

CARBON MOLECULAR SIEVES FOR HYDROCARBON SEPARATIONS BY ADSORPTION

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Introduction

This work presents the use of carbon molecular sieves (CMS) in Pressure Swing Adsorption (PSA) units focusing on two energy-consuming separations: propane-propylene and methane-nitrogen.

Propane-propylene separation is the most difficult separation practiced in petrochemical industry commonly performed at 243 K (cryogenic distillation) and 30 psig in columns containing over 200 trays. Adsorption has already been proposed for this separation [1]. Much of the literature published in this area was devoted only to adsorbent characterization. Most of the works dealt with zeolites and π -complexation adsorbents [2-3] and only a few with carbonaceous materials but activated carbons [4] and CMS [5-6] had poor selectivity towards propylene. We have previously published adsorption equilibrium and kinetics of pure gases onto CMS 4A from Takeda [7]. This adsorbent did not have high equilibrium selectivity, but large difference in adsorption kinetics was observed indicating the possibility of kinetic separation to be performed.

Methane-nitrogen separation appears in the context of natural gas for fuel usage. This separation is practiced by cryogenic distillation when large flowrates are available and helium can be obtained as a byproduct. In this topic much of the literature was also concerned with adsorbent characterization [3,5,9-11] but more works can be found specifically on PSA processes using carbon molecular sieves [12-13]. In these works, poor purity was obtained because the feed has high nitrogen molar fractions (>40%) for landfill gas applications. We already measured adsorption characteristics of pure methane and nitrogen on CMS 3K from Takeda [14], which has presented a good kinetic selectivity towards nitrogen, even when methane is the most adsorbed gas.

The challenging issue of a PSA process for these separations is that the size of the molecules involved is very close and they have very similar energetic characteristics. The use of CMS with a correct average pore size diameter can allow the partial exclusion of the larger molecules (methane and propane) with selective adsorption of propylene and nitrogen. The main difference between these two separations is that in the methane-nitrogen case we are proposing a cycle that allows methane recovery as a top product avoiding the recompression stage required in cryogenic distillation. In the case of propane-propylene separation, propylene is the heavy compound (most adsorbed) being inevitably recovered in the blowdown step at low pressure. For this reason, two different cycles were proposed accounting for different needs in each specific separation.

The modeling of a kinetically driven PSA separation is rather complex, particularly in the case of non-isothermal bulk separation [8]. The cycle for methane-nitrogen separation is of a Skarstrom type comprising pressurization, feed (500 kPa), counter-current blowdown (50 kPa) and counter-current purge with product (50 kPa). We have used a feed with 90% of methane and 10% of nitrogen, as an example and temperature of the feed, purge and pressurization streams were 308 K. In the case of propane-propylene separation, we used a five-step cycle that consists in: pressurization, feed (250 kPa), rinse (250 kPa), intermediate blowdown (50 kPa) and counter-current low-pressure blowdown (10 kPa). Experiments were done with a 52/48 (molar ratio) propylene-propane mixture at 373 K not because is the optimal temperature but to ensure that they will work inside the temperatures where adsorption of pure gases was measured (343-423 K).

Experimental

Carbon molecular sieves used are 3K and 4A for methane-nitrogen and propane-propylene separations, respectively, both kindly provided by Takeda Corp. (Japan). Adsorption equilibrium and kinetics of pure gases in these adsorbents have been previously reported [7,14].

The PSA laboratory unit already existing at the LSRE is a single column unit, completely automatic requiring attendance only for sampling. Collecting 11 samples taken in different steps defined by the operator we analyze the outlet composition of a hole cycle. As each chromatogram takes three minutes in the case of propane-propylene, a minimum interval of six cycles is expected. The 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 (0.17, 0.40 and 0.65 m from the inlet). The complete equipment set-up was reported elsewhere [15]

Air Liquide provided all gases used for this study: methane N35, nitrogen N50, propane N35 and propylene N25.

