

CARBON MOLECULAR SIEVES PRODUCTION AND PERFORMANCE ASSESSMENT IN CO₂ SEPARATION BY SELECTIVE ADSORPTION

Mădălina VĂDUVA¹, Vasile STANCIU²

Sitele moleculare din carbon (CMS) sunt adsorbanți carbonici de mare importanță. Această lucrare prezintă rezultatele studiului privind prepararea sitelor moleculare din carbon și modificarea structurii porilor. Proprietățile sitelor moleculare ale varietăților de cărbuni au fost studiate prin măsurarea capacității de adsorbție dinamică a dioxidului de carbon utilizând sistemul PSA (adsorbția la presiune variabilă). De asemenea, este prezentată separarea dioxidului de carbon din amestecul de N₂ – CH₄ – CO₂ și din gazul natural pe CMS preparați în laborator, proces bazat pe ciclul PSA..

Carbon molecular sieves (CMS) are carbonaceous adsorbants of increasing importance. This paper describes the results of the study concerning the carbon molecular sieves preparation and modification of the pore structure. Molecular sieving properties of various carbons were studied by measuring the dynamic adsorption capacity for carbon dioxide under pressure swing adsorption (PSA) conditions. Separation of carbon dioxide from N₂ – CH₄ – CO₂ mixture and from landfill gas on CMS prepared in a laboratory unit designed for this purpose based on PSA cycle is also reported.

Keywords: molecular sieves, adsorption, chromatography, coal.

1. Introduction

Carbon molecular sieves (CMS) belong to activated carbons family and can be obtained by various procedures leading to pores narrowing to smaller sizes than 10 Å. Pores narrowing increases diffusion speed for smaller molecules as compared to the larger, resulting in a fast gas separation caused by the differences in molecules sizes[1-6].

CMS preferentially retain O₂ from air by its rapid penetration into micro pores, thus enriching or separating N₂ from the air. In addition, other gas separations such as CO₂ and CH₄ separation are also achieved by CMS use [6-11].

The speciality literature [7-11] shows that CMS preparation is based on one of the following procedures:

¹ Prof., Dept. of Physics, "Ferdinand I" High School, Râmnicu Vâlcea, România;

² Ph.D Researcher, National R-D Institute for Cryogenics and Isotopic Technologies, Râmnicu Vâlcea, Romania

- controlled thermal treatment of carbonaceous substrate in inert gas atmosphere;
- impregnation of carbonaceous substrate with an organic polymer of >400 molecular weight, followed by a controlled thermal treatment of the polymer and its carbonisation. As a result of this process, the macro porous structure of carbonaceous substrate is blocked without diminishing micro pores retention capacity or diffusion through micro pores, specific for the substrate;
- organic substances cracking leading to the finely divided carbon deposit into carbonaceous substrate pores. The pores diameter can be adjusted to the desired sizes by modifying the treatment with cracking hydrocarbons.

Consequent to our own preoccupations in obtaining selective adsorbents of CMS type and in using them to separate gases, this paper presents:

- the achievement of carbons with molecular sieving properties for CO₂ separation from the landfill gas by selective adsorption;
- the results obtained regarding adsorption features on CO₂ separation;
- improved procedures to obtain CMS and assess performances on selective adsorption by use of PSA process.

We mention that the researches were conducted in an institute with mainly applicative activity and the specific parameters of CO₂ separation were established only for the selective adsorption period up to the breakthrough point.

2. Experimental

2.1. Preparation of carbonaceous substrate (CMS-HP Initial)

The speciality literature [7-11] shows that the raw materials for CMS preparation are deposit carbons (peat, lignite, pit coal, anthracite), wood, coconut shells, fruit kernels, petrol coke and coke obtained from plastic materials pyrolysis.

Our CMS preparation procedure used as raw material the Petrila pit coal, Hunedoara, Romania.

The experimental procedure followed for the production of CMS is represented by the flow chart shown in Fig. 1.

