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Layered Pressure Swing Adsorption for Methane Recovery from $CH_4/CO_2/N_2$ Streams

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Abstract. In this paper we discuss the performance of Layered PSA (Layered Pressure Swing Adsorption) for methane/carbon dioxide/nitrogen separation for methane upgrading from contaminated natural gas. A four-step PSA cycle was defined using extrudates of zeolite 13X (selective for carbon dioxide) and CMS 3 K (nitrogen selective) in a layered packed bed. Ternary breakthrough curves are reported as well as PSA experiments using a stream composition of 70% CH_4–20% CO_2–10% N_2. Purity of methane of 92% with no carbon dioxide contamination and 43.5% recovery was obtained.

Keywords: kinetic separation, natural gas, Layered Pressure Swing Adsorption

1. Introduction

Natural gas upgrading is being studied in the last years for methane usage as alternative fuel with two advantages: low cost and clean burning. The low quality of natural gas is due to some contaminants like nitrogen and carbon dioxide. To introduce methane into a transportation duct, some requirements are established and low-quality gas has to be upgraded to meet pipeline grade specifications: 4% for nitrogen and 2% for carbon dioxide (corrosive gas). Adsorption technology may offer a cheaper alternative than CO_2 absorption with MEA and cryogenic distillation for nitrogen removal. Some works using layered Pressure Swing Adsorption have been reported in literature; the idea of using layered beds consisting in different sorbents has become a reality in industrial practice for multicomponent gas separation by PSA (Park et al., 1998). This specific ternary separation was also studied in a layered bed using activated carbon, zeolite 13X and carbon molecular sieve (Dong et al., 1999).

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In this work we used a layered bed of zeolite 13X (CECA) and a second layer of carbon molecular sieve CMS 3 K (Takeda Corp.). Zeolite 13X is supposed to retain carbon dioxide and CMS 3 K performs the kinetic separation of nitrogen and methane. Carbon dioxide has to be removed completely in the zeolite layer because is more strongly retained in the CMS than methane and nitrogen affecting this separation. Ternary breakthrough experiments for model calibration and PSA experiments are reported. PSA experiments are four-step Skarstrom-type comprising: pressurization, feed, counter-current blowdown and counter-current purge with product. Simulations using different ratios of zeolite 13X to CMS 3 K are also presented.

2. Experimental

Layered breakthrough curves and PSA experiments were performed in a laboratory unit already existing at the LSRE. Experimental runs were performed at 305 K $\pm$ 0.2 K. Activation of the layered column was done at 523 K overnight under nitrogen flow. This equipment consists in a single column unit, completely

Table 1. Column and commercial sample parameters used in PSA experiments.

Adsorbent	Zeolite 13X	CMS 3 K
Column length (m)	0.20	0.60
Column radius (m)	0.008	0.008
Column density (Kg/m^3)	758	701
Column porosity	0.35	0.35
Pellet diameter (m)	1.6×10^{-5}	1.8×10^{-5}
Pellet porosity	0.54	0.46
Crystal radius (m)	0.7×10^{-6}	1.9×10^{-6}
C_p adsorbent (J/Kg.K)	920	880
Wall heat mass transfer coefficient (W/m^{2}K)	50	
Overall heat transfer coefficient (W/m^{2}K)	25	

automatic requiring operator only for sampling. Collecting 11 samples taken in different steps defined by the operator we analyzed the outlet composition of a whole cycle. As each chromatogram takes five minutes, a minimum interval of twelve cycles is expected. Gas detection was done in a Chrompack gas chromatograph with a fused silica PoraPLOT Q (Varian) column using TCD (Thermal Conductivity Detector) and FID (Flame Ionization Detector) in series. The PSA equipment is connected to a computer where the individual gas flowrates and pressures at the inlet and outlet of the column are stored together with temperature measured in three different points of the column (0.20, 0.41 and 0.63 m from the inlet). A full description of this laboratory unit was done elsewhere (Da Silva, 1999). Zeolite 13X extrudates were kindly given by CECA (France) and CMS 3 K by Takeda Corp. (Japan). Some parameters relative to the column are detailed in Table 1, together with some properties of the commercial zeolite 13X and CMS 3 K used in the experiments.

