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SELECTIVE CARBON DIOXIDE ADSORPTION FROM N_2-CH_4-CO_2 MIXTURE ON CARBON MOLECULAR SIEVES

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Cărbunii sită moleculară sunt adsorbanţi carbonici de o mare importanţă. Lucrarea prezintă rezultatele studiului privind prepararea cărbunilor sită moleculară şi modificarea tratamentului cu hidrocarburi care crachează. De asemenea se prezintă procesul de adsorbţie selectivă a dioxidului de carbon din amestecul N_2-CH_4-CO_2 *care se realizează într-un echipament special creat în acest scop, bazat pe procesul de adsorbţie la presiune variabilă.*

Carbon molecular sieves (CMS) are carbonaceous adsorbents of increasing importance. This paper presents the results of a study concerning the carbon molecular sieves (CMS) preparation which comprises the treating of carbonaceous substrate with a hydrocarbon splitting of carbon. Selective carbon dioxide adsorption from N_2-CH_4-CO_2 *mixture on CMS prepared in a device especially designed for this purpose based on a pressure swing adsorption (PSA) 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 [1-11].

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 [5,7,8,10,11].

CMS preferentially retain O_2 from air by its rapid penetration into micropores, 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.

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

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- the achievement of carbons with molecular sieving properties for CO_2 separation from the $N_2 - CH_4 - CO_2$ mixture and from landfill gas by selective adsorption [7,10,11];
- improved procedures to obtain CMS and assess performances on selective adsorptions.

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 carbonization. As a result of this process, the macro porous structure of carbonaceous substrate is blocked without diminishing micropores retention capacity or diffusion through micropores, specific for the substrate [4,6,9].
- 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.

2. Experimental

2.1. Obtaining CMS by use of lignite and pitcoal as raw material

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, pitcoal, 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.

Hydrogen is linked to carbon, oxygen, sulphur and nitrogen and does not exceed 7% of the weight.

Water content drops with the organic mass drop and comes from superficial infiltrations and from the water hygroscopically carbon attached.

The average composition of some carbon types of Romania is shown in Table 1.

Table 1

Approximate average composition of some carbon types

Carbon type	Formation geological Era	Water (%)	Ash (%)	Elementary composition of dry coal without ash (%)		
				C	H	O
Wood	-	30-50	0.5	50	6	44
Peat	Current	75-80	0.5	55-60	6	35-40
Lignite	Tertiary	40	5-15	50-60	4-5	25-30
Brown coal	Tertiary	30-60	3-8	65-70	5.5-6	4-15
Pitcoal	Carboniferous	2-4	2-20	80-90	4-5.5	4-15
Anthracite	Carboniferous	2	2	95	2-3	2-3

CMS sorts were prepared according to the flow chart shown in Fig.1.

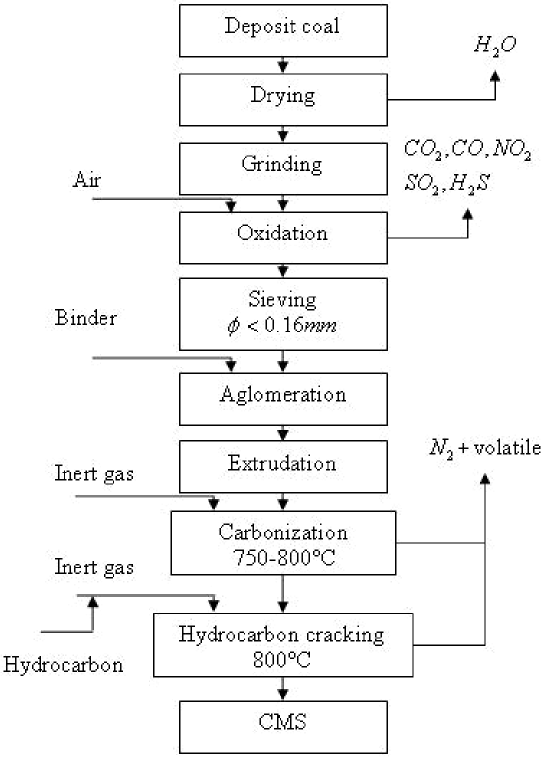

Fig.1. Procedure for CMS production

Drying removes the water content from the carbon by heating it to 120-130^o C.

The dry carbon is (0.5-2 mm) and then oxidized in fluidized bed at a lower temperature than that for carbon 300^o C. Oxidation has the role of removing a series of elements making up deposit coal composition H_2, O_2, N_2, S under the form of CO_2, CO, NO_2, SO_2, H_2S.

