Enrichment of Coal-Bed Methane by PSA Complemented with CO_2 Displacement

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A PSA cycle complemented with CO_2 displacement was studied for enriching coal-bed methane (CBM). The column was first pressurized to the adsorption pressure with feed gas, and then N_2 was produced at column top in step 2. The feed gas switched to CO_2 at the end of step 2, and the adsorbed CH_4 was displaced and pushed to column top by CO_2 becoming the second column-top product in step 3. The CO_2 stream was shut off before it broke through the sorption bed. Then bed regeneration followed. A series of CH_4/N_2 mixtures containing 17.62 to 51.33% CH_4 was used for feed gas. It was experimentally shown that the product concentration was higher than 90%, and methane recovery was higher than 98% even for the feed of low-methane concentration. Displacement at ambient pressure was shown more efficient than the displacement at adsorption pressure for the enrichment. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 645–654, 2011

Keywords: separation, coal bed methane, enrichment, PSA, CO_2 displacement

Introduction

Coal bed methane (CBM) is a kind of natural gas formed geologically or biologically in coal seams. The world's CBM resource buried in the top 2000 m of the earth is up to 2.4×10^{15} m^3, which is more than two times that buried in natural gas reservoirs.[1] Most CBM has not yet been exploited. High-quality CBM may serve as chemical raw stock or clean fuel; however, the poor quality CBM always is released to the atmosphere, which is hazardous to the environment because the greenhouse effect of CH_4 is 21 times higher than CO_2.[2] In order to serve as chemical raw stock, the CH_4 content in CBM must be higher than 80%, and higher than 90% in order to merge in the pipeline network of civil natural gas.[3] However, methane concentration in the usual seam drainage gas is in the range of 20–45%. The other constituents are mainly incombustible N_2 and CO_2. Therefore, the key problem for the utilization of CBM is the enrichment of CH_4 from its mixture with N_2 and CO_2. CO_2 may or may not exist in CBM, and the difference between CH_4 and CO_2 in separation is larger than that between CH_4 and N_2; therefore, the pair of key components for the enrichment is CH_4/N_2. Separation of CH_4/N_2 was considered as a challenge due to the similarity of the two gases in physicochemical properties.[4] Cryogenic distillation, membrane and PSA (pressure swing adsorption) are considered as the major technologies applicable for the separation presently. The cryogenic method may be applied for large-scale production since a huge investment and large-energy consumption are involved.[5] Membrane separation is a hot topic of research; however, there is still a distance to industrial application due to the poor selectivity and unsatisfactory working life of available membranes.[6,7] PSA is also a young separation technology since it did not appear in industry

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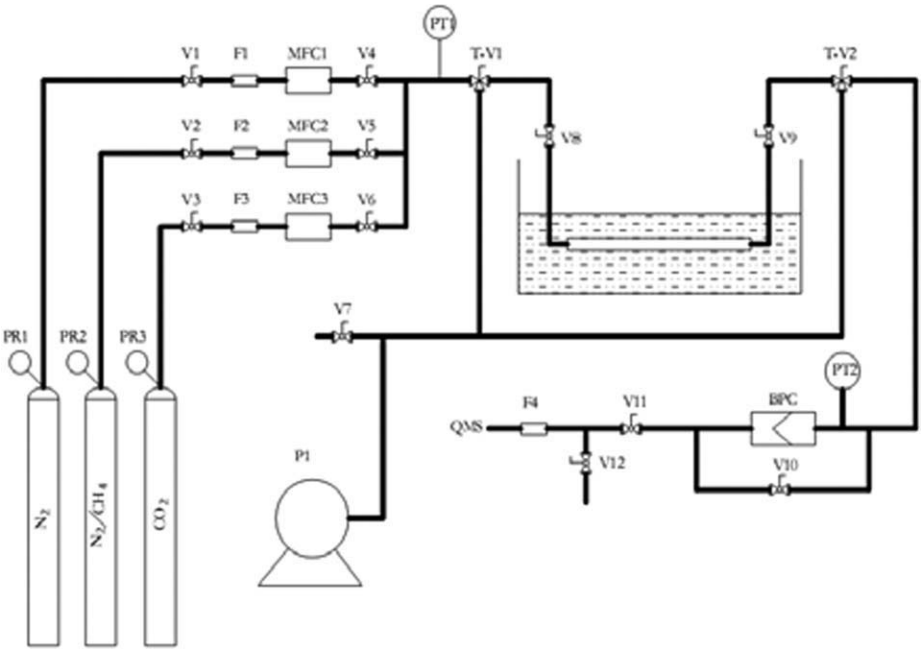

Chart 1. Flow chart of experimental setup.

Pressure regulator (PR), filter (F), valve (V), three-way valve (T-V), mass-flow controller (MFC), pressure transducer (PT), backpressure controller (BPC), pick-up pump (P1), and quadrapole mass spectrograph (QMS).

until the 1970s. However, it has been extensively used in petroleum, chemical and petrochemical or air separation industries in the following years. It operates at ambient temperature and a reasonable pressure. The equipment is simple and highly automated with large flexibility of operation. Investment in adsorbents may be large; however, the working life of adsorbents is usually long. Therefore, PSA attracts extensive interest for the separation of industrial gases due to the advantage of low cost and energy effectiveness.[4,8,9]