3. Adsorption Equilibrium and Kinetics of Pure Gases

Experimental adsorption equilibrium of pure methane, carbon dioxide and nitrogen was performed in a magnetic suspension microbalance (Rubotherm, Germany) operated in closed system using zeolite 13X extrudates (Cavenati et al., 2004) and CMS 3 K. Adsorption equilibrium of CH_4, CO_2 and N_2 at 308 K in both adsorbents is shown in Fig. 1. The solid lines correspond to the multisite Langmuir model (Nitta et al., 1984) using parameters shown in Table 2. The saturation capacity (q_{mi}) and the number of neighboring sites (a_i) are only fitting parameters and do not have specific physical meaning. Carbon dioxide is the most adsorbed gas in both samples.

Diffusivity parameters of pure CH_4, CO_2 and N_2 were also determined in by differential uptake curves (Cavenati et al., 2004). In the CMS sample, diffusion was shared by micropore resistance and a barrier resistance in the mouth of the micropores. The diffusion of methane in CMS is very slow when compared to the other gases.

The micropore and barrier coefficients have an exponential dependence with temperature described by:

$$\begin{aligned} D_{c,i} &= D^o_{c,i} \cdot \exp(-E_{A,i}/R_g T) \\ k_{B,i} &= k^o_{B,i} \cdot \exp(-E_{B,i}/R_g T) \end{aligned} \tag{1}$$

where D^o_c and k^o_B are the pre-exponential terms and E_A and E_B are the activation energy of micropore diffusion

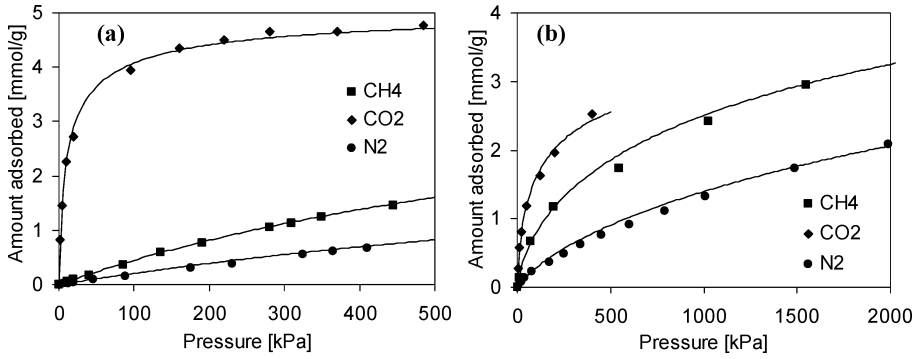

Figure 1. Adsorption equilibrium of methane (■), carbon dioxide (♦) and nitrogen (●) on zeolite 13X (a) and CMS 3 K (b) at 308 K. Solid lines are simulated multisite Langmuir model.

Table 2. Adsorption equilibrium and kinetic parameters for CH_4, CO_2 and N_2 in zeolite 13X and CMS 3 K at 308 K.

Gas	q_{mi}/(mol.kg^{-1})	k_i^0/kPa^{-1}	$(-\Delta H_i)$/(kJ.mol^{-1})	a_i	D_c/r_c^2 (s^{-1})	k_b (s^{-1})
			Zeolite 13X			
CH_4	28.871	4.34×10^{-7}	15.675	8.136	2.3×10^{-8}	
CO_2	17.901	3.20×10^{-11}	54.729	13.120	3.0×10^{-14}	
N_2	29.676	1.79×10^{-7}	15.716	7.917	1.0×10^{-9}	
			CMS 3 K			
CH_4	11.7973	2.48×10^{-10}	38.947	6.303	2.33×10^{-6}	1.0×10^{-4}
CO_2	8.9742	1.72×10^{-8}	33.674	8.287	4.99×10^{-4}	6.4×10^{-3}
N_2	10.6234	6.57×10^{-7}	15.930	7.000	1.05×10^{-3}	–

and the activation energy of surface barrier resistance. These parameters are also detailed in Table 2.

