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Bulk Separation and Purification of CH_4/CO_2 Mixtures on 4A/13X Molecular Sieves by Using Pressure Swing Adsorption

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Abstract

Results of bulk gas separation and purification of a CH_4/CO_2 mixture by pressure swing adsorption (PSA) are reported. Bulk gas separation and purification of CH_4/CO_2 mixture have direct application in landfill gases and tertiary oil recovery and effluent separations. ZMS-13X/4A with calculated kinetic selectivities equal to 0.604 and 0.601, respectively, were used as sorbents. The step times corresponding to various flow rates and compositions were chosen to allow sorption of CO_2 but preclude penetration of CH_4 into the micropores. By using a simulated biogas mixture (66% CH_4 and 34% CO_2) as a feed, the results for bulk gas separation for a PSA cycle between 1.2–36.0 P_H/P_L ratios over ZMS-13X adsorbent was 95% or more CH_4 in the raffinate, whereas with a 10/90 CH_4/CO_2 feed, purification over ZMS-4A at P_H/P_L ratios of 10–304 gave 85–90% CH_4 at 900 and 1800 mL/min flow rates.

INTRODUCTION

Pressure swing adsorption (PSA) is a process for the purification and partial or complete separation of gas mixtures on fixed beds of adsorbent by using pressure variation as the principal operating parameter. Two or more beds can be operated continuously in a cyclic manner. The operation of a typical two-bed PSA apparatus involves adsorption, cocurrent/countercurrent blowdown, purging, and repressurization steps. Separation of CH_4/CO_2 is required in two important applications:

(1) Landfill gases which contain up to 50% CO_2 as an impurity.
(2) Tertiary oil recovery where the effluent gas contains up to 20–80% CO_2 and CH_4 (*1*).

The possibility of kinetic separation of these mixtures has been suggested (*2*). Presently these separations are accomplished by membrane permeation. Landfill gases have received increasing attention as a renewable source of energy. They contain up to 40–60% CH_4 which is to be enriched to over 90% as pipeline quality. In the recent past, PSA has become a well-established industrial technique for both purification and bulk separation of various gaseous and liquid mixtures. PSA finds a number of applications in the chemical industry (*3–10*). PSA has advantages over other adsorption methods in that its cyclic operation can lead to process improvements because it does not require separate desorption steps which need heat input. Moreover, it runs continuously with virtually no adsorbent handling required. This paper reports a study of the bulk separation and purification of a CH_4/CO_2 mixture over ZMS-13X and ZMS-4A.

LITERATURE SURVEY

For reasons of environmental protection and for conservation of energy resources, it is important for many regions in the world to recover CH_4 from biogases, e.g., from landfill gases, savage gases, mine gases, and wellhead gases, in order to use the product gas for heating purposes in particular. These processes normally handle relatively small quantities of gas, so that basically a pressure swing system is suitable for these purposes. By using a carbon molecular sieves absorbent, a four-step process for CH_4 recovery from landfill gases was developed and successfully tested in two pilot plants (*11–13*). The first full-size plant for CH_4 recovery at the largest landfill site in the Netherlands was set up in 1988 (*14*). Bulk gas separation and purification of CH_4/CO_2 mixtures have received increasing attention in industry. Membrane processes were first commercialized for CH_4/CO_2 separation (*15*, *16*), and equilibrium PSA processes using vacuum desorption with 5A zeolite were only recently commercialized (*17*, *18*). Kinetic separation of CH_4/CO_2 mixtures by adsorption on carbon molecular sieves has been studied by Yang and Kapoor (*1*). Different separation methods, such as physical or chemical absorption of CO_2 in a solvent, selective permeability of CO_2 through a polymeric membrane, and selective adsorption of CO_2 on a solid adsorbent, may be used to achieve this goal (*19*).

THEORY

Selective adsorption of one or more components of the feed gas mixture on a solid adsorbent is the main basis of separation in PSA processes. This produces a gas stream enriched in the less selectively adsorbed component of the feed gas. The adsorbed components are then desorbed by reducing their superincumbent partial pressures to produce a gas stream enriched

in the more selectively adsorbed component of the feed gas. The desorption process also cleans the adsorbent for reuse. Consequently, a practical PSA process consists of some or all of the following basic steps:

(1) Pressurization
(2) Adsorption
(3) Cocurrent blowdown
(4) Countercurrent blowdown
(5) Purge