The oxidation and fluidizing agent of carbonaceous powder is instrumental air in lignite case, while for pitcoal we can use an air-N_2 oxidizing mixture with a 10-12% vol. content of O_2. The oxidizing agent speed ranges between $1.3 \times 10^{-2} \div 4.4 \times 10^{-2}$ m/s with a 4 hours oxidation time. After oxidation, a carbonaceous substrate is obtained which is then finely milled and sieved to a particle size of $ø < 0.16$ mm.

The carbonaceous powder is mixed with binders (pitch and starch) under certain conditions and to certain proportions until homogenization and the mixture is extruded as cylindrical pellets of 6-8 mm long and 5-6 mm diameter.

The carbon pellets are introduced in a stainless steel door mounted in a tubular retort of an electric oven.

A flow of inert gas (N_2 or Ar) is heated by 3-5°C/min up to 750°C. During this calcination phase the atmosphere has to be completely without O_2.

At 750°C, the inert gas is released over the carbonaceous substrate at a speed of $0.025 \div 0.045$ m/s at free section and heating is continued until 800°C.

This phase is aimed at fully removing the water vapours and the volatile substances from the coal.

At 800°C the coal is treated for the change of its internal structure with hydrocarbon decomposition.

Table 2 shows the conditions of the carbonization and hydrocarbon decomposition for CMS sorts prepared and submitted to the experiments for performances assessment.

Table 2

Data regarding CMS preparation conditions

CMS sort	Raw material used	Oven temp. for carbonization	Dosed hydrocarbon (gr/gr CMS)	Deposit time (min)	Contact time (sec)
CMS-I	Lignite	750 - 800	0.41	30	16
CMS-II	Lignite	750-800	0.28	60	10
CMS-III	Pitcoal	750-800	0.41	30	14
CMS-IV	Pitcoal	750-800	0.36	60	15
CMS-V	Pitcoal	750-800	0.16	20	15
CMS-VI	Pitcoal	750-800	0.52	25	9

2.2. Testing selective adsorbents made of lignite and pitcoal by use of $N_2 – CH_4 – CO_2$ mixture

To establish CO_2 dynamic adsorption capacity on CMS samples, the experimental apparatus shown in Fig. 2 was used.

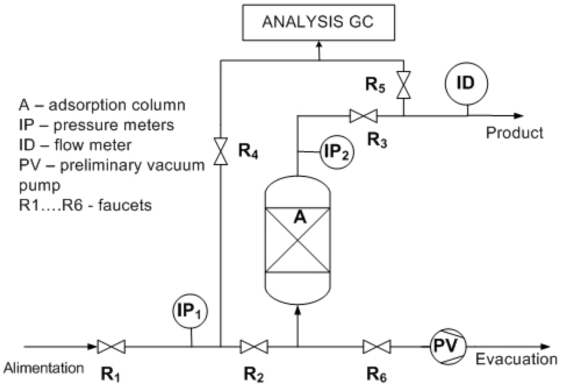

Fig.2. Flow sheet of selective adsorbents testing apparatus

The main components of this installation are:

- adsorption column A, fed with adsorbent sample
- flow meter ID
- pressure meters IP_1 and IP_2
- preliminary vacuum pump

The installation is made of metal, which offers it resistance up to a pressure of 25 bars. Adsorption column A, 200 mm long and 50 mm inner diameter, is made of stainless steel. The installation works in a dynamic regime and the variations of the components concentration in the $N_2 – CH_4 – CO_2$ gas mixture is monitored during the separation process by gas-chromatographic analysis.

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: pressurization, adsorption, detention and exhaustion by vacuuming.

We used the $N_2 – CH_4 – CO_2$ mixture for the experiments, showing the main components of the raw gas coming from the natural sources of Romania.

The $N_2 – CH_4 – CO_2$ mixture was prepared by partial pressures method and the components share was checked by the gas-chromatographic analysis (Fig. 3).

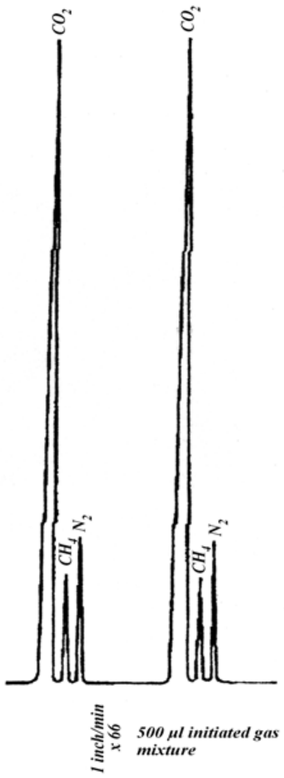

Fig.3. Chromatograms of the N2 – CH4 – CO2 gas mixture at adsorber inlet

The concentration values were: N_2 – 9.43% vol; CH_4 – 11.03% vol; CO_2 – 79.33% vol.