The pitcoal was first crushed (10-30 mm), dried at 150°C for 4 hours and milled to a particle size of 0.5 -2 mm. This granular mass was subjected to partial air oxidation in fluidised bed at 240 - 250°C, in a laboratory device, for 4 - 5 hours. The air flow rate was 40 l/h. Oxidized coal was milled to powdered mass and sieved to a particle size ≤ 0.16 mm. Oxidized coal powder was mixed with 11.5 wt% pitch dissolved in benzene and 11.5 wt% starch as binder and then extruded to 6 ÷ 8 mm x 6 mm cylindrical pellets in a pneumatic press. After

drying at $120 \div 130^\circ\text{C}$ for 4 hours, these pellets were carbonized in the reactor (350 mm length and 50 mm i.d.) with one preheater at $700 \div 750^\circ\text{C}$ (Fig. 2) in N₂ flow for 30min.

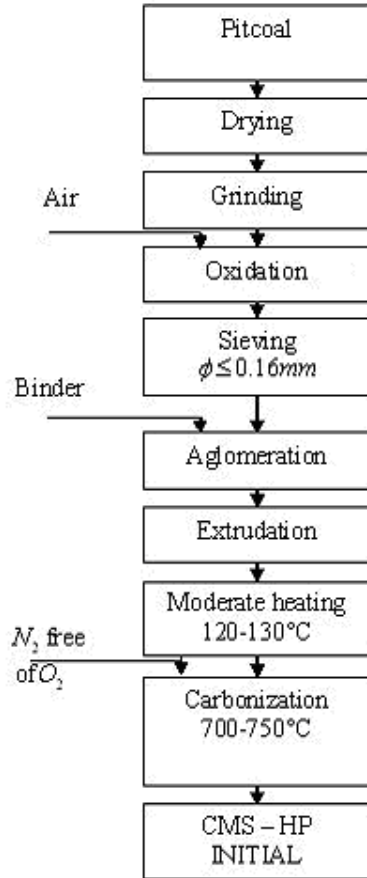


Fig. 1 Procedure for the CMS-HP Initial production

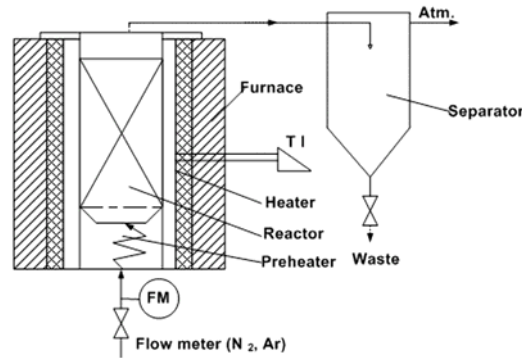


Fig. 2 Schematic diagram of reactor assembly

The N₂ flow rate was $60 \div 80$ l/h and the average heating rate was $5^\circ\text{C}/\text{min}$. The temperature of the sample in the reactor is indicated by a temperature indicator connected to a precalibrated Chromel - Alumel thermocouple. The gas flow was measured and controlled with the help of precalibrated manometer and regulator. After carbonization for a known duration, the heater was switched off and the reactor was allowed to cool in N₂. The product, CMS-HP Initial was removed at room temperature ($25 \div 30^\circ\text{C}$).

2.2. Changing initial CMS-HP for better CO₂ separation performance

In order to improve CO₂ separation performances, the CMS-HP carbon with sieving features initially obtained were submitted to some treatments to change their inner structure. CMS-HP initial, prepared according to the flow chart of Fig. 1, was submitted, after some preliminary trials, to a structural change by impregnation with a polymer and thermally treated according to the procedure whose flow chart is shown in Fig. 3, getting CMS-HP Modified.

We noticed that, out of the tested gas, the adsorbent CMS-HP Initial submitted only once to inner structure modification showed the best CO₂ separation performances.

The sieve character of the CMS-HP Initial was improved by impregnation with a 2 wt % solution of polystyrene in benzene. The amount of polymeric impregnated used to block the substrate macro pores will vary with the gas selectivity desired. Carbonaceous substrate (500 gr) was impregnated for 2 hours with a solution containing 2 wt% polystyrene in 1000 gr of benzene.