Complimentary steps like pressure equalization, where a part of the void gas from one adsorbent bed is directly transferred to another bed for preservation of the lighter component in the void gas, and pressurization, whereby the adsorbent bed is brought back from its lowest pressure level in the cycle to the highest pressure level, are also practiced in various combinations. These steps are usually carried out by using two or more adsorbent beds so that when one or more beds are undergoing the adsorption steps, the other beds are carrying out the desorption and the complimentary steps of the process in order to get ready for a new adsorption step. Every bed goes through each step of the process cyclically. Thus each bed operates at steady state in a cyclic manner. A typical cycle time for the PSA process is fixed on the basis of the breakthrough curves, and it is given by

$$t = t_H + t_L + t_p \tag{1}$$

where t_H = time for adsorption step, t_L = time for blowdown step, and t_p = time for purge step. The various steps and valve sequence used in this study are shown in Table 1.

EXPERIMENTS

A schematic diagram of the apparatus is shown in Fig. 1. Each adsorption column consists of a stainless steel pipe (355 mm long, 38 mm i.d.) fitted

TABLE 1
Sequence of Valve Operation

No.	Valves open	Bed 1	Bed 2
1	2, 6	Pressurization	Cocurrent blowdown
2	2, 5, 4	Adsorption	Countercurrent blowdown
3	3, 5	Cocurrent blowdown	Pressurization
4	1, 3, 6	Countercurrent blowdown	Adsorption

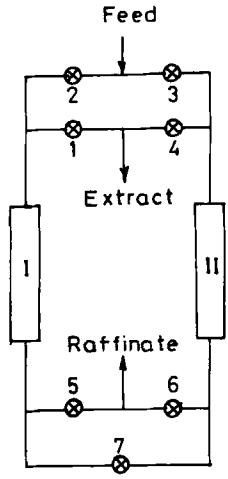

FIG. 1. Schematic diagram of PSA setup.

with a pressure transducer. SS flanges at both ends are provided with openings for gas flow. The columns are packed with adsorbent ZMS-13X/4A, manufactured by IPCL, CATAD Division. Details are included in Table 2.

Various PSA steps were carried out by use of a set of solenoid valves operated at desired cycle times by the use of a specially designed pro-

TABLE 2
Physical Parameters

Feed gas composition	66% CH_4, 34% CO_2	10% CH_4, 90% CO_2
Column length, cm	35	35
Cross-sectional area (A_{cs}), cm^2	11.401	11.401
Bed voidage	0.4	0.4
Temperature, °K	298	298
Adsorbent	ZMS-13X	ZMS-4A
Particle size	1.5–3.0 mm pellets	1.5–3.0 mm pellets
Bulk density (ρ_b), g/L	530	650
Equilibrium constant for Co_2 (K_A)	75.1	40.0
Equilibrium constant for CH_4 (K_B)	6.67	3.0
Effective diffusivity for CO_2, cm^2/s	1.25×10^{-3}	5.035×10^{-4}
Effective diffusivity for CH_4, cm^2/s	2.08×10^{-3}	8.343×10^{-4}

grammable sequential timer. The various steps of the PSA cycle were carried out as shown in Table 1. In the present work the need for a purge step was eliminated because the adsorption carried out at low pressure produced a comparatively clean bed for the subsequent cycles. Gas samples were collected and analyzed by using a gas chromatograph on the TCD mode with a Porapak-N 80/100 SS column (3.2 mm i.d., 2000 mm length) with helium as the carrier gas (25 mL/min at ambient temperature). Prior to actual PSA experiments, the following data were collected:

(1) Adsorption isotherms for pure CO_2 and CH_4 over ZMS-13X at 298 K.
(2) Adsorption isotherms for pure CO_2 and CH_4 over ZMS-4A at 298 K.
(3) Breakthrough curves for pure CO_2 and CH_4 and their mixtures over ZMS-13X/4A.

Adsorption isotherm data were obtained by using a Carlo-Erba Strumentazione DRU Mod. 804 Sorptometer.