Modeling and simulations

In this work, the multisite Langmuir model [16] was used for the description of pure component adsorption equilibrium data previously reported. This model can be expressed as:

$$\left(\frac{q_i^*}{q_{\max,i}} \right) = K_i P y_i \left[1 - \left(\frac{q_i^*}{q_{\max,i}} \right) \right]^{a_i} \quad (1)$$

where $q_{\max,i}$ is the maximum amount adsorbed of component i , a_i is number of neighboring sites occupied by a molecule of component i and K_i is the adsorption constant which has an Arrhenius exponential temperature dependence as $K_i = K_i^0 \exp(-\Delta H_i / R_g T_s)$ where K_i^0 is the adsorption constant of component i at the limit of $T \rightarrow \infty$ and $-\Delta H_i$ is the isosteric heat of adsorption of component i at zero coverage [17]. The parameters used for the fitting are shown in Table 1. The saturation capacity

of each component is imposed by the thermodynamic constraint $a_i q_{mi} = \text{constant}$ [17]. The advantage of this model over the Toth model previously used is its direct (theoretical) extension to multicomponent mixtures, presenting also a very good fitting of single component isotherms.

Table 1 – Adsorption equilibrium and kinetic parameters of pure gases

Gas	$q_{\text{max}i}$ (mol/kg)	K_i^0 (kPa ⁻¹)	a_i (-)	$-\Delta H_i$ (kJ/mol)	$D_{c,i}^0/r_c^2$ (s ⁻¹)	$E_{A,i}$ (kJ/mol)	$k_{b,i}^0$ (s ⁻¹)	$E_{B,i}$ (kJ/mol)
CH ₄	11.797	2.48×10^{-10}	6.303	38.947	$D_c(308\text{K}) =$		$k_B(308) =$	
N ₂	10.623	6.57×10^{-7}	7.000	15.930	356.35	34.732	6.40×10^{-2}	5876.8
C ₃ H ₆	2.197	6.10×10^{-7}	4.700	93.931	1.0441	14.507	-	-
C ₃ H ₈	2.065	3.33×10^{-6}	5.000	32.088	0.3087	23.086	-	-

The adsorption kinetics of pure gases at infinite dilution was also previously reported [7,14]. In the case of propane and propylene in CMS 4A the mass transfer was controlled by micropore diffusion while in the case of methane and nitrogen, micropore diffusion together with a film mass transfer in the mouth of the micropores controls mass transfer. The micropore and film mass transfer coefficients have an exponential dependence with temperature described by:

$$D_{c,i} = D_{c,i}^0 \cdot \exp(-E_{A,i}/R_g T) \quad k_{B,i} = k_{B,i}^0 \cdot \exp(-E_{B,i}/R_g T) \quad (2)$$

where D_c^0 and k_B^0 are the pre-exponential terms and E_A and E_B are the activation energy of micropore diffusion and the activation energy of surface barrier resistance. As a first approximation 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:

$$K_{LDF,i}^C = \frac{1}{\frac{1}{k_{B,i}} + \frac{r_c^2}{15D_{c,i}}} \quad K_{LDF,i}^P = \frac{15D_{p,i}}{R_p^2} \quad (3)$$

For the simulations of the PSA behavior, mass, energy and momentum balances were solved simultaneously using the gPROMS (PSA, UK) package. Details of the model were published elsewhere [15]. The model was solved using orthogonal collocation method on finite elements (OCFE) with 25 finite elements and two interior collocation points in each element of the adsorption bed.

Results and Discussion

We will start with the propane-propylene separation. For the correct modeling of a non-isothermal bulk PSA process, many parameters have to be estimated (axial dispersion, film mass transfer coefficient and energetic parameters) and checked. These parameters, as well as the validity of the model (bi-LDF) were verified by means of

binary breakthrough experiments in the column where PSA experiments were performed. As an example of this “model calibration”, molar flowrate at the exit of the column and temperature in 3 points of the column from a binary breakthrough curve are shown in Figure 1. Note that temperature increase due to adsorption is very high and cannot be ignored. Temperatures of the bottom and middle correspond to the temperature of the pellets while the top temperature was measured on the column wall. Also, the temperature excursion due to propane and propylene adsorption can be separately observed. Another information is that the temperature waves travel at a similar velocity than the concentration waves. The lines in Figure 1 correspond to the model. The conditions of the breakthrough curve reported in Figure 1 together with relevant column and adsorbent properties are shown in Table 2.