CO_2 adsorption monitoring is done by taking gas flow samples at the absorber outlet and by their gas-chromatographic analysis (Fig. 4).

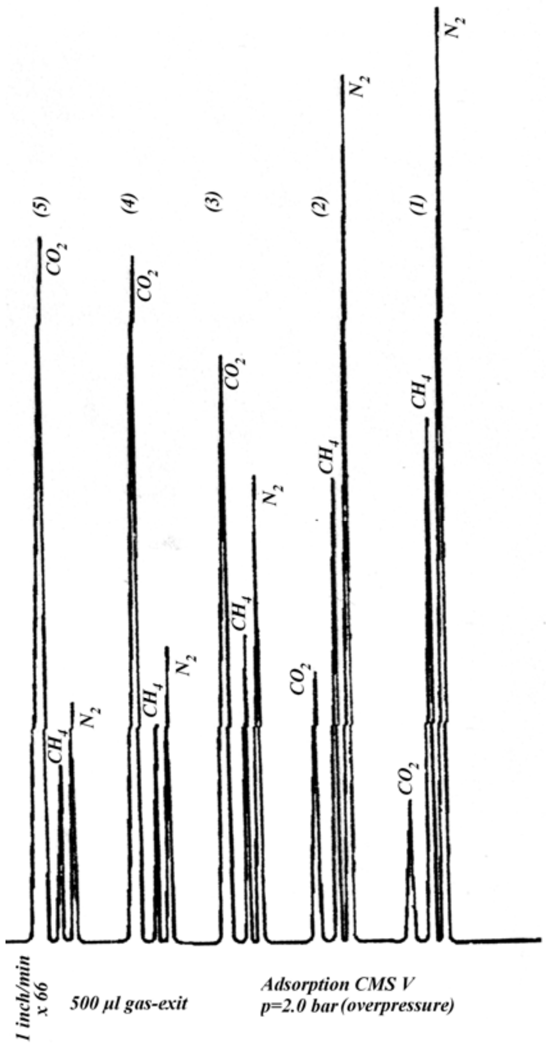

Fig.4. Chromatograms of the $N_2 – CH_4 – CO_2$ gas mixture at adsorber outlet

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} bar. CO_2 desorption takes place during the recovery phases.

The experiments were done at pressure values ranging between 1÷8 bars and a consistent gas flow through the absorber (9Nl/h), that is a gas speed in the free section of $0.12 \cdot 10^{-2}$ m/s.

Adsorption capacity was calculated with the formula:

$$a = \frac{Q \cdot p(c_i - c_f) \cdot t}{m} \tag{1}$$

where:

$a =$ adsorption capacity, cm^3/g;
$Q =$ gas exit flow rate through adsorber, cm^3/s;
$p =$ adsorption pressure, bar;
$c_i =$ CO_2 feed concentration, % fraction;
$c_f =$ CO_2 exit concentration up to adsorbent saturation, % fraction;
$t =$ breakthrough time, s;
$m =$ CMS quantity fed into adsorber, g.

3. Results and discussion

Fig. 5 shows the $N_2 - CH_4 - CO_2$ concentration variation in the adsorber exit gas flow for an adsorption at 2 bar on CMS-V.

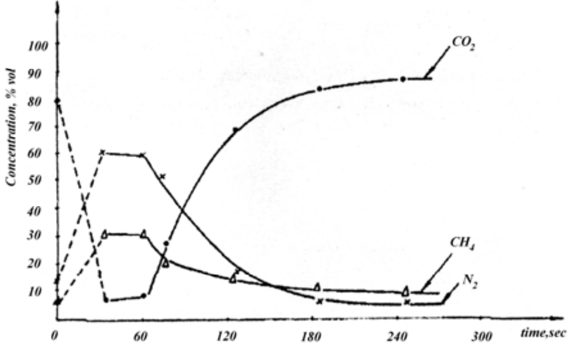

Fig.5. $N_2 - CH_4 - CO2$ concentration variation in adsorption gas flow

For 60 seconds, the CO_2 concentration in the feeding gas flow was reduced by adsorption from 79.33% vol to 7.98 % vol.

Table 3 shows the CO_2 adsorption capacities for CMS types considered for the study.