RESULTS AND DISCUSSION

Preliminary observations of CH_4/CO_2 adsorption isotherms (Figs. 2 and 3) and calculated values of separation factors showed that ZMS-13X and ZMS-4A are good adsorbents for the selective removal of CO_2 from CH_4/CO_2 mixtures. Kinetics selectivities based on diffusivities of CO_2 and CH_4

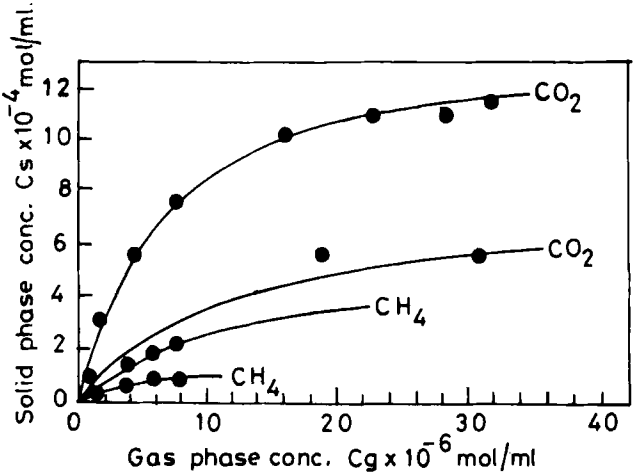

FIG. 2. Adsorption isotherm data for CO_2 and methane at 298 K.

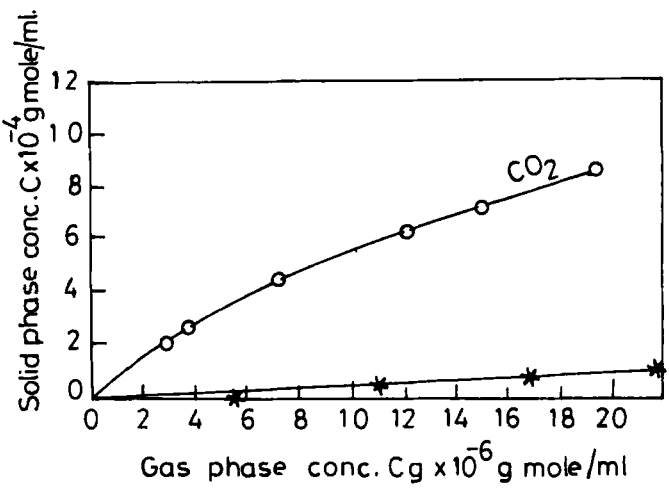

FIG. 3. Adsorption isotherms for CO_2 and CH_4 at 298 K.

for ZMS-13X and ZMS-4A were calculated to be 0.604 and 0.601, respectively.

Experimental data for breakthrough curves of pure CO_2 and CH_4 over ZMS-13X were obtained in the pressure range 1.0–4.5 kg/cm^2 and for CH_4/CO_2 mixtures in the pressure range 1.0–1.8 kg/cm^2 and flow rates of 300–1500 mL/min. The results are plotted in Figs. 4, 5, and 6.

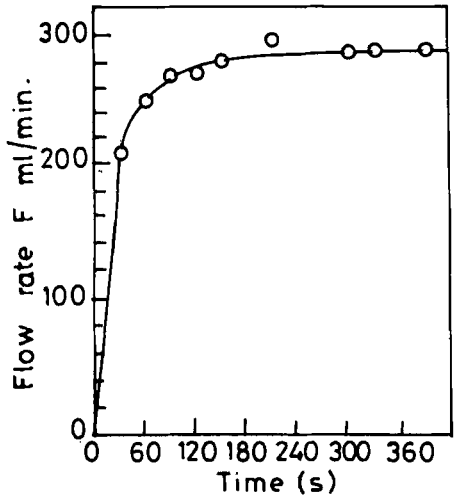

FIG. 4. Breakthrough curve for carbon dioxide at 298 K.

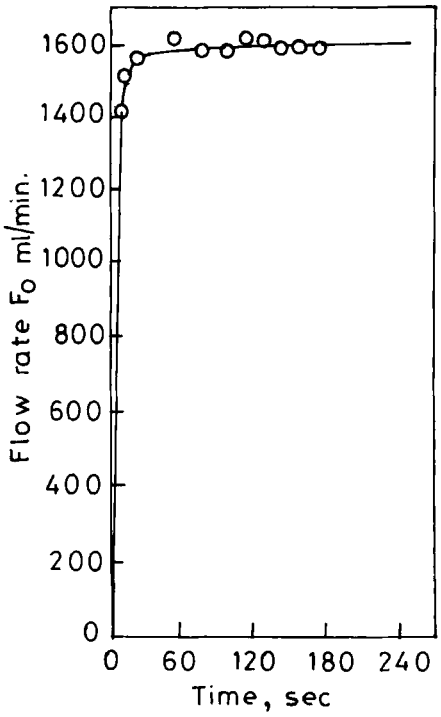

FIG. 5. Breakthrough curve for methane at 298 K.

