsorption (VSA) cycle. This unique cycle obviates the need to cool, dry or pressurize the feed stream and has the potential to produce a stream enriched in CO_2 at high recovery. Using a rigorous PSA process simulator, a parametric study is performed to examine the effects of the purge-to-feed ratio, the cycle step time (with all four steps of equal time), and the pressure ratio on the process performance in terms of the CO_2 recovery and enrichment at constant throughput. Results are reported for 125 different PSA cycle conditions.

PSA Process Description

The PSA (or VSA) cycle consists of four interconnected beds each undergoing four cycle steps in tandem. The four steps are high-pressure (P_H) adsorption with feed gas (step II) just above atmospheric pressure, countercurrent blowdown (evacuation) from P_H to a lower (vacuum) pressure (P_L) (step III), countercurrent low-pressure desorption with light product purge under vacuum (step IV), and repressurization from P_L to P_H (step I) with light product gas. The heavy product (CO_2) is enriched and recovered in steps III and IV, whereas the inert light product (mainly N_2 and H_2O) is recovered in step II. The purge and pressurization gases used in steps IV and I come directly from the other bed as the light product of step II, retaining their time-dependent composition and temperature.

The periodic state PSA process performance is judged by the CO_2 recovery (R), CO_2 enrichment (E), and throughput (θ). R is defined as the number of moles of CO_2 leaving the bed during steps III and IV divided by the number of moles of CO_2 entering the bed in step II. E is defined as the average mole fraction of CO_2 leaving the bed during steps III and IV divided by the mole fraction of CO_2 in the feed. Since the four cycle steps are all of equal duration in the PSA cycle studied here, θ is defined as the amount of feed fed to one

column during step II divided by the cycle time and the mass of adsorbent in one column.

Mathematical Model

The rigorous PSA process simulator utilized in this study was the same as that developed by Liu et al. (1999); they provide specific details including assumptions and equations. The process parameters and conditions used in this mathematical model are shown in Table 1. The bench-scale column dimensions and corresponding heat transfer coefficient were taken from an experimental setup described by Liu et al. (1998).

The mass transfer coefficients for CO_2 in this HTlc adsorbent were estimated by Ding and Alpay (2001). Figure 1 shows the experimental adsorption isotherm data for CO_2 on a K-promoted HTlc at four different temperatures (Ding and Alpay, 2000, 2001). These data were fitted to a temperature dependent Langmuir isotherm model shown in the figure. The isosteric heat of adsorption, ΔH_i, was estimated from the temperature dependence of the isotherm parameter, b_i. N_2 and H_2O were considered to be inert for this HTlc adsorbent.

Table 1. Bed characteristics, adsorbent properties, transport properties, and operating parameters investigated.

Bed length (L)	0.2724 m
Bed radius (r_b)	0.0387 m
Bed porosity (ε)	0.48
Particle radius (r_p)	0.001375 m
Particle density (ρ_p)	1563 kg/m^3
Particle heat capacity ($C_{P,p}$)	0.850 kJ/kg/K
Isosteric heat of adsorption (ΔH_i)	2.22 kcal/mol
Heat transfer coefficient (h)	0.00067 kW/m^2/K
Mass transfer coefficient: ads (k_a), des (k_d)	0.0058 s^{-1}, 0.0006 s^{-1}
High pressure (P_H)	137.9 kPa
Pressure ratio ($\pi_T = P_H/P_L$)	4, 6, 8, 10, 12
Feed flow rate (V_f)	1.0 L STP/min
Feed mole fractions: CO_2, N_2, and H_2O	0.15, 0.75 and 0.10
Throughput (θ)	14.4 L STP/hr/kg
Feed temperature (T_f)	575 K
Wall temperature (T_o)	575 K
Purge to feed ratio (γ)	0.50, 0.75, 1.00, 1.25, 1.50
Cycle step time (t_s)	100 s, 200 s, 300 s, 400 s, 500 s
Total cycle time (t_c)	400 s, 800 s, 1200 s, 1600 s, 2000 s