Many adsorbents have been tested for the CH_4/N_2 separation. If the separation is based on the difference of components at equilibrium adsorption, activated carbon was usually applied.[10] Yang and coworkers reached a selectivity ratio of 4.25 by grafting MoO_2 on high-surface carbon; however, the selectivity ratio decreased with pressure, and leveled off to about 3 at 12 atm.[11] Olajossy and coworkers used activated carbon in a VPSA process and enriched methane from 55.2% to 96–98%.[12] A simulation study showed that lower-adsorption pressure was preferred for the PSA separation between CH_4 and N_2.[13] Methane is always adsorbed more strongly than nitrogen at equilibrium; therefore, it cannot be obtained at column top as long as the separation is based on the difference of equilibrium adsorption. As a bottom-product, both concentration and recovery of methane are limited not to mention the loss of pressure. Fortunately the kinetic property difference of the two gases allows methane to be collected at column top[14] when carbon molecular sieves (CMS),[15–17] synthesized zeolites,[18–21] clinoptilolites and their modified species[22–26] are used as adsorbents. Because N_2 shows more adsorption preference over these materials, CH_4 is obtained at column top. It was shown for 4A zeolite that improvement was observed only at relatively low-temperature (253 K);[20] however, a product with higher than 90% CH_4 was obtained at 273 K.[21] Yang and coworkers published a series of CBM enrichment studies on using clinoptilolites and their modified species as adsorbents. The original clinoptilolites increased the methane content from 85% to 97.3%; however, methane recovery was only 53.2%. Other studies worked on ZSM-5, SAPOs, ETS-4, β-zeolite and silicalite,[27–31] did not reach satisfactory enrichment either. Although this kind of adsorbents can switch over the adsorption preference of methane and nitrogen, its potential for industrial application is not promising due to the nonideal selectivity and low-adsorption capacity. Activated carbon is actually most suitable for industrial enrichment of CBM. The disadvantage of using activated carbon in PSA processes is that methane cannot be the column-top product; however, as shown it is possible to switch methane to column top by complementing conventional PSA cycle with a step of CO_2 displacement in this study. Compared to CH_4, CO_2 is more strongly adsorbed on activated carbon; therefore, it can displace the adsorbed methane and push it up to the column top. As a column-top product, the enriched coal-bed methane can reach higher concentration and recovery even for the CBM of low-methane content. In addition, the product stream maintains its mechanical energy and yields low-energy cost in succeeding transportation.

Experimental

Apparatus

The experimental study on the proposed PSA process addressing to CBM enrichment was carried out in a setup shown schematically in Chart 1. A stainless steel tube with dimension of 250 mm long and 10 mm i.d. was used for the adsorption column, and activated carbon of 40–60 mesh was packed in. A backpressure regulator controlled the

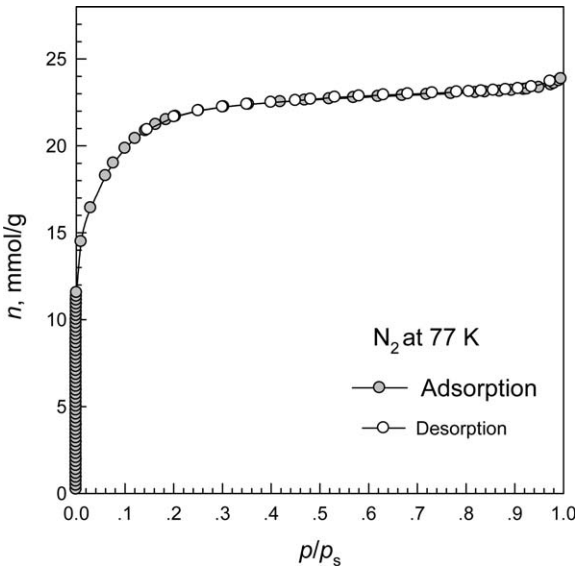

Figure 1. Adsorption/desorption isotherms of N_2 at 77 K.

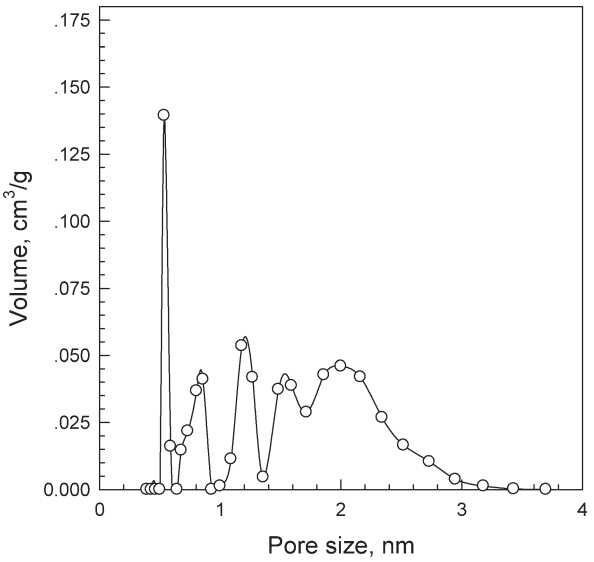

Figure 2. Pore-size distribution of carbon sample.

adsorption pressure, and the pressure drop over the adsorption bed was set at 0.2 MPa. Pressure was measured and transmitted to a computer by pressure transmitters model SY-9411 provided by Advantech Co., Ltd. Beijing. The full measurement scale was 1 MPa with precision ±0.1% F.S. The gas-flow rate was measured and controlled by mass flow controllers model SY-9312 provided by the same company. The full scale of measurement was 400 cm^3/min of precision ±1.5% F.S. Composition of the effluent stream was analyzed by a quadrapole mass spectrograph made in Stanford Research Systems, Inc. USA. All units were connected by stainless steel capillary tube of 2 mm i.d. and 0.5 mm wall thickness. The adsorption column was put in a thermostat with temperature constant to ±0.1 K.