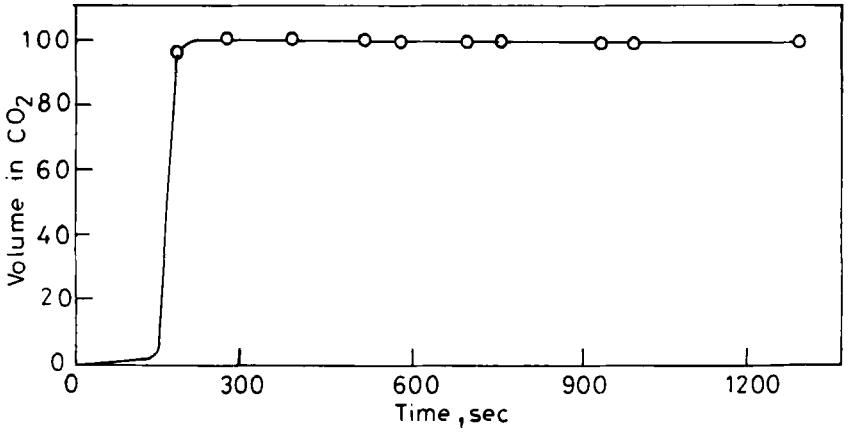

FIG. 6. Breakthrough curve for CO_2–CH_4 mixtures at 298 K.

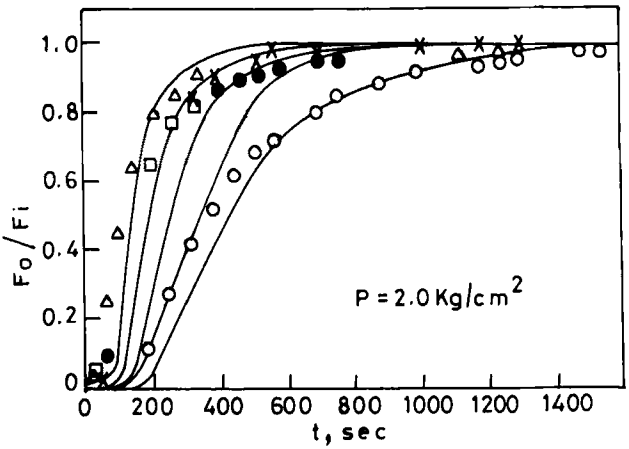

FIG. 7. Breakthrough curves for CO_2.

Breakthrough data for CO_2 and CH_4/CO_2 mixtures were collected in the pressure range 1.0–2.0 kg/cm^2 at flow rates of 600–1800 mL/min over ZMS-4A. A few breakthrough curves are shown in Figs. 7 and 8.

Breakthrough times for pure CO_2 and CH_4 and their mixtures decrease with an increase in pressure and flow rates, as shown in Figs. 4–9. Also, breakthrough time increases with an increase in CH_4 percentage in a CH_4/CO_2 mixture, as shown in Fig. 10.

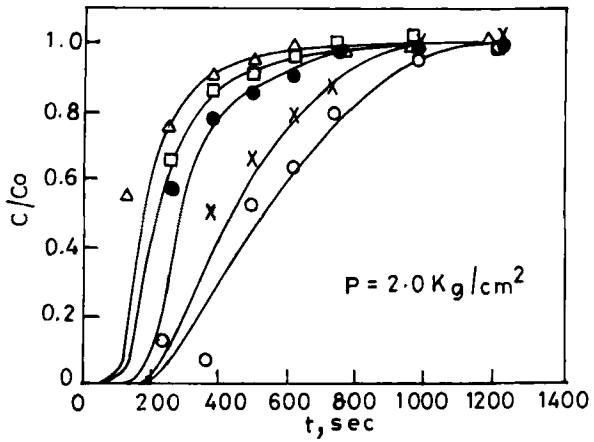

FIG. 8. Breakthrough curves for CH_4–CO_2 mixture (10% CH_4).

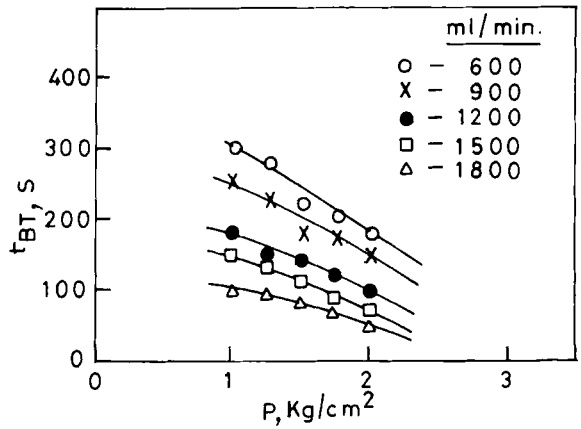

FIG. 9. Effect of pressure on breakthrough time for CH_4–CO_2 mixture (10% CH_4).