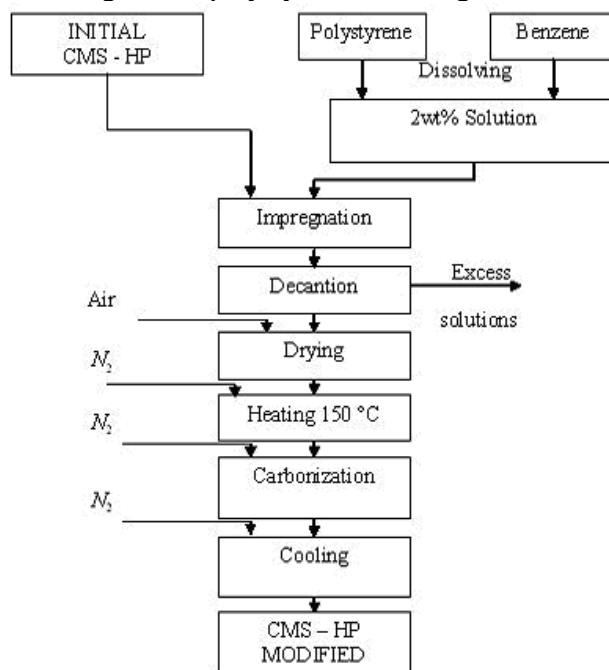


Fig. 3. Procedure for the CMS-HP Modified

Excess solution was decanted and the substrate was dried in air flow (40 ÷ 60 l/h) for 12 ÷ 16 hours. After drying, this impregnated substrate was heated for 30 min. at 150°C in the reactor (Fig. 2) and then carbonized at 750 ÷ 800°C in N₂

flow ($60 \div 80$ l/h) for 30 min. The average heating rate was $5^{\circ}\text{C}/\text{min}$. After carbonization, the heater was switched off and the reactor was allowed to cool in N₂. The product, CMS-HP Modified was removed at room temperature ($25 \div 30^{\circ}\text{C}$).

2.3. Adsorption measurements

Performance tests for separation of CO₂ on CMS-HP Initial and CMS-HP Modified were carried out by using of CO₂-He mixture (76.60 vol% \div 23.40 vol %) on a PSA single adsorber (Fig. 4).

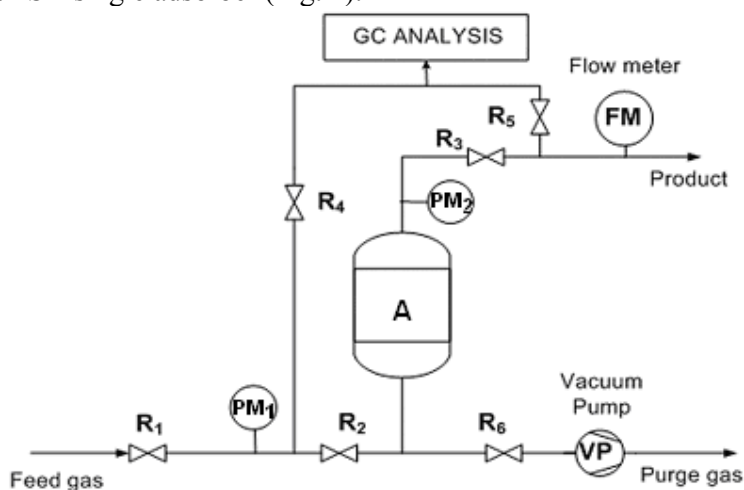


Fig. 4. Flow sheet of the PSA apparatus

The main components of this installation are: adsorbent A, fed with adsorbent sample, flow meter FM, pressure meters PM₁ and PM₂, preliminary vacuum pump.

The installation is made of metal, which offers it resistance up to a pressure of 25 bars. Adsorbent A, 200 mm long and 50 mm inner diameter, is made of stainless steel. The installation works based on a separation system flow sheet by adsorption at variable pressure with an adsorbent, showing the successive phases of the PSA process.