Materials

The activated carbon used in the experiments was prepared in the authors' laboratory. A carbon sample was analyzed based on nitrogen adsorption and desorption isotherm at 77 K collected on Micromeritics ASAP 2020 and shown in Figure 1. The BET surface area, pore volume and the bed-packing parameters are shown in Table 1. The pore-size distribution determined by the DFT model[32] is shown in Figure 2. The activated carbon used in experiments is basically microporous as illustrated in Figures 1 and 2. The adsorption isotherms of CH_4, N_2 and CO_2 on the carbon at 298 K were collected on a volumetric apparatus and shown in Figure 3. Details of the measurement were previously described.[33] The adsorbed amount of CO_2 was much higher than that of CH_4 and N_2. The breakthrough curves of gas mixture He/CH_4/N_2 were also collected at 298 K and shown in Figure 4. A separation coefficient between CH_4 and N_2 was determined as 3.5 based on the breakthrough curves. Details of the breakthrough experiment and calculation of the separation coefficient were described in the literature.[26] The carbon was dried *in vacuo* at 393 K for 8 h before experiments. All gases used in the experiments were provided by Liufang Gas Co. Tianjin. The purity of He and CH_4 is higher than 99.99%, and higher than 99.9% for N_2 and CO_2. The composition of feed gases prepared for simulating real CBM is shown in Table 2.

Table 1. Carbon and Adsorption Bed Parameters

Parameter	Values
BET surface, m^2/g	1700
Pore volume, cm^3/g	0.83
Carbon weight in bed, g	7.29
Bulk density, g/cm^3	1.94
Void space, ε	0.77

Procedure

The proposed PSA cycle was composed of four steps: pressurization, adsorption, CO_2 displacement, and regeneration. It

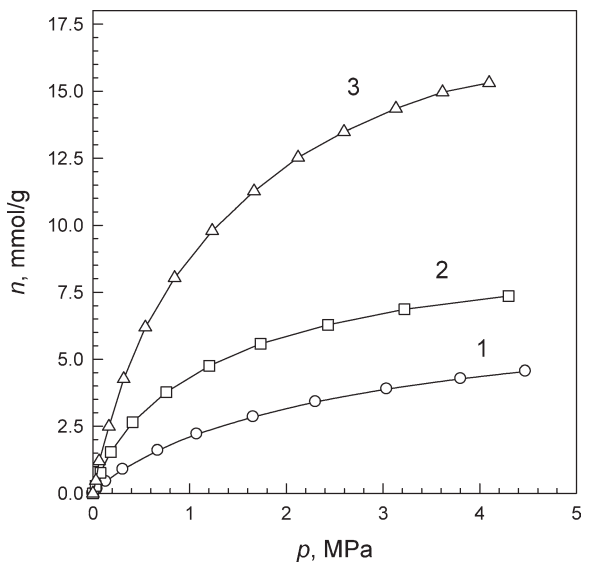

Figure 3. Adsorption isotherms of CH_4, N_2 and CO_2 at 298 K.

(1) N_2, (2) CH_4, and (3) CO_2.

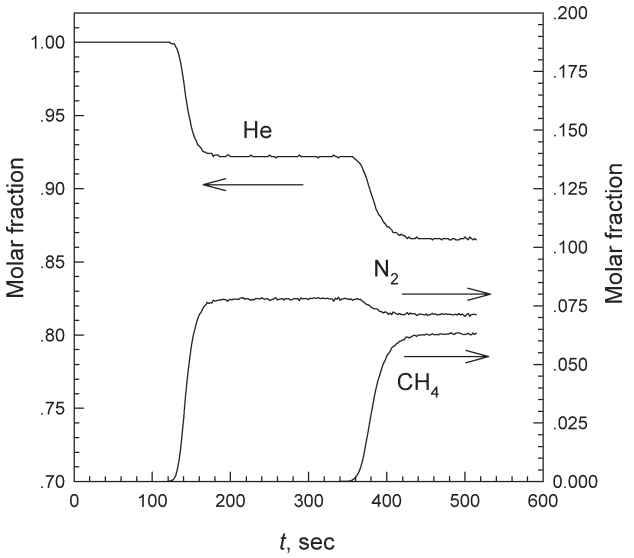

Figure 4. Breakthrough curves of the $He/N_2/CH_4$ mixture passing the carbon bed at 298 K.

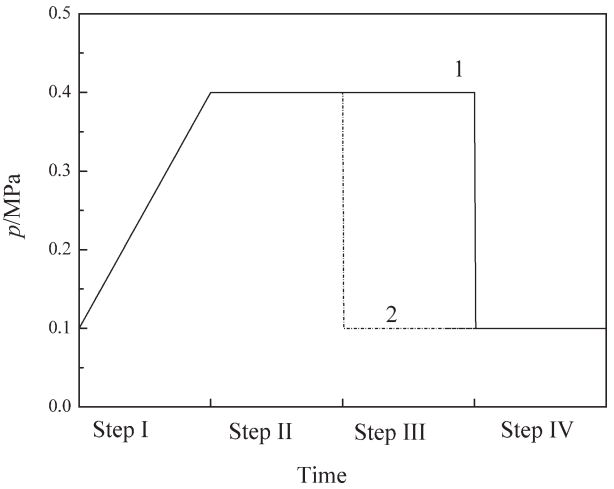

Figure 5. Pressure histories of a cycle.

(1) Displacement at 0.4 MPa, and (2) displacement at 0.1 MPa.

featured inclusion of a CO_2 displacement step in a conventional PSA cycle. Compared to CO_2, CH_4 became the weakly adsorbed component and was displaced and pushed up to the column top by CO_2. The column pressure at each step is shown for a cycle in Figure 5. The column was first pressurized to the adsorption pressure (0.4 MPa) with feed gas in step 1. The feed gas continued to feed the column at the pressure, and pure N_2 was obtained at column top in step 2. The third step was CO_2 displacement; however, there are two modes of displacement. One mode was to switch the feed gas to CO_2 at the same pressure as adsorption. The CO_2 stream was shut off before it broke through the sorption bed, and the bed pressure was released cocurrently to the ambient pressure at the end of step 3 as shown by branch 1 of Figure 5. Another mode was to release the bed pressure cocurrently to ambient at the end of step 2, and then to allow CO_2 stream to feed the sorption bed at ambient pressure, and to shut off the CO_2 stream at the end of step 3 as shown by branch 2 of Figure 5. Two concentration profile borders, N_2/CH_4 and CH_4/CO_2, were formed in the sorption bed during step 3 as shown in Chart 2 no matter which displacement mode was applied. Nitrogen was still the column top product in the early time of step 3; however, both borders moved toward the column top following the feeding of CO_2, and methane became the second column top product of step 3 when the profile front of CH_4 broke through the bed. The sorption bed was saturated by CO_2 when the front of CO_2 profile reached bed top at the end of step 3; therefore, the forth step was regeneration. Two regeneration methods were tested in experiments: purging by pure nitrogen previously obtained or by evacuation.