BULK SEPARATION

PSA experiments for bulk separation were performed over ZMS-13X at different P_H/P_L ratios and flow rates with a simulated biogas mixture (66% CH_4 and 34% CO_2) by fixing the step times from gas mixture breakthrough experiments. More details about the work are given in the literature (*20*). The PSA results over ZMS-13X are shown in Table 3.

The raffinate stream purity achieved on the basis of the chosen step time was more than 95% in the first cycle in all cases. The fall in CH_4 content

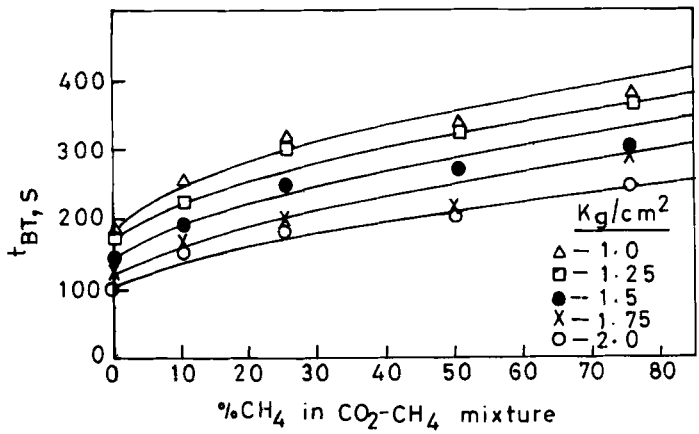

FIG. 10. Effect of CH_4 content in CH_4–CO_2 mixture on breakthrough time.

TABLE 3
Results of PSA Experiments over ZMS-13X

No.	Conditions	P_H/P_L	% CH_4 in cycle no. 1	2	3	4	5
1	$P_H = 1.2$, $P_L = 1.0$, $F = 600$	1.2	99.2	99.1	80.4	70.9	70.1
2	$P_H = 1.6$, $P_L = 1.0$, $F = 600$	1.6	95.4	83.7	80.2	77.0	76.0
3	$P_H = 1.8$, $P_L = 1.0$, $F = 600$	1.8	95.3	80.1	75.2	74.8	74.9
4	$P_H = 5.0$, $P_L = 1.0$, $F = 900$	5.0	93.2	83.2	71.5	70.9	70.8
5	$P_H = 1.6$, $P_L = 0.05$, $F = 600$	32.0	95.4	96.2	95.0	96.7	97.8
6	$P_H = 1.8$, $P_L = 0.05$, $F = 900$	36.0	96.8	94.7	97.6	97.3	97.8

in subsequent cycles is attributed to the poor CO_2 desorption at 1.0 kg/cm^2. To overcome this difficulty, the P_H/P_L ratio was increased in later experiments by lowering the blowdown pressure by vacuum. The CH_4 content obtained at higher P_H/P_L values was 95% or more in all cycles.

PURIFICATION

PSA experiments for the purification of a CH_4/CO_2 mixture (10% CH_4) were performed over ZMS-4A by fixing the step times from gas mixture breakthrough experiments. The PSA results over ZMS-4A are summarized in Table 4.

In the first cycle the purity of CH_4 in raffinate could be enhanced to 95% or more CH_4 from 10% CH_4 in the feed. The CH_4 content of the raffinate stream was higher at higher P_H/P_L ratios; i.e., when the P_H/P_L ratio was raised from 10 to 40, the CH_4 content in the raffinate increased from 71.9 to 86.3% at steady state. Beyond a P_H/P_L of 40, there was no

