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Carbon molecular sieves production and performance assessment in carbon dioxide separation

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Carbon molecular sieves (CMS) are carbonaceous adsorbents 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 N_2 – CH_4 – CO_2 mixture and from landfill gas on CMS prepared in a laboratory unit designed for this purpose based on PSA cycle is also reported.

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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 [1-10].

Gas separation by variable pressure adsorption is achieved by the differences between adsorption balances or adsorption speeds of the individual components of a given adsorbent [11-18]. Production of some selective adsorbents, both in laboratory, and industrially, from the carbons category with molecular sieve properties which should eclipse adsorbents from PSA systems is a field of great scientific and practical interest.

CMS preferentially retain O_2 from air by its rapid penetration into micro pores, thus enriching or separating N_2 from the air. In addition, other gas separations such as CO_2 and CH_4 separation are also achieved by CMS use [11-18].

The speciality literature [1-10] shows that CMS preparation is based on one of the following procedures:

- 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 CO_2 separation from the landfill gas by selective adsorption;
- the results obtained regarding adsorption features on CO_2 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 CO_2 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 [1-10] 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 complex of substances called "deposit carbon" is made of the organic mass composed of carbon, hydrogen, oxygen, nitrogen, sulphur and the organic mass composed of the mineral substances turned into oxides and water by burning. The carbon content is rising with the deposit carbon age in the following order: peat, lignite, pit coal, anthracite. The oxygen, nitrogen and hydrogen content is inversely evolving as to the carbon one. The oxygen takes the form of some oxygenated compounds specific to carbon, in carbonyl, hydroxyl and carboxyl groups. Water content drops with the organic mass rise and comes from superficial infiltrations and from the water hygroscopically attached to carbon.

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

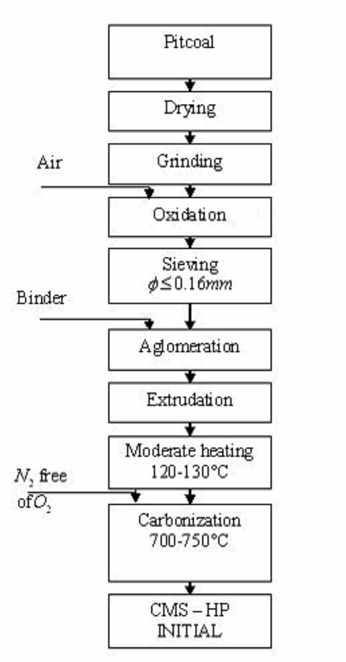

Fig. 1. Procedure for the CMS-HP INITIAL production.

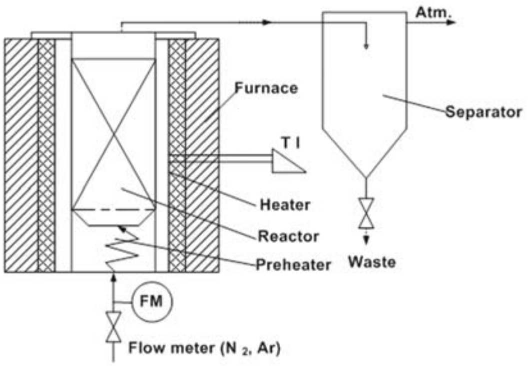

Fig. 2. Schematic diagram of reactor assembly.

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 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 ÷130°C for 4 hours, these pellets were carbonized in the reactor (350 mm length and 50 mm i.d.) with one preheater at 700 ÷750°C (Fig. 2) in N_2 flow for 30min.

The N_2 flow rate was 60 ÷80 l/h and the average heating rate was 5°C/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 N_2. The product, CMS-HP Initial was removed at room temperature (25 ÷30 °C).

2.2. Changing initial CMS-HP for better CO_2 separation performance

In order to improve CO_2 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 CO_2 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.