Table 2. Composition of Testing Gases

Mixture	CH_4 %	N_2 %	He %
$He/CH_4/N_2$	6.30	7.12	86.58
CH_4/N_2	17.62	82.38	–
CH_4/N_2	22.30	77.70	–
CH_4/N_2	32.06	67.94	–
CH_4/N_2	40.28	59.72	–
CH_4/N_2	51.33	48.67	–

Performance evaluation

To evaluate the performance of the proposed PSA cycle, aside from product concentration, some other performance indices were defined. Methane recovery was defined as

$$\text{CH}_4 \text{ recovery} = \frac{V_{\text{out}} c_{\text{out}}}{F_{\text{in}} c_{\text{in}} \left(t_{\text{pr}} + t_{\text{ads}}\right)} \times 100\% \tag{1}$$

Where V_{out} is the product volume per cycle, c_{out} is the methane concentration in product, F_{in} is the flow rate of feed gas, c_{in} is the methane content in feed gas; t_{pr} and t_{ads} are the time for pressurization and adsorption, respectively. The adsorbent productivity is defined as the volume of feed gas processed per unit mass/volume of adsorbent per unit time

$$C_M = \frac{F_{\text{in}} \left(t_{\text{pr}} + t_{\text{ads}}\right)}{t_{\text{tot}} m_{AC}} \tag{2}$$

$$C_V = \frac{F_{\text{in}} \left(t_{\text{pr}} + t_{\text{ads}}\right)}{t_{\text{tot}} V_{AC}} \tag{3}$$

where C_M and C_V are the adsorbent productivity per unit mass and unit volume, respectively; t_{tot} is the time for a cycle period, m_{AC} is the mass of adsorbent packed in column, and V_{AC} is the volume of adsorbent bed. To evaluate the effectiveness of the purging regeneration method, an index of regeneration cost C_{reg}, was defined as the ratio of purging gas used for decreasing the CO_2 content in tail gas down to 10% over the nitrogen available in a cycle

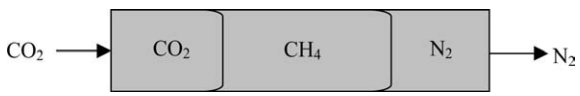

Chart 2. The two concentration profiles along the adsorption bed in step 3.

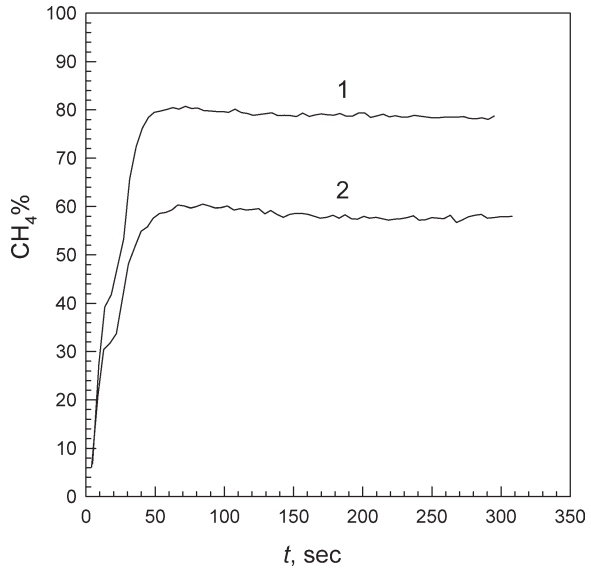

Figure 6. Methane concentration in the desorbed gas (adsorption pressure = 0.4 MPa, and bed regeneration by evacuation).

(1) Releasing pressure cocurrently, and (2) releasing pressure counter-currently.

$$C_{\mathrm{reg}} = \frac{F_{\mathrm{pg}} t_{\mathrm{pg}}^{0.1}}{F_{\mathrm{in}} c_N \left(t_{\mathrm{pr}} + t_{\mathrm{ads}}\right)} \tag{4}$$

Where F_{pg} is the flow rate of purging gas; $t_{\mathrm{pg}}^{0.1}$ is the purging time required for decreasing the CO_2 content in tail gas down to 10%; c_N is the concentration of nitrogen in feed gas. When the sorption bed was regenerated by evacuation, the degree of regeneration D_{reg}, was defined as the ratio of breakthrough times

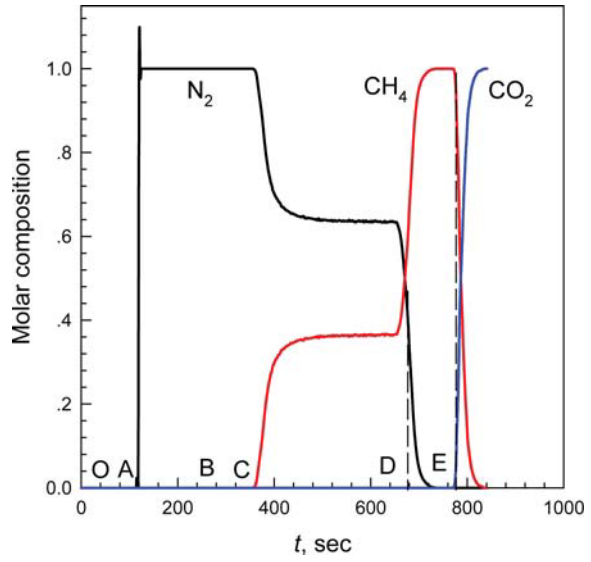

Figure 7. Composition variation of the effluent stream for CO_2 displacement at adsorption pressure 0.4 MPa.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