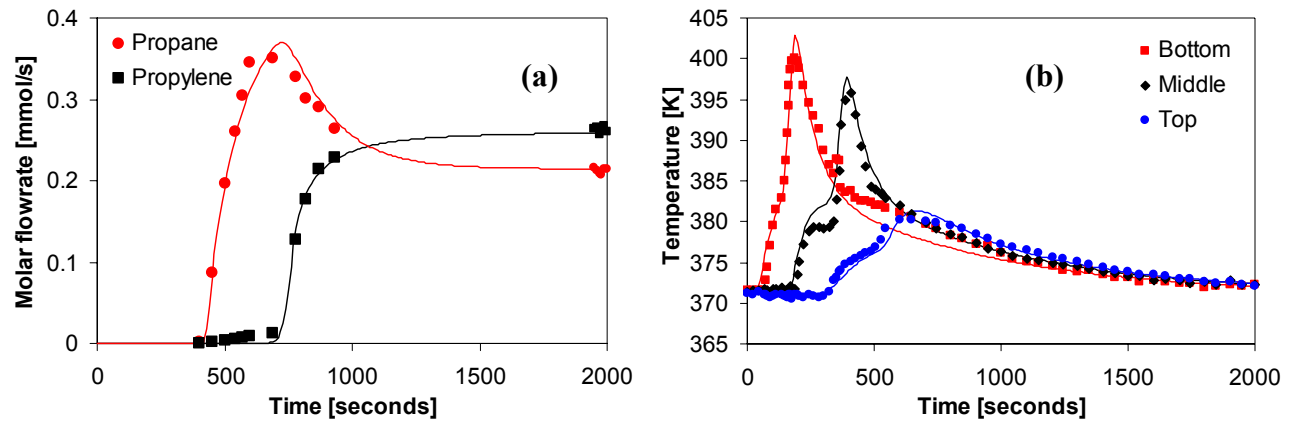


Figure 1. Binary propane-propylene breakthrough curve on CMS 4A at 373 K and 250 kPa: (a) molar flowrate and (b) temperature at 0.17, 0.4 and 0.65 m of entrance

Table 2 – Experimental conditions for breakthrough experiments, column and adsorbent properties			
Temperature, K	373	Column radius, m	0.0105
Pressure, kPa	250	Column density, kg/m ³	678.3
Flowrate, SLPM	0.70	CMS heat capacity, J/kg.K	880
C ₃ H ₆ molar fraction	0.52	Particle density, kg/m ³	900
C ₃ H ₈ molar fraction	0.48	Pellet porosity	0.315
Column length, m	0.83	Pellet tortuosity	2.0
Column porosity	0.246	Pellet radius, m	1.1x10 ⁻³

Once verified that the model that uses pure component parameters (determined in separated experiments) can correctly describe the column behavior with the binary mixture, we can proceed to the PSA modeling. As this process involves five steps we have initially fixed the operative variables (temperature, step pressures, flowrate and molar fractions) and concentrate in the effect of different step times in the overall performance of the unit trying to maximize purity and recovery of propylene. The starting condition is the column filled with nitrogen (considered inert) at 373 K and 120 kPa. Many of the simulations performed are shown in Table 3. Initially, some of the parameters (intermediate and counter-current blowdown) were based on previous work

with zeolite 4A. In this case, when the intermediate blowdown step is used, instead of a further enrichment of propylene in the column (step for pre-purification of the product), much of the propylene is lost. For this reason, this step was initially diminished and further omitted.