As a first approximation in PSA modelling we will consider these diffusion coefficients invariant with concentration. Also mass transfer kinetics was described by a bi-LDF approximation for macropore-micropore resistances. The LDF constants are calculated by:

$$K^C_{\mathrm{LDF},i} = \frac{1}{1/k_{B,i} + r_c^2/15D_{c,i}} \quad K^P_{\mathrm{LDF},i} = \frac{15D_{p,i}}{R_p^2} \quad (2)$$

4. Ternary Layered Breakthrough Curves; Model Calibration

For PSA modeling and simulation it is common practice to start from pure component gas adsorption parameters and simulate the mixture behavior. Even though considering that the adsorption behavior of the mixture does not deviate from multicomponent predictions, there are many estimated heat and mass transport parameters that have to be checked and/or calibrated. For this purpose a set of four ternary breakthrough experiments were performed at the same temperature. Total gas flowrates were varied from 0.9 to 1.35 SLPM. As there is a continuous flow of nitrogen in the column, prior to each measurement, a pure flow of methane was passed for 1 hour in order to desorb nitrogen from both adsorbents. Then this stream is switched to the ternary feed composed by 70% of methane, 20% of carbon dioxide and 10% of nitrogen. The total bed length is 0.8 m. The layer of zeolite 13X is in the initial 0.2 m while the rest is CMS 3 K. An example of these ternary breakthrough curves is shown in Fig. 2. Concentration of gases at the outlet of the column and temperature in the three different points of the column are shown. Note that temperature fluctuations in the zeolite adsorbent due to carbon dioxide adsorption are much higher than in the case of CMS 3 K. Solid lines in these figures are the model using the bi-LDF approximation, axially dispersed flow, Ergun equation for pressure drop and energy balances in the gas, solid and column wall (Da Silva, 1999). The model successfully described the data and based in these curves the heat parameters mentioned in Table 1 were obtained. In Fig. 2 we also show the simulation of the concentration of each gas at the outlet of the zeolite 13X layer that cannot be experimentally measured.

5. Layered Pressure Swing Adsorption: Experiments and Simulation

This layered bed PSA has the specific purpose of separating carbon dioxide in the first zeolite 13X layer by large difference in adsorption equilibrium isotherms and to perform the kinetic separation of methane and nitrogen in the CMS 3 K layer by partial size exclusion of methane from the micropores. Also if carbon dioxide passes through the CMS layer it adsorbs more strongly than nitrogen affecting its separation from methane. Several experiments were performed with the aim of obtaining pipeline grade methane starting from a stream of 20% of carbon dioxide and 10% of nitrogen.

Starting conditions were the column filled with methane (flow of one hour prior to experiment start) at 120 kPa. Overall gas flowrate in the pressurization and feed steps was 1.26 SLPM while 0.51 SLPM of pure methane was used in the purge. By default, blowdown pressure was 10 kPa, although other experiments