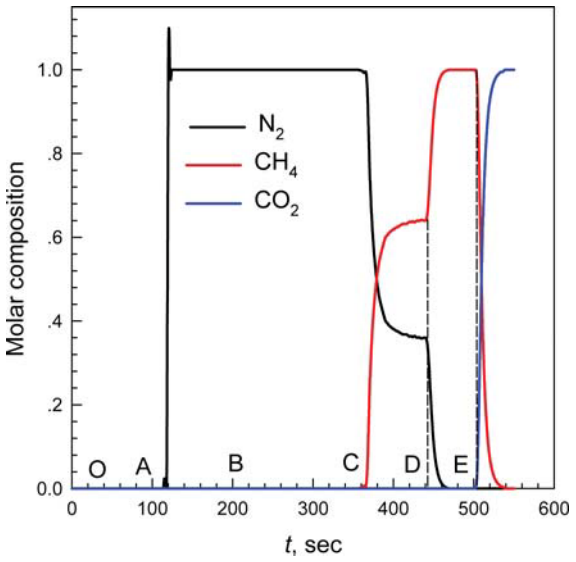

Figure 8. Composition variation of the effluent stream for CO_2 displacement at ambient pressure 0.1 MPa.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$D_{reg} = \frac{t_{re}}{t_1} \tag{5}$$

Where t_{re} is the breakthrough time after regeneration, and t_1 is the breakthrough time when a gas mixture passes through a fresh sorption bed.

Results and Discussion

Enrichment without CO_2 displacement

Methane as the stronger adsorbed component is concentrated in adsorbent, and can merely be a column-bottom product on

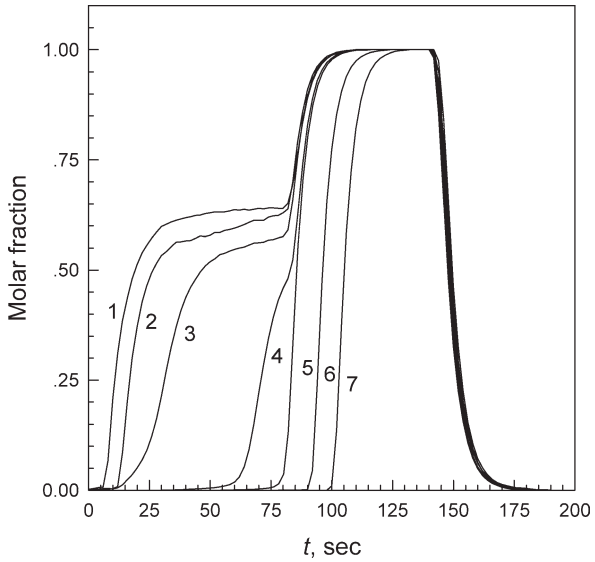

Figure 9. Effect of adsorption time on displacement consequence (displacement at 0.1 MPa).

(1) t_{ads} = 360 s, (2) t_{ads} = 240 s, (3) t_{ads} = 180 s, (4) t_{ads} = 150 s, (5) t_{ads} = 140 s, (6) t_{ads} = 120 s, and (7) t_{ads} = 100 s.

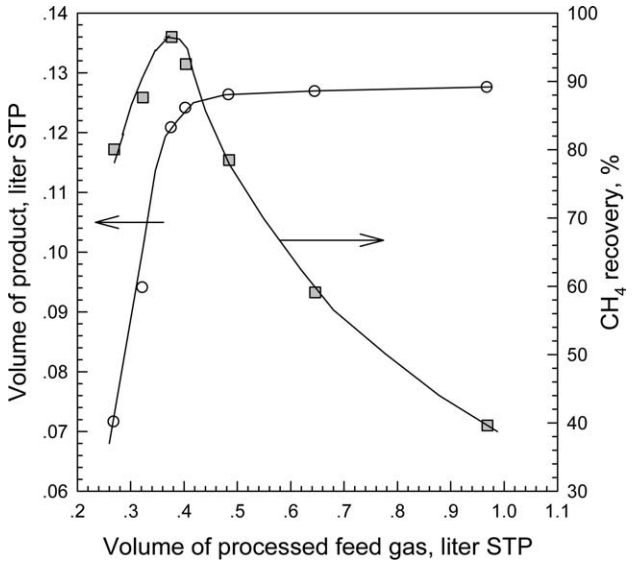

Figure 10. Effect of processed feed gas per cycle on product quantity and methane recovery (CO_2 displacement at 0.1 MPa).

releasing bed pressure and/or on the following evacuation without CO_2 displacement. However, the product concentration cannot be higher than 80% as shown in Figure 6 for the enrichment of feed gas containing 32.06% CH_4.

Enrichment with CO_2 displacement

In the proposed PSA cycle, the step of adsorption was followed by a step of CO_2 displacement. Because CO_2 is more strongly adsorbed than CH_4 on activated carbon, the adsorbed CH_4 was displaced by the incoming CO_2 and enriched in gas phase. Figure 7 illustrates the displacement procedure when it takes place at the pressure of adsorption. The figure ordinate is the molar composition of the effluent stream. The OA period corresponded to the pressurization step, and the bed pressure increased from 0.1 to 0.4 MPa without any effluent stream. The AB period corresponded to the adsorption step, and nitrogen broke through the bed when the feed gas continued to enter at pressure 0.4 MPa. The feeding stream switched from feed gas to CO_2 at point B, and the displacement step began. Nitrogen was still the "column-top" product until point C, where the methane profile front broke through the bed. However, the tail of the nitrogen profile had not left the bed yet, and a mixture of N_2 and CH_4 flew out of the bed until point D, where the tail of the nitrogen profile left and a concentrated methane stream obtained at column-top. The feeding CO_2 was shut off at point E, where the profile front of CO_2 had just reached the bed top, and the fourth step began. The concentrated CO_2 stream after point E was recorded during bed regeneration. A plug-flow regime was certainly provided for the displacement procedure. Figure 8 shows the same procedure for the CO_2 displacement occurring at ambient pressure. Comparing the two figures, it is observed that the time for the CD period considerably decreased if the displacement occurs at ambient pressure; therefore, less mixture of N_2 and CH_4 was produced. Due to pressure release, the methane content in the mixture for period CD becomes higher than that shown in Figure 7.