Run	t_{pres} , s	t_{feed} , s	t_{rinse} , s	$t_{bint-blow}$, s	t_{ccblow} , s	C_3H_6 purity (%)	C_3H_6 recovery (%)
1	100	100	75	40	220	80.8	22.5
2	100	100	75	40	300	80.3	26.1
3	100	150	75	40	300	81.3	19.8
4	100	100	75	10	300	80.0	53.0
5	100	100	90	10	300	82.2	40.8
6	100	100	90	0	300	83.6	84.4
7	100	75	75	0	300	78.8	95.3
8	100	125	25	0	300	71.9	93.1
10	100	125	25	0	250	72.3	92.4
11	100	125	50	0	300	78.1	94.8
12	100	100	75	0	300	80.8	95.7

* Conditions: Pressure feed: 250 kPa; Intermediate blowdown pressure: 50 kPa; Counter-current blowdown pressure: 10 kPa;

Total feed flowrate: 0.7 SLPM; Rinse with pure propylene. Column and adsorbent properties detailed in Table 4.

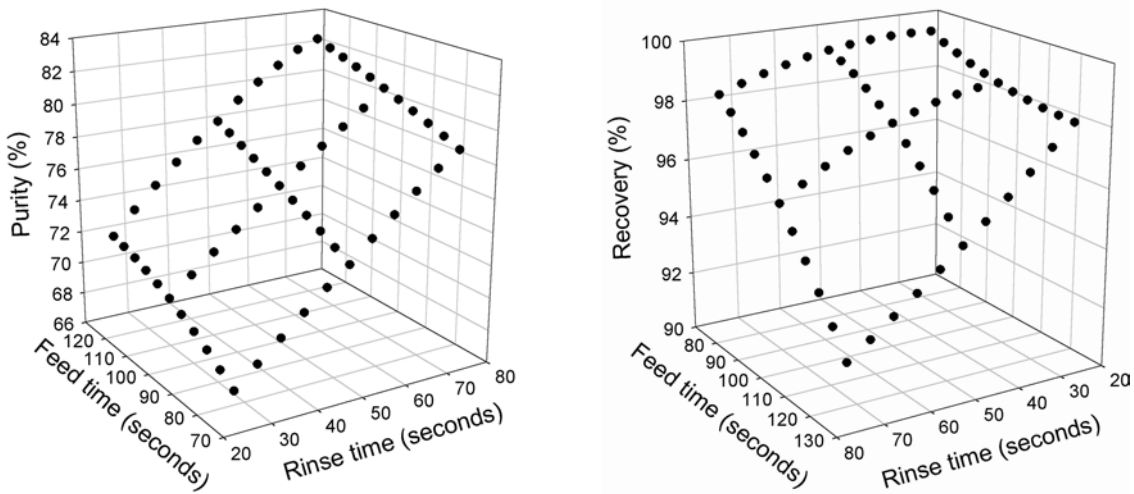


Figure 2. Performance parameters of C_3H_6/C_3H_8 PSA cycle for different feed and rinse step times: purity and recovery. $t_{press} = 100s$; $t_{ccblow} = 300s$.

The effect of blowdown time is not very important in terms of purity (less than 0.5%) but has larger influence in the recovery (4% difference between runs 1 and 2). For this reason was kept at 300s. For a better visualization of the effects of feed and rinse timings we show in Figure 2 the purity and recovery variations when $t_{press} = 100s$ and $t_{ccblow} = 300s$.

From Table 3 we took simulation 12 as an example to perform in the PSA unit. The molar flowrate of the first cycle and of the cyclic steady state (CSS) are shown in Figure

3. Temperature histories at the bottom, middle and top of the column are also plotted in this figure. The solid lines correspond to the model employed. Cyclic steady state was reached after 20 cycles. As can be seen, the model fits the experiment very well confirming the validity of conclusions taken from simulations presented in Figure 2 and Table 3. The purity around 80% obtained in all the simulations is far away of the 99.5% required for polymer degree propylene but operating conditions were not optimized. Also an important issue is the temperature excursion of around 30 K in one cycle. This variation has to be diminished for a better equipment performance.