The complete cycle of a laboratory PSA plant is based on different adsorption kinetics, consists of the following steps: pressurization of the adsorber with feed gas, adsorption and production, counter - current depressurization, evacuation by vacuum pump.

The initial mixture and the samples collected were analysed by GC with thermal conductivity detector using Porapak Q + Porapak R column at oven and detector temperatures of 100°C and 120°C respectively. The influence of the

operating parameters (pressure and flow rate) on the breakthrough curves was investigated. Dynamic adsorption capacity for CO₂ was measured in the pressure range 2 ÷ 8 bar and calculated with the formula:

$$a = \frac{Q \cdot p (c_i - \overline{c_e})}{m} \quad (1)$$

where: a - dynamic adsorption capacity (cm³ CO₂/g CMS);

Q - gas exit flow rate (cm³/s);

p - adsorption pressure (bar)

c_i - CO₂ feed concentration (fraction %);

$\overline{c_e}$ - mean CO₂ concentration up to breakthrough time (adsorbent saturation start) at adsorber exit (fraction %);

t - the breakthrough time (s);

m - utilized CMS quantity (g).

Separation efficiency was calculated by:

$$\eta = \frac{c_a}{c_i} \cdot 100 \quad (2)$$

where: η - separation efficiency (%);

c_a - concentration of CO₂ adsorbed (vol.%);

c_i - CO₂ feed concentration (vol.%);

CO₂ adsorption monitoring is carried out by taking gas flow samples at the absorber outlet and by their gas-chromatographic analysis. The time elapsed between two successive sample taking is set up depending on the components retention time from the sample analyzed on the separation gas-chromatograph column and on the working parameters of the experimental installation.

The adsorbant saturation is revealed when the gas-chromatographic analysis shows a CO₂ concentration in the gas flow at absorber outlet about equal to that from the inlet. The adsorbant can be used in a new experiment only after a recovery made by depressurization, exhaustion and vacuuming for 10 min at 10⁻² bars. CO₂ desorption takes place during the recovery phases.

2.4. Recovery of carbon dioxide

To get a technological flow of CO₂ separation from landfill gas by selective adsorption, the experimental plant shown in Fig. 5 was designed and built.

Landfill gas was drawn from Cusmed -Harghita county, Romania, and was analysed by G.C. with a T.C. Detector, using a Porapak Q + Porapak R and Molecular Sieve 5Å columns.

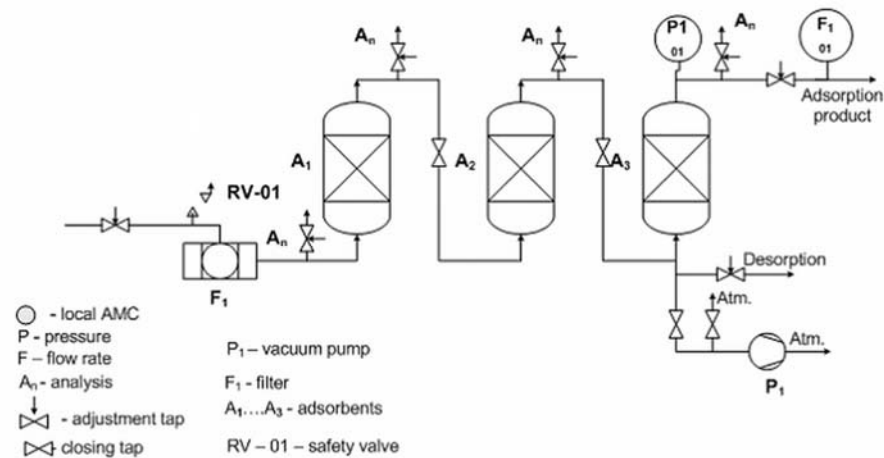


Fig. 5. Flow sheet of experimental PSA plant for CO₂ separation from landfill gases

- Landfill gas contain (vol%): CO₂=77.80; CH₄=12.22; N₂=9.0; O₂=0.38; He=0.10; C_{2,3}=0.35, H₂O=0.15.