Selection of adsorption time

The CD period in either Figures 7 or 8 corresponds to a mixture of CH_4 and N_2 coexisting in the effluent stream. Obviously, the shorter is the CD period, the better is the cycle productivity, and the higher is the product concentration. The CD period can be compressed to the utmost by controlling the time allocated for adsorption. The coexisting gas mixture decreased, and finally disappeared with the decrease of adsorption time from 360 s to 140 s as shown in Figure 9 for the displacement occurring at ambient pressure as an example. With disappearance of the CD period, an effluent stream of high-methane content was obtained. Because the amount of feed-gas processed per cycle is largely determined by the time of adsorption, there is optimal process productivity correspondingly, at which both product volume and methane recovery show the largest value as shown in Figure 10. The optimal adsorption time is 140 s and the corresponding optimal quantity of feed gas processed per cycle is 0.377 L STP for CO_2 displacement at 0.1 MPa, and that for CO_2 displacement at 0.4 MPa is 210 s and 0.565 L STP, respectively. However, the productivity per unit mass of adsorbent is larger if the displacement occurred at 0.1 MPa as shown in Table 3. The composition of effluent stream during a cycle at the optimal operation regime is shown in Figure 11 for the displacement at 0.1 MPa as an example. OA marks the pressurization period, and AB the adsorption period. The bed pressure was released to ambient at point B, and CO_2 displacement took place till point E. The "top product" was N_2 for period BD, and it switched to CH_4-enriched gas for period DE. The period CD disappeared and no mixture was produced.

Relationship between product concentration and methane recovery

The relationship between product concentration and methane recovery was affected by methane content in the feed gas and the mode of CO_2 displacement. When the displacement occurred at the adsorption pressure, methane recovery declined initially moderately following the increase of product concentration, and the decline accelerated at high concentrations. However, if the CO_2 displacement occurred at ambient pressure, methane

Table 3. Effect of Methane Content in Feed Gas on Adsorption Time and Process Productivity

		Displacement at 0.4 MPa		Displacement at 0.1 MPa	
Run	c_{in}, %	t_{ads}, sec	C_M, l/Kg.h (STP)	t_{ads}, sec	C_M, l/Kg.h (STP)
1	51.33	200	262.6	130	270.7
2	40.28	200	275.5	130	289.1
3	32.06	210	300.0	140	320.7
4	22.30	210	306.7	140	327.8
5	17.62	210	314.1	140	335.8

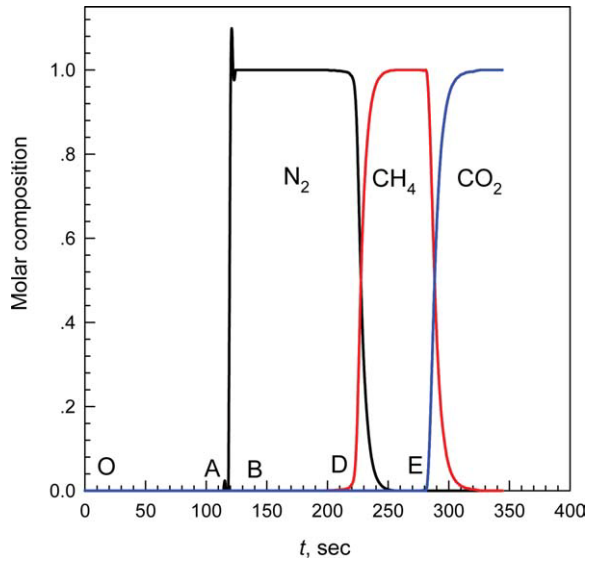

Figure 11. Effluent stream composition at the optimal operation regime (CO_2 displacement at 0.1 MPa).

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

recovery maintained a high level until the product concentration reached to an upper limit, and then the recovery fell down to the bottom as shown in Figures 12 and 13 for the two modes of CO_2 displacement.

Effect of feed-gas concentration on enrichment

Methane content in the drainage gas of coal mining is generally 20–45%. Five compositions of feed gas were tested in this study, and the methane content ranges in 17.62–51.33% as shown in Table 2. As shown in Figures 12 and 13, the methane content in feed gas showed remarkable effect on the reachable product concentration and methane recovery. Higher feed-gas concentration reaches higher product concentration and higher methane recovery; however, a product containing more than 90% CH_4 was obtained with recovery higher than 98% even for a feed gas with low-methane concentration (17.62%) as shown in Figure 13. In addition, the optimal adsorption time also varies with feed-gas concentration as shown in Table 3. Shorter adsorption time applied for the feed gas of higher methane content, which resulted in less quantity of feed gas processed per cycle, and less adsorbent productivity.

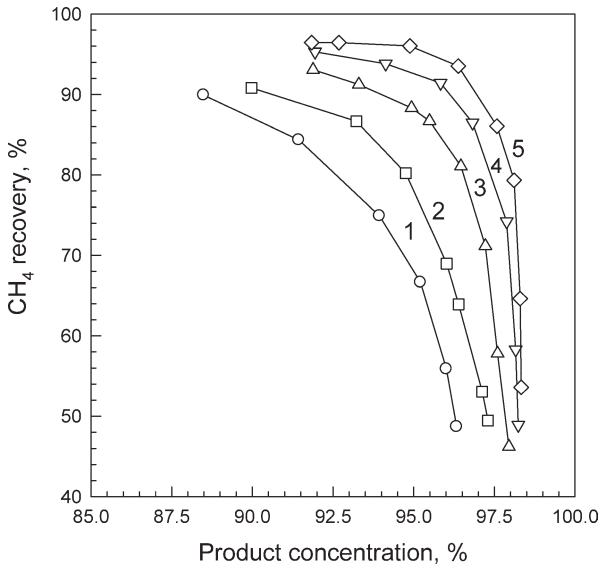

Figure 12. Product concentration and methane recovery for CO_2 displacement at 0.4 MPa with feed-gas concentration of (1) 17.62%, (2) 22.30%, (3) 32.06%, (4) 40.28, and (5) 51.33%.