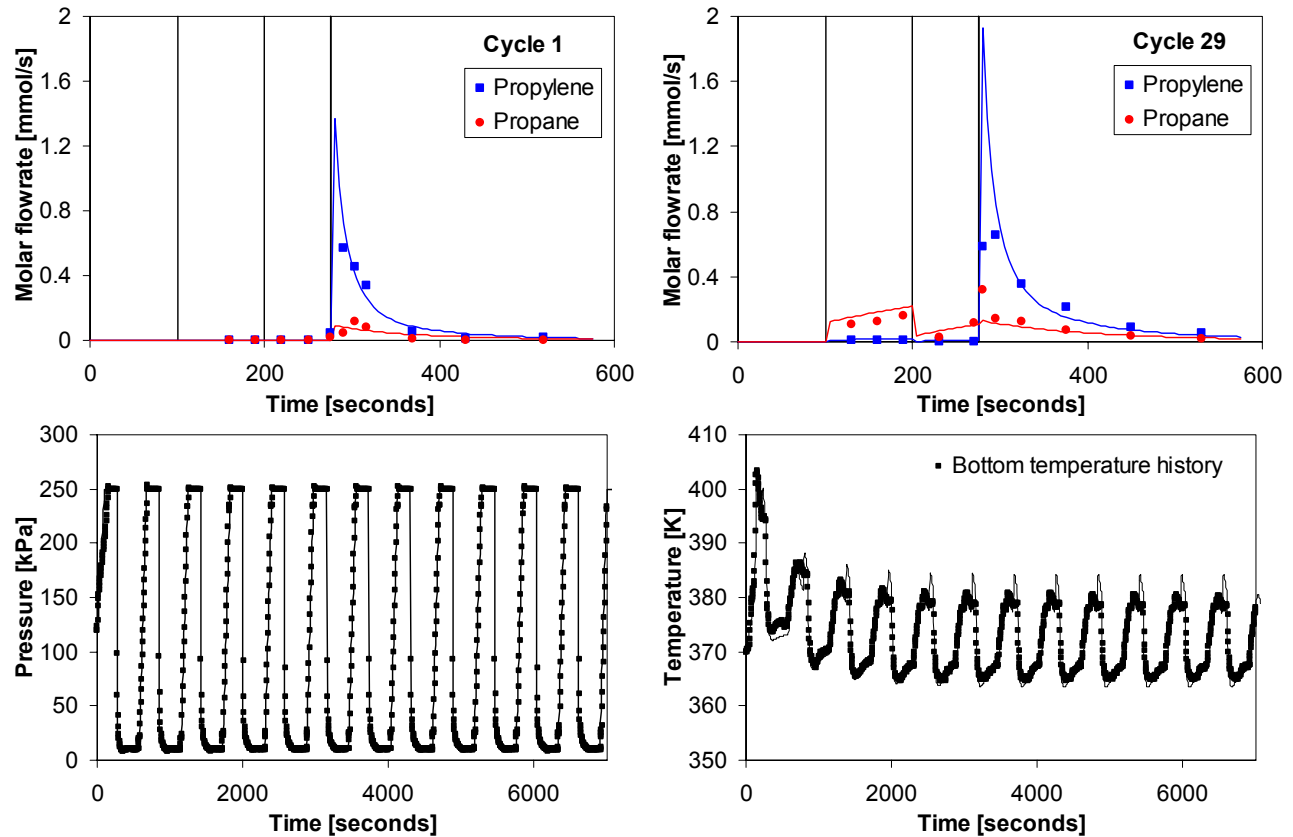


Figure 3. PSA experiment of propane-propylene separation (for conditions see simulation 12, Table 5): molar flowrate in the first cycle and in cyclic steady state, history of pressure at the exit of the column and temperature in the bottom thermocouple.

Another topic of this article deals with the methane-nitrogen separation. In this case, methane is the most adsorbed gas that is being partially excluded from the micropores, giving an effective kinetic selectivity towards nitrogen [14]. A four-step Skarstrom type cycle: counter-current pressurization with product, feed (500 kPa), counter-current blowdown (50 kPa) and counter-current purge with product (50 kPa) was simulated based on pure component behavior. The bed length in this case was 0.75 m. Temperature was fixed at 308 K, molar fractions in the feed stream are 0.1 for nitrogen balanced by methane and total flowrate of feed and purge was fixed in 0.5 SLPM (standard liters per minute). Pressurization was done with 1.2 SLPM of pure methane. Many simulations were performed varying the step timings to obtain good performance