The plant is made of:

- filter F₁ to keep the mechanical particles in suspension from the feeding gas;
- adsorber A₁ for gas drying to remove wetness from the feeding gas with molecular sieve of 13x(415 g);
- adsorber A₂, with activated carbon (280 g) for separation of hydrocarbons C₂, C₃ ;

Adsorbants regeneration from A₁ and A₂ adsorbers is independently carried out by the installation.

- adsorber A₃ , with selective carbon, CMS-HP Modified (740g) to separate CO₂ by selective adsorption under pressure from the N₂ – CH₄ – CO₂ mixture left after the landfill gas passage through A₁ and A₂; regeneration is done by adsorbant depressurization at air pressure, followed by coupling to the preliminary vacuum pump (10⁻² bar).
- local AMC elements, allowing the plant control as regards adsorption pressure, gas flow rate and vacuum value.

The installation works continuously or the filtering, drying and C₂, C₃ fractions, and discontinuously for the CO₂ selective adsorption, meaning that the specific phases of a PSA process are in succession inside absorber A₃.

The separation is monitored in the three absorbers by gas-chromatographic analysis, with samples taken from “A_n” points.

CO₂ separation from the natural gas was achieved in the following conditions: *adsorption pressure*: 4-6 bar; *temperature*: ambient; *gas flow rate*

through absorber: 64.4; 72.0; 96.0 l/h; desorption pressure: $6 - 8 \times 10^{-2}$ bar; adsorption time: 3 min; gas flow speed at absorber A_3 free section: 9.12×10^{-3} m/s $\div 1.4 \times 10^{-2}$ m/s.

Absorbers A_1 and A_2 reach a balance as to CO_2 in about 35 min. and then the gas composition with N_2 , CH_4 , CO_2 at absorber A_3 is about the same as that of the natural gas at the plant inlet. For every set of experimental conditions, the chromatographic gas review monitored the N_2 , CH_4 , CO_2 concentration at absorber A_3 outlet.

2.5. Recovery of methane

In the last years landfill gas is more and more being utilized as alternative energy source by direct combustion in heating boilers and gas engines for production of heat and electric power.

Another method for utilization of landfill gases is up-grading and recovery of methane by separation from carbon dioxide and nitrogen. Landfill gas was drawn from Cadaciu -Harghita county, Romania and was analysed by GC. Landfill gas contains (vol. %): $\text{CO}_2 = 44.33$; $\text{CH}_4 = 37.82$; $\text{N}_2 = 16.94$; $\text{O}_2 = 0.16$; $\text{He} = 0.10$; $\text{C}_{2,3} = 0.50$; $\text{H}_2\text{O} = 0.15$.

Purification and subsequent gas separation with CMS-HP Modified based PSA - technology is an attractive process for recovery of CH_4 from landfill gases.

Dynamic separation tests were performed in previously described experimental plant (Fig. 5).

Before CO_2/N_2 , CH_4 - separation landfill gas is purified in two stages. In the first stage, water is removed by adsorption onto molecular sieve 13X (Adsorber A_1).

In the second purification stage hydrocarbons $\text{C}_{2,3}$ are removed by adsorption onto activated carbon (Adsorber A_2). After purification, the clean landfill gas was fed to the PSA-adsorber A_3 . Operating conditions of experimental plant were: adsorption pressure: 4 bar; gas exit flow rate: $24.74 \div 195.21 \text{ l}\cdot\text{h}^{-1}$; desorption pressure: $6 \div 8 \times 10^{-2}$ bar.

CO_2 and part of N_2 are adsorbed at 4 bar onto CMS-HP Modified, so that non-adsorbed CH_4 and N_2 are produced at the top of the adsorber A_3 . CO_2 and N_2 are desorbed by depressurization and subsequent evacuation with vacuum pump before start of a new PSA - cycle with repressurization and adsorption.