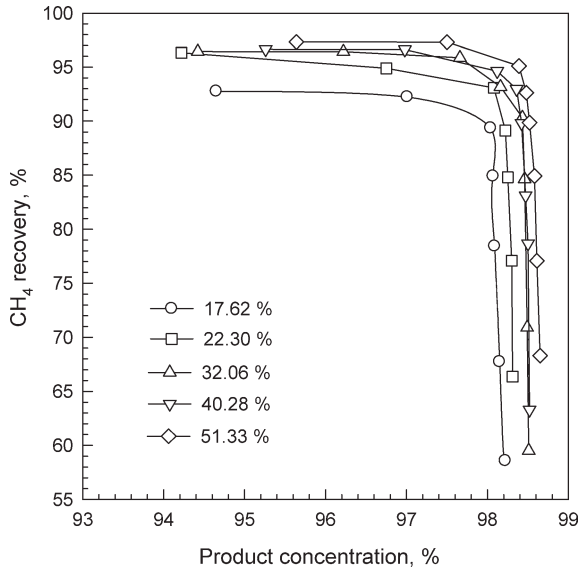

Figure 13. Product concentration and methane recovery for CO_2 displacement at 0.1 MPa with different feed-gas concentrations.

Studies on regeneration

The regeneration performance of adsorbent is very important for a PSA process since it greatly affects the operation cost and the productivity of process. Two regeneration methods were tested in experiments. One method was purging the CO_2-saturated sorption bed with a N_2 stream counter-currently at ambient pressure; another method was to evacuate the bed when the bed pressure had been released. Variation of CO_2 content in the tail gas is shown in Figure 14 for different purging rates. The purging time decreases as purging rate increases; however, the index of regeneration cost gradually increased as shown in Figure 15 for two modes of CO_2 displacement. A trade-off between purging time and regeneration cost must be made, and a purging rate of 200 cm^3/min was selected for subsequent experiments. The C_{reg} for the displacement at ambient pressure is larger than that for the displacement at the adsorption pressure due to the large difference in adsorption time. For example, the adsorption time was 140 s for the displacement at ambient pressure, and that for the displacement at adsorption pressure was 210 s; however, the purging time was the same for the two displacement modes. The fact that C_{reg} is larger than unity means

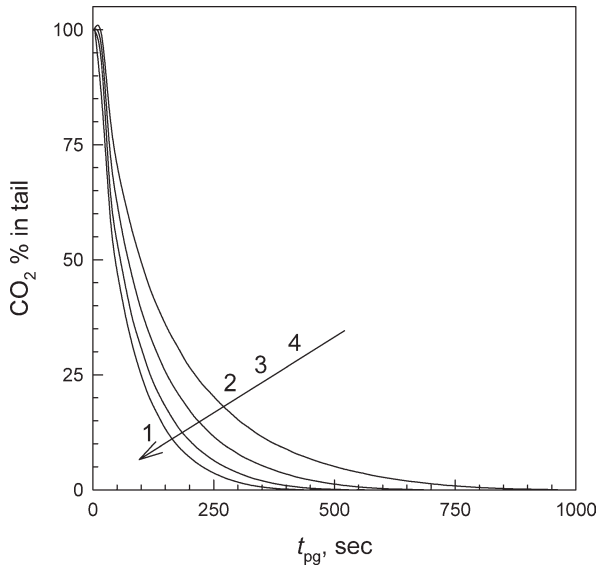

Figure 14. CO_2 concentration in tail gas at different purging rates.

(1) 250 cm^3/min, (2) 200 cm^3/min, (3) 150 cm^3/min, and (4) 100 cm^3/min.

the quantity of nitrogen produced in a cycle is not enough for purging; however, a separation between CO_2 and N_2 is required and both CO_2 and N_2 are reused. This separation may not contribute much to the total cost of CBM enrichment due to the limited volume of the CO_2/N_2 mixture, and the fact that the separation between CO_2 and N_2 is easier than the separation between CH_4 and N_2. In case that CO_2 is a component of CBM, the separation is no longer superfluous. The CO_2-saturated sorption bed can also be regenerated by evacuation. For a given evacuation rate, the longer the evacuation time the larger the regeneration degree. The dependence of regeneration degree on evacuation time is shown in Table 4. Apparently, the CO_2-saturated bed can be fully regenerated by evacuation, and the desorbed CO_2 can be reused after compression.

Table 4. Effect of Evacuation Time on Regeneration Degree

t_{vac}, sec	t_{brk}, sec	D_{reg}, %
60	284	87.92
180	311	96.28
300	317	98.14
420	321	99.38
630	323	100
660	323	100

Note: t_{vac} is the time of evacuation, and t_{brk} is the breakthrough time after regeneration.

Test on consecutive cycling

Consecutive cycling was carried out at the optimal condition determined in previous sections aiming to verify the stability of the proposed PSA process. The CO_2 displacement took place at ambient pressure, and both purging and evacuation methods were tested for bed regeneration. Product concentration and methane recovery are shown in Figure 16 for both regeneration methods. As shown in the figure, both regeneration methods result in almost the same process performance, and the process can be operated continuously.