conditions with the fixed parameters mentioned above, as shown in Table 4. As an example, we show in Figure 4 the molar fraction of methane and nitrogen at the end of each step when cyclic steady state was achieved corresponding to simulation 2 (pressurization: 60s; feed: 120s; blowdown: 60s; purge: 60s). The temperature variation in the entire cycle is not higher than one Kelvin degree indicating that the process can be considered as isothermal. In this case due to the very low diffusivity of methane, the CSS is reached only after 200 cycles requiring large computing time (near 10 hours in a Pentium IV with 1.00 MB RAM memory). Pipeline methane (less than 4% nitrogen) was obtained in all the simulations, although recovery is around 30%. Different parameters (feed and blowdown pressures as well as temperature) may result in better methane recovery.

Run	t_{pres} , s	t_{feed} , s	t_{blow} , s	t_{purge} , s	CH ₄ purity (%)	CH ₄ recovery (%)
1	60	120	120	60	97.73	14.39
2	60	120	60	60	97.63	14.61
3	60	140	60	60	96.79	26.86
4	60	120	90	60	97.69	14.49
5	60	140	90	60	96.85	26.45
7 ^a	60	140	60	60	96.58	28.81

* Conditions: Pressure feed: 500 kPa; Blowdown pressure: 50 kPa; Total feed flowrate: 0.5 SLPM; Pressurization flowrate: 1.0

SLPM; Bed Length: 0.75 m. a) Blowdown and purge pressure: 1.0 bar

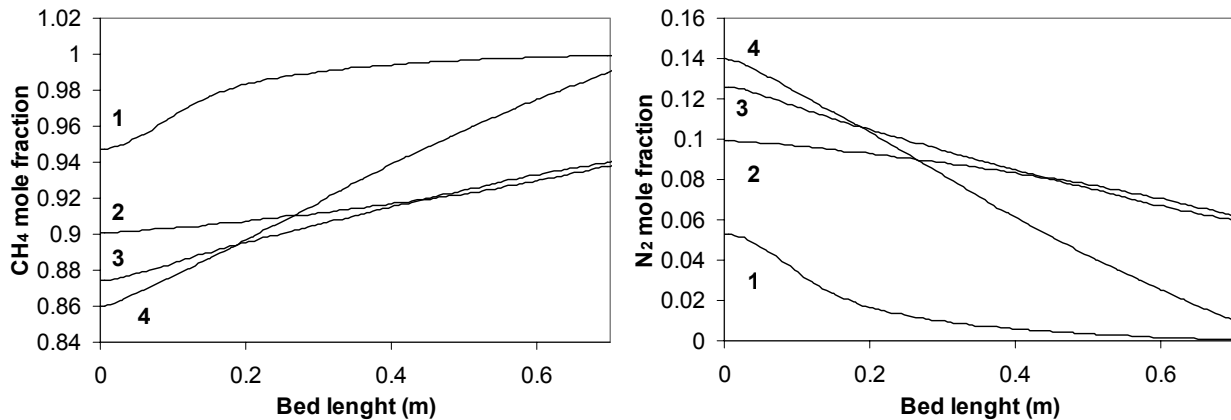


Figure 4. Methane and nitrogen profiles inside the column at the end of each step (1-pressurization, 2-feed, 3-blowdown, 4-purge)

Conclusions

Two difficult separations, methane-nitrogen and propane-propylene, were studied using Pressure Swing Adsorption, PSA, as an alternative process to cryogenic distillation. Two different cycles were proposed for these separations and step time effect were evaluated in PSA performance (purity and recovery) at constant operative variables. In the case of propane-propylene, starting from a mixture 48/52 C₃H₈-C₃H₆ we obtained by

simulations purities around 82% with 87% recovery and make experiments to confirm these results. For the case of methane-nitrogen with a mixture of 90% methane balanced with nitrogen only simulation studies were performed and purity higher than 96.5 was obtained with maximum recovery of methane around 30%. The results obtained here, although not optimized, indicates that PSA can be applied to these separations, although better conditions should be found to achieve higher recovery of methane and higher propylene purity.

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