Results and Discussion

A total of 125 simulations were carried out, all at constant throughput $\theta = 14.4$ L STP/hr kg. At each of five pressure ratios, five cycle step times and five purge to feed ratios were investigated. The base case conditions for the purge to feed ratio (γ), cycle step time (t_s), and pressure ratio ($\pi_T = P_H/P_L$) are underlined in Table 1. With the feed flow rate (V_f) fixed at 1.0 L STP/min, γ was changed by changing the purge flow rate; and with P_H fixed at 137.9 kPa, π_T was changed by changing P_L. All simulations were started from a clean bed containing only inert gas and carried out until the periodic state was reached. The results from 13 simulations

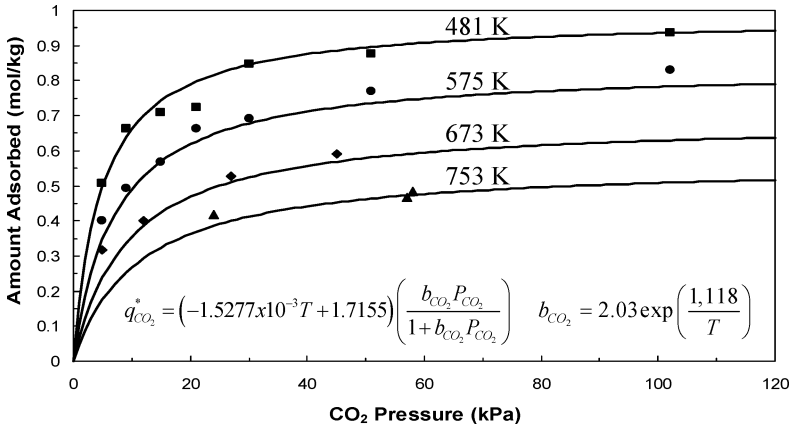

Figure 1. CO_2 adsorption isotherms for K-promoted HTlc (Ding and Alpay, 2000, 2001). Symbols: experiment; lines: model.

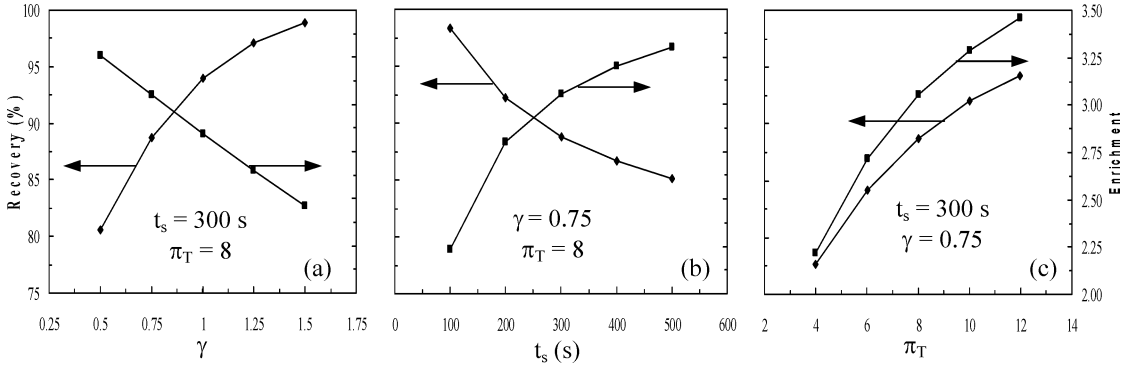

Figure 2. Effect of the (a) purge to feed ratio (γ), (b) cycle step time (t_i), and (c) pressure ratio (π_T) on the process performance in terms of the CO_2 recovery (R) and CO_2 enrichment (E). Base case conditions used for the non-varying parameters. The throughput $\theta = 14.4$ L STP/hr/kg.

carried out at the base case conditions (i.e., $\gamma = 0.75$, $t_s = 300$ s and $\pi_T = 8$ for the base case, non-varying parameters) are shown in Fig. 2. Qualitatively similar trends were observed for conditions outside of the base case conditions (not shown).

Figure 2(a) shows the effect of γ on R and E with $\pi_T = 8$ and $t_s = 300$ s. R increased, but E decreased, as γ increased. Since the purge gas was taken from the light product gas and used to sweep the low pressure column during the countercurrent purge step, more CO_2 left the column as enriched product. Also, the light product purge regenerated the adsorbent; thus, the adsorbent was able to adsorb more CO_2 in the subsequent adsorption step, thereby allowing less CO_2 to breakthrough into the light product. Both caused R to increase with increasing γ. However, since more of the light product was returned to the low pressure column as purge with increasing γ, it diluted the CO_2 in the heavy product, which caused E to decrease with increasing γ.