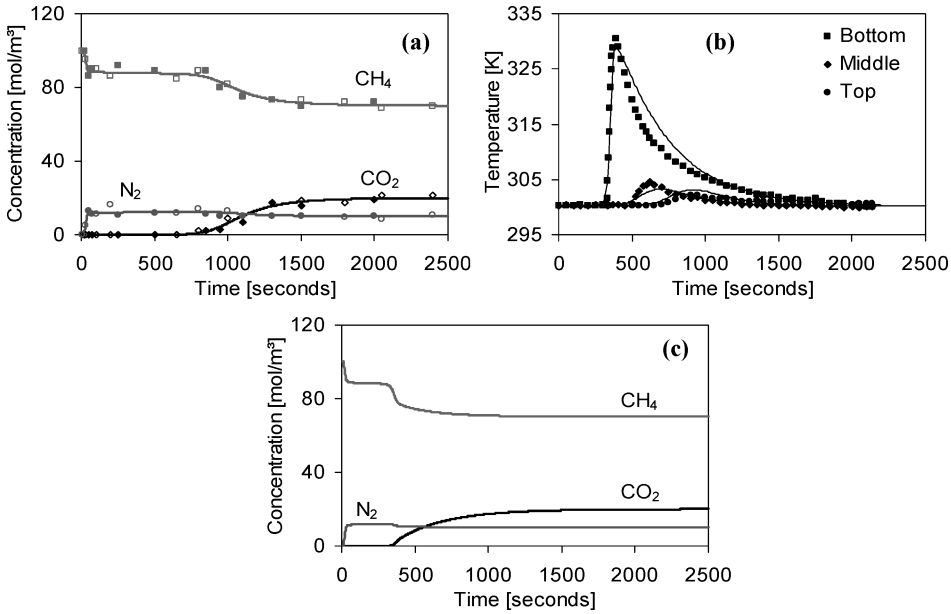

Figure 2. Ternary breakthrough curve of 70% CH_4, 20% CO_2 and 10% N_2 in a layered bed of zeolite 13X (0.2 m) and CMS 3 K (0.6 m) at 300 K with a total gas flowrate of 1.16 SLPM: (a) concentration of gases at the end of the column; (b) temperature profile in three different points (0.20, 0.41 and 0.63 m from inlet); (c) simulated concentration of gases at the end of the 13X layer.

with pressures around that value were performed. All the experimental runs are presented in Table 3. In that table results of simulations with different ratios of zeolite 13X to CMS 3 K are presented. To describe a PSA experiment we will use run 5 as example. In Fig. 3 the temperature in the three different positions of the column (0.20, 0.41 and 0.63 m) in cyclic steady state (CSS) are shown. The first thermocouple was inserted in the contact point of both adsorbents. If there is some particle migration, some errors may happen in that point because gradients of temperature are large, as mentioned by the simulated values in 0.195 and 0.20 m. Temperature in the large portion of the CMS layer is almost constant in all the experiment. The pressure profile at the end of the column and the molar flowrate are plotted in Fig. 4. There is a small variation of pressure at the beginning of the purge step because the vacuum pump used has a certain delay in retire the methane input.

Note that in this case some carbon dioxide passes to the CMS layer. The amounts of methane and carbon dioxide adsorbed in the column in cycle 50 are also plotted in Fig. 5. The process has attained the cyclic steady state by cycle 50. Nitrogen separation in this case suffers from two major problems. First, carbon dioxide passed to the CMS bed. The other problem is inherent to the adsorbent. Although the diffusivity of methane is very small, by making many cycles, methane is

Table 3. Performance parameters of experimental runs together with blowdown pressure, adsorbent layer ratio and step times.

Run	P_{low} (kPa)	13X/CMS	t_{press} (s)	t_{feed} (s)	t_{blow} (s)	t_{purge} (s)	Purity (%)	Recovery (%)
1	8	0.25	55	20	60	40	90.5	41.4
2	10	0.25	55	20	60	40	89.5	41.7
3	15	0.25	55	20	60	40	88.2	42.1
4	10	0.25	55	20	60	40	88.7	41.1
5	10	0.25	55	40	60	40	84.9	61.9
6	10	0.375	55	40	60	40	92.5	54.5
7	10	0.5	55	40	60	40	89.1	43.5

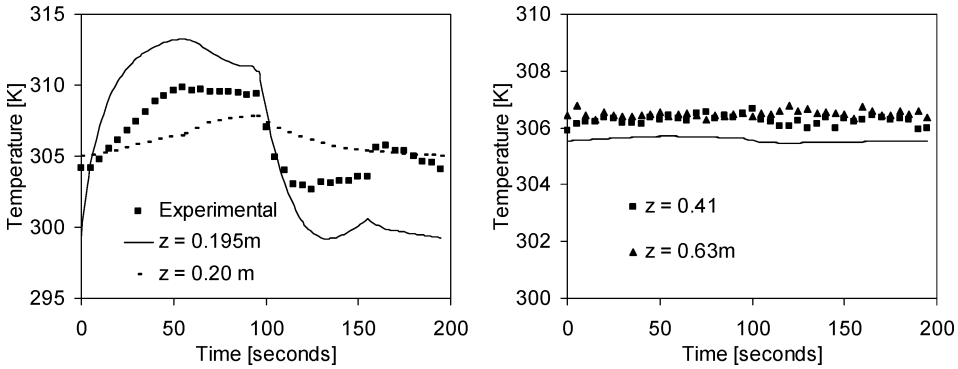

Figure 3. Temperature profiles inside the column at cycle 50 (cyclic steady state) at 0.20, 0.41 and 0.63 m for run 5 (see Table 3 for details). Solid lines are simulations of the experiment.