The samples collected were analysed by G.C. Using the concentration values were calculated:

- Separation efficiency (η) by formula (2).
- Methane recovery, by

$$R_{CH_4} = \frac{\overline{C}_{e(CH_4)} - C_{i(CH_4)}}{C_{i(CH_4)}} \cdot 100 \quad (3)$$

where:

- R_{CH_4} -methane recovery (%);
- $\overline{C}_{e(CH_4)}$ - mean CH₄ concentration up to breakthrough at adsorber exit (fraction %);
- $C_{i(CH_4)}$ - methane feed concentration (fraction %).
- Productivity (cm³ CH₄/cm³ CMS-HP· h) which was calculated for every gas exit flow rate.

3. Results and discussion

For every set of experimental conditions: adsorbent – working pressure – gas flow inlet through absorber, the analysis followed the variation in time of CO₂ concentration at absorber outlet in view of drawing saturation curves.

The curves show a horizontal layer along which CO₂ concentration in the gas flow at absorber outlet is approximately constant until the breakthrough point, after which it goes up towards the initial value, which proves the adsorbent saturation (Figs.6 and 7).

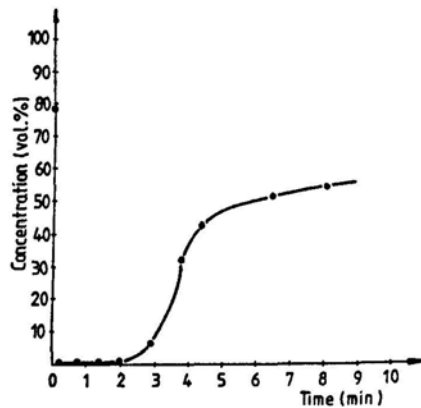


Fig.6 Carbon dioxide breakthrough curve for CMS-HP Initial (Q=13.1 l/h, adsorption pressure = 4 bar)

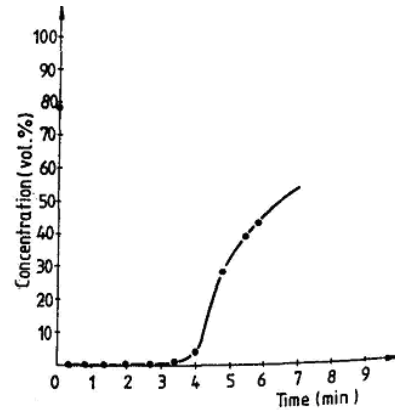


Fig.7 Carbon dioxide breakthrough curve for CMS-HP Modified (Q=12 l/h, adsorption pressure =4 bar)

CO₂ separation features by selective adsorption at p = 4 bar on CMS-HP Initial and Modified are given in Table 1.

Table 1

Separation specific features of CO₂

Parameters	CMS-HP Initial	CMS-HP Modified
Adsorption capacity, a, cm ³ /g	3.55	14.53
Separation efficiency, η , (%)	99.50	99.60÷99.94
The breakthrough time, t (s)	120	198
Mean CO ₂ concentration up to breakthrough at adsorber exit, c_e (vol. %)	max. 0.8	max 0.04

The specific CO₂ separation parameters were established for the selective adsorption period until the breakthrough point. They were used to design and achieve the experimental pilot installation for CO₂ separation from the natural gas by a PSA process (Fig. 5).

Table 2 and Table 3 show a part of the experimental quantitative results of CO₂ separation from natural gas by selective adsorption and the working conditions on the given experimental installation.

Nitrogen, methane and carbon dioxide concentrations values at PSA adsorber A₃ exit for Q = 64,4 l/h and pressure adsorption = 4 bar are presented in Table 2.

In Table 3 the CO₂ concentration measured at desorption is presented for different desorption pressure.

Lab results showed that CO₂ cannot be upgraded to a high purity if it is desorbed immediately after previous adsorption. The reason for this is that N₂ and CH₄ are coadsorbed into CMS-HP Modified. Therefore the adsorbant was purged after adsorption and before desorption with a CO₂- rich gas, which has a higher CO₂-content then the feed so that N₂ and CH₄ are displaced from the adsorbant and die voids.