Comparison with literature

A comparison with other studies is made and summarized in Table 5, where the feed gas containing 32.06%CH_4 was taken as representative of this technology because this methane content is in the middle of the CH_4 content range tested. Although this study deals with the lowest feed concentration, the product concentration, methane recovery and adsorbent

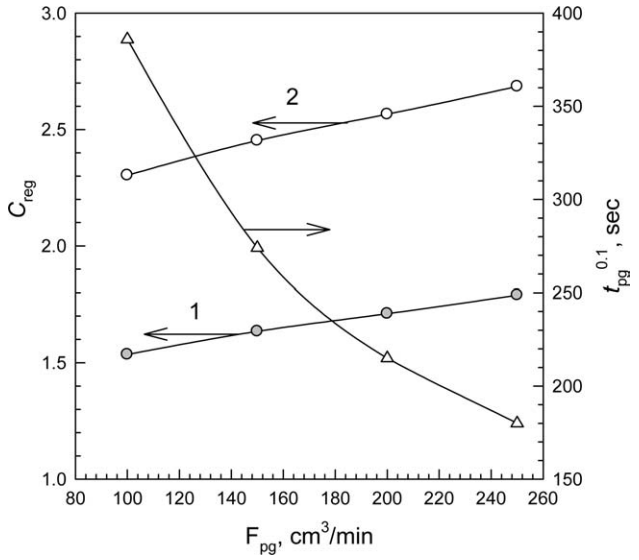

Figure 15. Effect of purging rate on purging time and regeneration cost (evaluated for 10% of CO_2 content in tail gas).

(1) CO_2 displacement at 0.4 MPa, and (2) CO_2 displacement at 0.1 MPa.

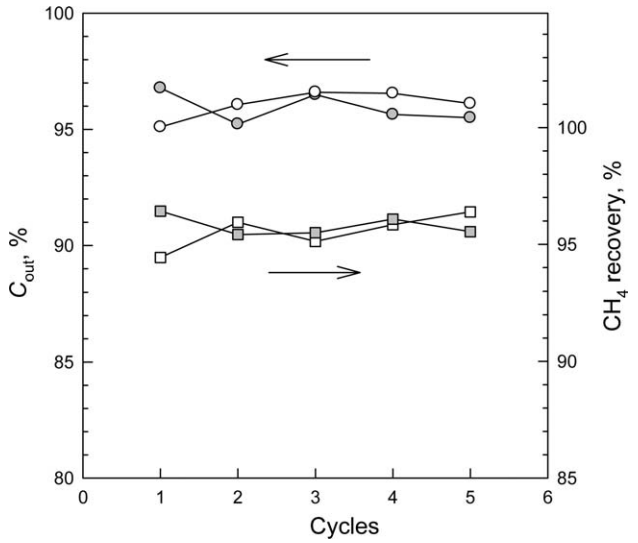

Figure 16. Product concentration and methane recovery in consecutive cycles.

White points (purging), gray points (evacuation), and CH_4 content in the feed gas is 32.06%.

Table 5. Comparison of Enrichment Result with Literature

Method	Adsorbent	CH_4% of Feed	T, K	p, MPa	CH_4 % in product	CH_4 % Recovered	Productivity l./kg.h (STP)	P/F
Present	AC[a]	32.06	298	0.4	97.66	95.87	320.7	–
PSA[11]	AC	50	298	0.2	98.43	59.75	200	0.5
VPSA[12]	AC	55.2	278	0.3	96–98	86–91	–	1.8-2.1
PSA[15]	CMS[b]	50	298	0.2	79.2	48.5	–	–
PSA[16]	CMS	60	298	0.3	75.84	75.52	–	1.79
PSA[25]	ETS-4	85	295	0.7	97.2	53.2	–	–
	Clinop[c]				95.4	73.1		
	Mg-Clinop[d]				93.3	41.65		
PSA[34]	Solialite	85	298	0.12	96	74	106.8	–
LPSA[35]	CMS	60	301	0.25	86	52.6	–	–

Note: [a]Activated carbon;[b]Carbon molecular sieve;[c]Clinoptilolites;[d]Mg- Clinoptilolites.

productivity are at the top level. The excellent enrichment result must be attributed to the inclusion of CO_2 displacement into the PSA cycle.

Conclusion

1. Inclusion of CO_2 displacement into a conventional PSA process succeeded to switch methane from column bottom to column top provided that the separation was based on equilibrium adsorption.

2. As a result of CO_2 displacement, a low-concentration feed gas (methane content 17.62%) was enriched to concentrated gas containing more than 90% CH_4 with methane recovery higher than 98%.

3. The CO_2 displacement at ambient pressure results in higher product concentration, higher methane recovery, and higher adsorbent productivity than the displacement occurring at the adsorption pressure.

4. Both purge with nitrogen and evacuation can fully regenerate the activated carbon saturated by CO_2.

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Notation

C_M = adsorbent productivity per gram, cm^3 (STP)/g. min
C_{reg} = index of regeneration cost
C_V = adsorbent productivity per unit volume, 1/min
c_{in} = methane concentration in feed gas, %
c_N = concentration of N_2 in feed gas, %
c_{out} = methane concentration in product, %
D_{reg} = degree of regeneration, %
F_{in} = flow rate of feed gas, cm^3/min
F_{pg} = flow rate of purging gas, cm^3/min
m_{AC} = mass of adsorbent packed in column, g
n = adsorbed amount, mmol/g
P/F = purging ratio, defined as the ratio of the column-top component contained in purging stream to that contained in feed stream for a cycle
p = adsorption pressure, MPa
p_s = saturation pressure, MPa
T = temperature, K
t_1 = time for breaking through a fresh sorption bed, s
t_{ads} = adsorption time, s
$t_{pg}^{0.1}$ = purging time required for decreasing the CO_2 content in tail gas down to 10%, s
t_{pr} = time for pressurization, s
t_{re} = breakthrough time after regeneration, s
t_{tot} = time for a cycle period, s
V_{AC} = volume of adsorbent bed, cm^3
V_{out} = product volume per cycle, cm^3

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