Table 3

CO_2 adsorption capacity on CMS

Adsorbent	Pressure, bar	Adsorption capacity, cm^3/g
CMS – I	1	0.75
	2	1.15
	3	1.34
	4	1.56
	5	1.72
	6	1.80
	7	1.92
	8	2.12
CMS – II	1	0.86
	2	1.24
	3	1.58
	4	1.82
	5	1.98
	6	2.30
	7	2.51
	8	2.72
CMS – III	1	0.62
	2	0.85
	3	1.16
	4	1.52
	5	1.78
	6	2.01
	7	2.18
	8	2.34
CMS – IV	1	0.44
	2	0.66
	3	0.84
	4	1.05
	5	1.14
	6	1.30
	7	1.54
	8	1.75
CMS – V	1	1.27
	2	2.46
	3	3.55
	4	4.05
	5	4.55
	6	4.92
	7	5.25
	8	5.52

CMS-V is seen to have a higher adsorption capacity than CMSI-VI types.

CO_2 as a result of a selective adsorption separation process under variable pressure is obtained at desorption. Table 4 and Figs. 6 and 7 show the results of the gas flow analysis at desorption in case of CMS-IV and CMS-V types used at 4 and 6 bars, respectively.

Table 4

Gas flow analysis at desorption

Adsorbent	Desorption pressure, bar	Desorption concentrations, % vol		
		N_2	CH_4	CO_2
CMS – IV	3	3.92	16.75	79.05
	2	5.32	13.12	81.28
	1	6.15	8.93	84.64
	0.5	6.98	7.82	84.92
	0.2	6.70	7.81	85.20
CMS – V	5	9.81	17.97	71.93
	4	6.09	14.30	79.33
	3	3.17	11.84	84.71
	2	0.73	9.80	89.19
	1.5	0.37	8.37	90.98
	1.0	0.61	6.94	93.66
	0.7	0.94	5.31	93.67
	0.5	1.13	4.69	93.89
	0.2	1.20	3.88	94.56

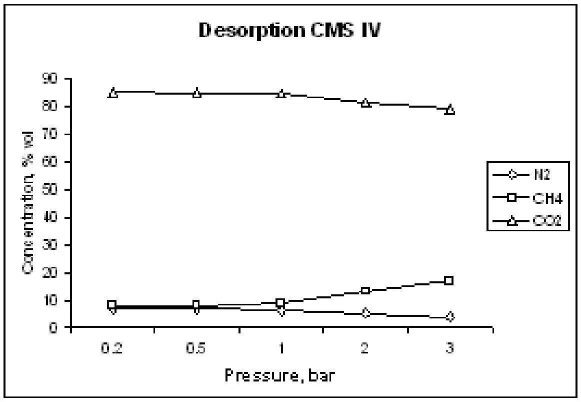

Fig.6. Variation of N_2, CH_4 and CO_2 concentration in gas flow at desorption on CMS-IV

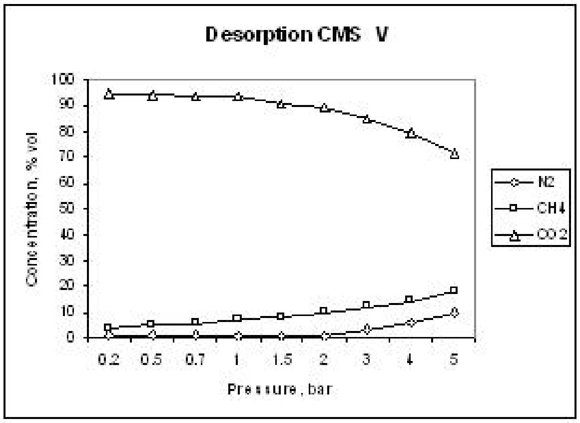

Fig.7 Variation of N_2, CH_4 and CO_2 concentration in gas flow at desorption on CMS-V

It can be seen that CO_2 concentration in the exit gas flow at 1 bar pressures ranges between 84.64 ÷ 85.20 % vol on CMS-IV and 93.66÷94.56% vol on CMS-V.

4. Conclusions

Results demonstrate that Carbon Molecular Sieves for CO_2/CH_4 separation can be prepared from Romanian pitcoal.

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.

High dynamic absorption capacity and CO_2 separation efficiency indicate their suitability for packing PSA-columns for recovery of CO_2 and CH_4, from landfill gases.

Based on the experimental data obtained from CO_2 selective adsorption from the *N_2- CH_4-CO_2 mixture*, adsorption features were established for CMS prepared and studies.

This paper opens new ways of continuing the research, both in the domain of producing and altering the internal structure of the CMS, and concerning the research in the process of separation through selective adsorption of carbon dioxide and of other gases too, with the deepening of the aspects concerning the growing of selectivity and preparing some experimental equipment of increasing capacity.

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