TABLE 4
Results of PSA Experiments over ZMS-4A

No.	Conditions	P_H/P_L	% CH_4 in cycle no. 1	2	3	4	5	6
1	$P_H = 2.0$, $P_L = 0.007$, $F = 900$	304.0	95.5	83.5	83.1	86.3	79.5	81.4
2	$P_H = 2.0$, $P_L = 0.07$, $F = 900$	30.4	97.9	90.5	89.1	88.9	89.5	88.9
3	$P_H = 2.0$, $P_L = 0.198$, $F = 900$	10.1	96.5	86.0	70.3	71.9	69.3	68.9
4	$P_H = 2.0$, $P_L = 0.1$, $F = 900$	20.0	94.9	88.6	81.2	84.8	82.3	83.7
5	$P_H = 2.0$, $P_L = 0.05$, $F = 900$	40.0	93.5	81.9	87.3	86.3	87.2	86.9
6	$P_H = 2.0$, $P_L = 0.07$, $F = 1200$	30.4	95.1	87.1	85.6	84.8	83.3	85.5
7	$P_H = 2.0$, $P_L = 0.07$, $F = 1500$	30.4	94.7	89.8	87.1	89.6	87.5	85.8
8	$P_H = 2.0$, $P_L = 0.07$, $F = 1800$	30.4	94.4	89.1	83.7	88.7	87.8	88.9

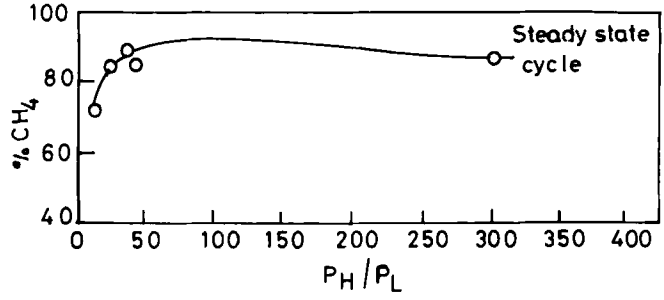

FIG. 11. Effect of P_H/P_L ratio on percent CH_4 in raffinate.

substantial gain in the purity of CH_4, as shown in Fig. 11. Experiments were carried out at a P_H/P_L ratio equal to 30.4 for flow rates of 900–1800 mL/min. There was no substantial change in CH_4 purity in the raffinate with a change in flow rates. At steady state the CH_4 content of the product obtained was 85–90% at a P_H/P_L ratio of 30.4. PSA recovery results according to the binary linear isotherm (BLI) theory (*21*) and those obtained experimentally are shown in Fig. 12. The BLI theory predicts recovery of the light component as given by

$$R_{TH} = (1 - \beta)[1 - 1/P(1 - y_F)]$$

$$= \frac{[\epsilon + (1 - \epsilon)k_B]}{[\epsilon + (1 - \epsilon)k_A]} \tag{2}$$

where $P = P_H/P_L$.

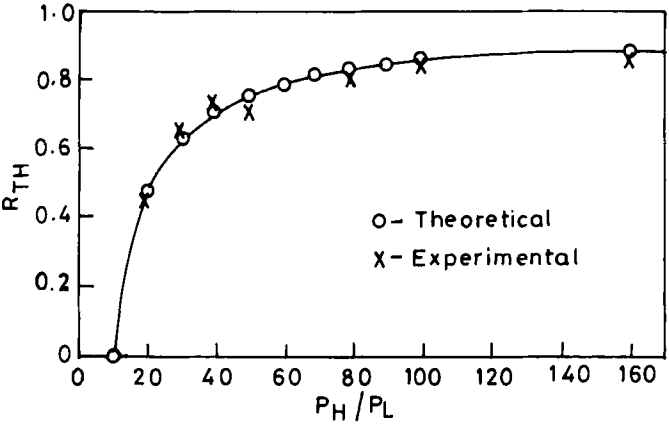

FIG. 12. Recovery of CH_4.

CONCLUSION

Experimental results have shown that PSA can be used for bulk separation as well as purification of CH_4/CO_2 mixtures. In this study a CH_4/CO_2 mixture was separated to give a product consisting of 95% or more CH_4. Purification of a CH_4/CO_2 mixture (10% CH_4) gave up to 85–90% CH_4 in the raffinate. There is little deviation in the values of percentage recovery of CH_4 as obtained experimentally and as predicted by BLI theory.

NOMENCLATURE

A_{cs}	cross-sectional area of bed (cm^2)
F	flow rate (mL/min)
K_i	slope of equilibrium isotherm Component i (dimensionless)
L	length of column (cm)
P	PSA cycle pressure ratio (dimensionless)
P_H	bed pressure during adsorption (kg/cm^2)
P_L	bed pressure during desorption (kg/cm^2)
R_{TH}	theoretical recovery
t_H	time for adsorption step (s)
t_L	time for desorption step (s)
t_p	time for purge step (s)
y_F	mole fraction of A in the feed gas

Greek Letters

β	separation factor
ϵ	adsorbent bed void fraction
ρ_b	bulk density (kg/m^3)

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