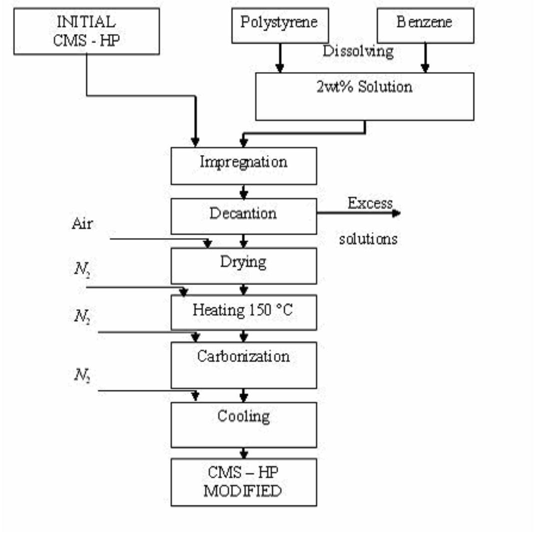

Fig. 3. Procedure for the CMS-HP Modified.

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 N_2 flow (60 ÷80 l/h) for 30 min. The average heating rate was 5°C/min. After carbonization, the heater was switched off and the reactor was allowed to cool in N_2. The product, CMS-HP Modified was removed at room temperature (25 ÷30 °C).

General properties of CMS-HP Modified were measured using pycnometry method. The results are given in Table 1.

Table 1. General properties of CMS-HP modified.

CMS – HP Modified	
Apparent density (g/cm^3)	0.96
True density (g/cm^3)	1.42
Packed density (g/cm^3)	0.47
Porosity (cm^3/cm^3)	0.33
Void fraction	0.67
Pore volume (cm^3/g)	0.35

2.3. Adsorption measurements

Performance tests for separation of CO_2 on CMS-HP Initial and CMS-HP Modified were carried out by using of CO_2-He mixture (76.60 vol% ÷ 23.40 vol %) on a PSA single adsorber (Fig. 4).

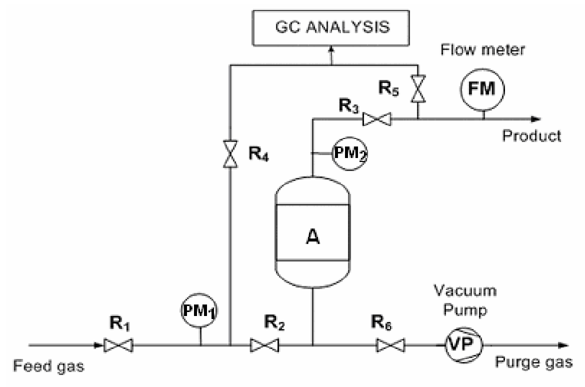

Fig. 4. Flow sheet of the PSA apparatus.

The main components of this installation are:

- adsorbent A, fed with adsorbent sample
- flow meter FM
- pressure meters PM_1 and PM_2
- 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 CO_2 was measured in the pressure range 2 ÷ 8 bar and calculated with the formula:

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

where:

a - dynamic adsorption capacity (cm^3 CO_2/g CMS);
Q - gas exit flow rate (cm^3/s);
p - adsorption pressure (bar)
c_i - CO_2 feed concentration (fraction %);
$\overline{c_e}$ - mean CO_2 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:

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

where:

η -separation efficiency (%);
c_a - concentration of CO_2 adsorbed (vol.%);
c_i - CO_2 feed concentration (vol.%);

CO_2 adsorption monitoring is done 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 adsorbent saturation is revealed when the gas-chromatographic analysis shows a CO_2 concentration in the gas flow at absorber outlet about equal to that from the inlet. The adsorbent can be used in a new experiment only after a recovery made by depressurization, exhaustion and vacuuming for 10 min at 10^{-2} bars. CO_2 desorption takes place during the recovery phases.

2.4. Recovery of carbon dioxide

To get a technological flow of CO_2 separation from landfill gas by selective adsorption, the experimental plant shown in Fig. 5 was designed and built.

Landfill gas was drawed 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.