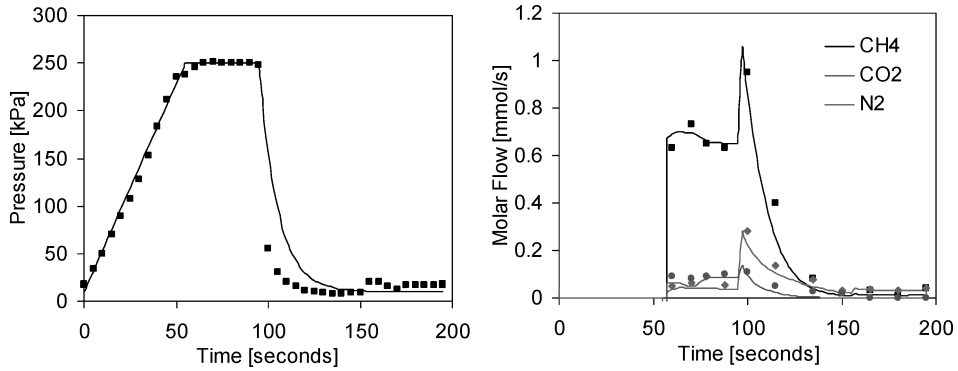

Figure 4. Pressure and molar flowrate of gases at the outlet of the column in cycle 50 (cyclic steady state) for run 5 (see Table 3 for details). Solid lines are simulation of the experiment.

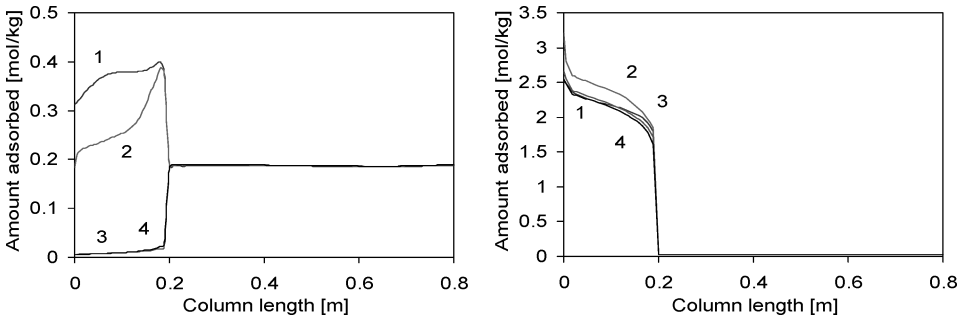

Figure 5. Methane and carbon dioxide concentration profiles inside the column at the end of each step in cyclic steady state: 1. pressurization; 2. feed; 3. counter-current blowdown; 4. purge.

adsorbing more displacing the amount of nitrogen adsorbed to very low values.

In order to improve the purity of methane, we have made simulations with larger zeolite 13X layers as mentioned in Table 3. Using a layer of 0.3 m of zeolite 13X, carbon dioxide was completely removed and nitrogen separation was improved. Even though, purity was 92.5% by nitrogen contamination. No carbon dioxide exits the column with methane. If the layer of zeolite 13X is increased to 0.4 m (half bed) the purity of the stream diminishes because the amount of CMS is not enough to split methane and nitrogen,

suggesting the existence of an optimum ratio of adsorbents.

6. Conclusions

Layered Pressure Swing Adsorption for methane upgrading using zeolite 13X and Carbon Molecular Sieve 3 K was investigated. Carbon dioxide was completely removed from a 20% starting contamination although 10% nitrogen contamination was diminished to 7% indicating the need of a more selective adsorbent for nitrogen/methane separation. Simulation of different ratio of zeolite 13X to CMS 3 K suggests the existence of a point where maximum purity is obtained. The best result obtained by this study is a cycle with methane purity of 92.5% and almost 55% recovery. This work suggested the attractive possibility of methane purification using a single unit to remove two different contaminants. Even though, an extensive set of variables have to be optimized to achieve better process performance and/or new more selective adsorbents have to be employed.

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