Table 2

Carbon dioxide adsorption from landfill gases on CMS-HP Modified; Q=64.4 l/h; p=4 bar

Time		Concentration, % vol		
min	s	N ₂	CH ₄	CO ₂
-	15	50.45	47.55	0.005
-	45	55.75	42.60	0.005
1	15	58.93	39.06	0.005
2	-	59.95	38.05	0.005
2	30	59.77	38.22	0.005
3	15	58.28	39.72	0.005
4	15	-	-	0.005
6	15	-	-	0.20
8	30	23.60	31.88	42.51
10	-	17.92	24.78	55.28
11	30	14.54	19.26	64.20
17	30	13.90	18.70	65.42

Table 3

Carbon dioxide desorption

Desorption pressure, bar	CO ₂ concentration in gas flow at desorption,% vol
4	73.12
3	76.85
2	80.96
1	88.64
0.5	92.0
0.2	92.28
>0	92.0

After purging and preevacuation from adsorption pressure (4 bar) to an intermediate pressure (2 bar), the adsorber was then further evacuated to a final pressure (> 0 bar), during this step CO₂ was obtained with high purity as product gas. In this mode CO₂ can be recovered from landfill gases with a purity of better than 97,5 vol. %. The values showing N₂, CH₄ and CO₂ concentrations in gas exit flow from PSA adsorber at recovery of CH₄ from Cadaciu landfill gases are presented in Table 4.

Table 4

Carbon dioxide adsorption from Cadaciu landfill gases

Q (l·h ⁻¹)	V (m·s ⁻¹)	Breakthrough time (min.-s)	Concentration (Vol %)		
			N ₂	CH ₄	CO ₂
24,74	0,39	7-50	27,12	71,40	0,24
44,32	0,68	6-45	27,32	71,24	0,24
73,20	1,02	6-	27,64	71,02	0,24
97,60	1,35	5-	27,86	70,63	0,24
122,80	1,70	4-	28,14	70,35	0,24
147,60	2,05	3-	28,38	70,12	0,27
164,80	2,28	2-30	29,01	69,58	0,44
195,21	2,71	1 -30	28,72	69,12	0,67

In Table 5 experimental data are presented for CH₄ production, CO₂ adsorption efficiency, CH₄ recovery and productivity of PSA – plant.

Table 5

Recovery of CH₄ from landfill gases

Q (l·h ⁻¹)	CH ₄ production (l·h ⁻¹)	CO ₂ adsorption efficiency (%)	CH ₄ recovery (%)	Productivity (cm ³ CH ₄ /cm ³ CMS ·h)
24,74	17,93	99,46	88,68	25,61
49,32	35,63	99,46	88,08	50,90
73,20	52,78	99,46	87,68	75,40
97,60	69,68	99,46	86,80	99,54
122,80	87,70	99,46	85,91	125,28
147,60	103,49	99,38	84,80	147,80
163,80	115,70	99,02	83,88	165,28
195,21	136,84	98,15	82,66	195,48

Methane production and productivity increase when gas exit flow increases. Carbon dioxide adsorption efficiency and CH₄ recovery decrease when gas exit flow increases.

The flexibility of PSA systems with regard to flow rate and purity makes it easy to meet the requirements on the consumers' side. To produce high-purity CH₄ can be used a PSA-plant with additional after-cleaning using partial condensation.

4. Conclusions

1. Results demonstrate that Carbon Molecular Sieves for CO₂/CH₄ separation can be prepared from Romanian pitcoal.

2. In order to further reduce the pore size, a carbon deposition technique was used by carbonaceous substrate impregnation with a solution of polystyrene and carbonization in N₂ atmosphere at 750-800°C.

3. High dynamic absorption capacity and CO₂ separation efficiency indicate their suitability for packing PSA-columns for recovery of CO₂ and CH₄ from landfill gases.

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