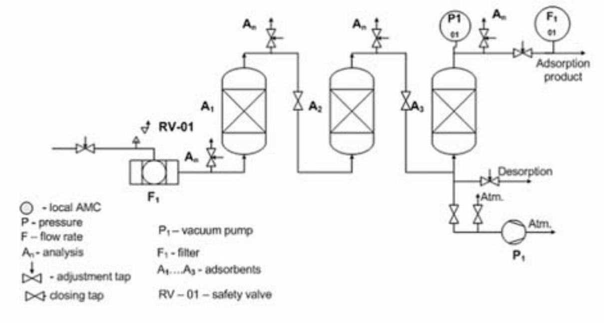

Fig. 5. Flow sheet of experimental PSA plant for CO_2 separation from landfill gases.

Landfill gas contain (vol%): CO_2=77.80; CH_4=12.22; N_2=9.0; O_2=0.38; He=0.10; $C_{2,3}$=0.35, H_2O=0.15.

The plant is made of:

- filter F_1 to keep the mechanical particles in suspension from the feeding gas;
- adsorber A_1 for gas drying to remove wetness from the feeding gas with molecular sieve of 13x(415 g);
- adsorber A_2, with activated carbon (280 g) for separation of hydrocarbons C_2, C_3 ;

Adsorbents regeneration from A_1 and A_2 adsorbers is independently done by the installation.

- adsorber A_3 , with selective carbon, CMS-HP Modified (740g) to separate CO_2 by selective adsorption under pressure from the $N_2 – CH_4 – CO_2$ mixture left after the landfill gas passage through A_1 and A_2; regeneration is done by adsorbent 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 C_2, C_3 fractions, and discontinuously for the CO_2 selective adsorption, meaning that the specific phases of a PSA process are in succession inside absorber A_3.

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

CO_2 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 x 10^{-2} bar
- adsorption time: 3 min.
- gas flow speed at absorber A_3 free section: 9.12 x 10^{-3} m/s ÷1.4 x 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.

Fig. 6 shows an example of a diagram obtained at the gas flow analysis at absorber A_3 outlet during CO_2 selective adsorption, adsorbent saturation and CO_2 desorption on depressurization.

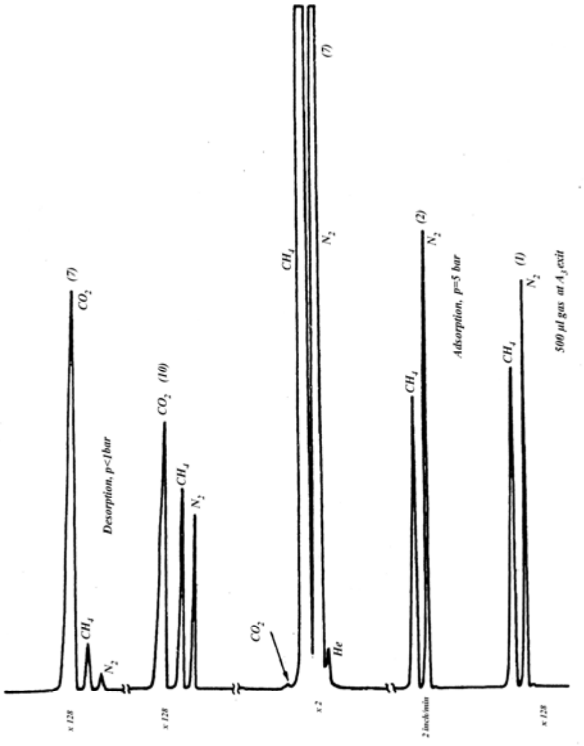

Fig. 6. Chromatograms of the N_2 - CH_4 - CO_2 mixture at adsorber A_3 exit.

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 CO_2 concentration at absorber outlet in view of drawing saturation curves.

The curves show a horizontal layer along which CO_2 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 (Fig. 7 and 8).