Figure 2(b) shows the effect of t_s on R and E with $\pi_T = 8$ and $\gamma = 0.75$. R decreased, but E increased, as t_s increased. Since CO_2 entered the column during the feed step, more CO_2 entered the system as t_s increased; thus, it was more likely for CO_2 to breakthrough into the light product, which decreased R with increasing t_s. However, as more CO_2 entered the system, more CO_2 was adsorbed by the hydrotalcite; hence, more CO_2 desorbed during the blowdown and low pressure purge steps and exited the system in the enriched product gas, which caused E to increase with increasing t_s.

Figure 2(c) shows the effect of π_T on R and E with $t_s = 300$ s and $\gamma = 0.75$. Both R and E increased with increasing π_T. Since t_s and P_H were fixed, the amount of CO_2 entering the system during the feed step was also fixed, as was the periodic state loading of CO_2 on the HTlc at the end of the feed step. Hence, the observed increases in R and E with increasing π_T were actually caused by P_L decreasing, i.e., a deeper vacuum was being applied to the system, which had two effects. For a fixed γ (i.e., the ratio of the purge gas to feed gas velocities), a lower P_L meant less purge gas was used to clean the bed, which caused R to increase. The use of less purge gas also resulted in less dilution of the heavy product, which caused E to increase. In effect, the working capacity of the adsorbent increased, because larger pressure swings allowed for a greater change in the loading, as gleaned from the large slope changes in the low pressure regions of the HTlc isotherms shown in Fig. 1.

The results in Fig. 2, not surprisingly, implied that a compromise exists between the CO_2 recovery and enrichment. In other words, the set of PSA process conditions that simultaneously maximizes both R and E is not necessarily the same set of conditions that maximizes R or E independently. The results in Fig. 3, which show the effect of the purge to feed ratio (γ) and cycle step time (t_s) on the (a) CO_2 recovery (R) and (b) CO_2 enrichment (E) for 25 simulations carried out at a pressure ratio $\pi_T = 8$ and throughput $\theta = 14.4$ L STP/hr/kg, in terms of 3-D contour plots tend to reveal the conditions that produce this optimum behavior better than simple 2-D plots (Fig. 2). The results in Fig. 3(a) clearly show that R increased monotonically with increasing γ and decreasing t_s with $R = 100\%$ for numerous sets of conditions. In contrast, the results in Fig. 3(b) reveal much more complex behavior: E increased monotonically with increasing γ,

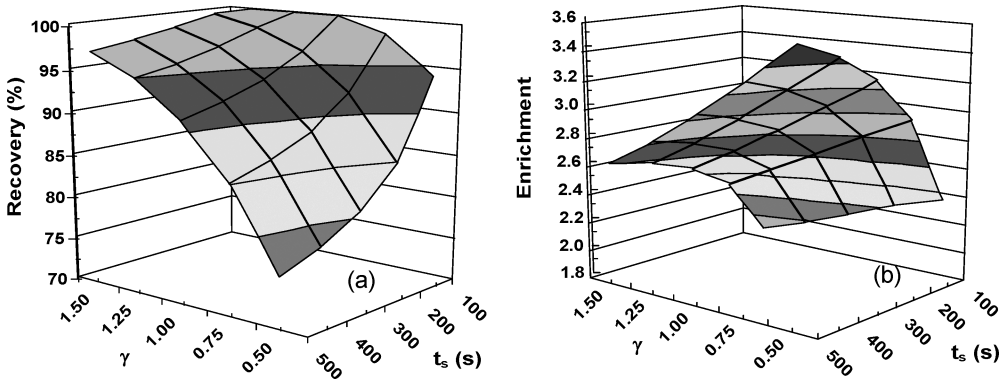

Figure 3. Effect of the purge to feed ratio (γ) and cycle step time (t_s) on the process performance in terms of the (a) CO_2 recovery (R) and (b) CO_2 enrichment (E). Results from 25 simulations are shown with $\pi_T = 8$ and $\theta = 14.4$ L STP/hr/kg.

but only at the lower values of t_s; it clearly went through a maximum at the higher values of t_s. Moreover, at the lower values of γ, E decreased with decreasing t_s, whereas at the higher values of γ, E increased with increasing t_s. Nevertheless, it is clear that a set of γ and t_s exists that maximizes both R and E, an effect that could not be ascertained from Fig. 2.

The results in Fig. 3 provide a convenient, but somewhat limited methodology, to evaluate the simulations, because only a fraction of them can be plotted. The results from all 125 simulations are easily evaluated, however, by constructing a plot or R versus E, as shown in Fig. 4. Performance curves are shown for a feed flow rate of 1.0 L STP/min (i.e., $\theta = 14.4$ L STP/hr/kg). Each line corresponds to five runs with t_s increasing from right to left. Each family of lines correspond to a constant γ with π_T increasing as their fan spreads from left to right. From this graph, it is easy to pinpoint the conditions that maximize both R and E. In this case, an $E = 3.89$ at $R = 86.8\%$ was obtained with $\gamma = 0.5$, $t_s = 500$ s and $\pi_T = 12$, which correspond to the smallest γ, longest t_s and highest π_T investigated, possibly an expected outcome with a bit of hindsight. The conditions that optimized E or R independently clearly were not the same, but could readily be identified from such a plot. For example, the best CO_2 enrichment dropped to $E = 2.79$ to achieve an $R = 99.99\%$, but now with $\gamma = 1.5$, $t_s = 400$ s and $\pi_T = 12$. Since all 125 simulations were obtained at the same throughput θ, other θs will shift these lines accordingly.

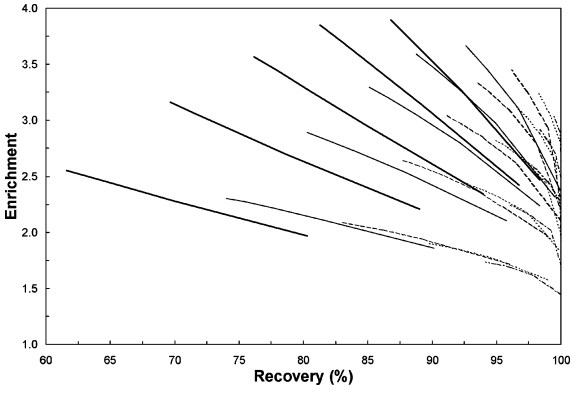

Figure 4. Performance curves for a feed flow rate of 1.0 L STP/min ($\theta = 14.4$ L STP/hr/kg) and purge to feed ratios (γ) of 0.50 (bold line), 0.75 (thin line), 1.00 (dashed line), 1.25 (dotted line), and 1.5 (dot-and-dash). Each line corresponds to five runs with t_s increasing from right to left. Each family of lines of constant γ corresponds to π_T increasing as their fan spreads from left to right.

Conclusions

A rigorous PSA process simulator was used to study a new, high temperature PSA cycle, based on the use of a K-promoted HTlc adsorbent and a simple, 4-step, Skarstrom-type, vacuum swing cycle designed to process a typical stack gas effluent at 575 K containing (in vol%) 15% CO_2, 75% N_2 and 10% H_2O. The effects of the purge-to-feed ratio (γ), cycle step time (t_s) (with all four steps of equal time), and pressure ratio (π_T) on the process performance was studied in terms of the CO_2 recovery (R) and enrichment (E) at a constant throughput θ of 14.4 L STP/hr/ kg. The results from 125 simulations, carried out at five different purge-to-feed ratios, cycle step times and pressure ratios showed that R increased with increasing γ and π_T and decreasing t_s, while E increased with increasing t_s and π_T and decreasing γ. The highest E of 3.9 was obtained at

$R = 87\%$ with $\gamma = 0.5$, $\pi_T = 12$ and $t_s = 500$ s, apparent optimum condition for E but not R. In contrast, at $R = 100\%$ the highest E of 2.8 was obtained at $\gamma = 1.5$, $\pi_T = 12$ and $t_s = 500$ s, apparent optimum conditions for R but not E. Different feed flow rates, i.e., different θs, will result in different sets of optimum, possibly better, conditions. Hence, these results are very encouraging and show the potential of a high temperature PSA cycle for CO_2 capture.

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