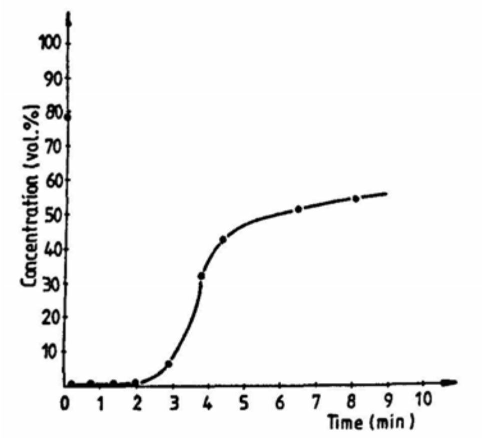

Fig. 7. Carbon dioxide breakthrough curve for CMS-HP Initial (Q=13.1 l/h, adsorption pressure = 4 bar).

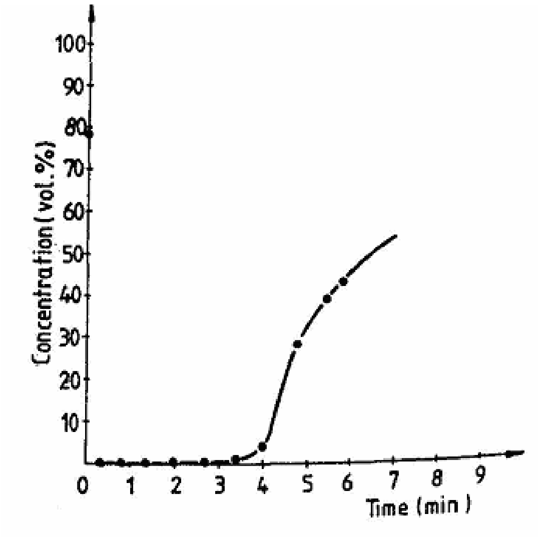

Fig. 8. Carbon dioxide breakthrough curve for CMS-HP Modified (Q=12 l/h, adsorption pressure =4 bar).

CO_2 separation features by selective adsorption at p = 4 bar on CMS-HP Initial and Modified are given in Table 2.

Table 2. Separation specific features of CO_2.

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 CO_2 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 CO_2 separation from the natural gas by a PSA process (Fig. 5).

Table 3 and table 4 show a part of the experimental quantitative results of CO_2 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 A_3 exit for Q = 64,4 l/h and pressure adsorption = 4 bar are presented in Table 3.

In Table 4 the CO_2 concentration measured at desorption is presented for different desorption pressure.

Lab results showed that CO_2 cannot be upgraded to a high purity if it is desorbed immediately after previous adsorption. The reason for this is that N_2 and CH_4 are coadsorbed into CMS-HP Modified. Therefore the adsorbent was purged after adsorption and before desorption with a CO_2- rich gas, which has a higher CO_2-content then the feed so that N_2 and CH_4 are displaced from the adsorbent and die voids.

Table 3. 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 4. 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 CO_2 was obtained with high purity as product gas. The schematic diagram for obtained of CO_2 as product gas is presented in Fig. 9.

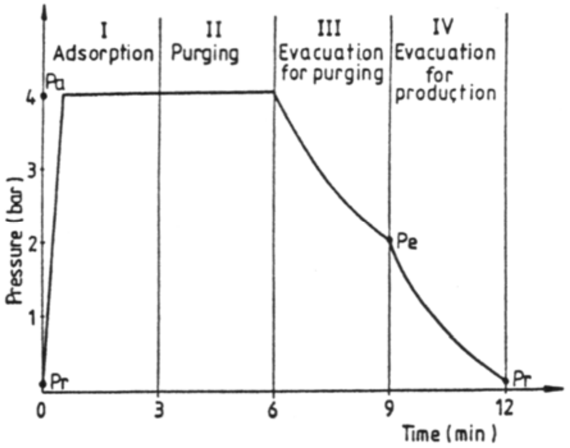

Fig. 9. PSA – Process for recovery of CO_2 from landfill gases.

In this mode CO_2 can be recovered from landfill gases with a purity of better than 97,5 Vol. %.

4. Conclusions

1. Results demonstrate that Carbon Molecular Sieves for CO_2/CH_4 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 N_2 atmosphere at 750-800°C.

3. High dynamic absorption capacity and CO_2 separation efficiency indicate their suitability for packing PSA-columns for recovery of CO_2, from landfill gases.

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