SEPARATION OF NITROGEN FROM AIR

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Carbon molecular sieves (CMS) are used on a wide scale for the separation of air into its components. Air separation its one of the most important applications of Pressure Swing Adsorption (PSA). In this paper a brief review of the results got in recent experimental studies on the sorption kinetics of oxygen from air by CMS used PSA process single column (700 mm length, 50 mm i.d.). The molecular sieves properties of O_2 selective carbon molecular sieves CMS-HP (O_2), prepared under different conditions, where studied by measuring dynamic adsorption capacity from O_2.

INTRODUCTION

Air separation is one of the most important applications of PSA (Pressure Swing Adsorption) technology.[1-11] Separation principle is based on the difference between Oxygen and Nitrogen adsorption speed on CMS.

PSA air separation systems with CMS are mainly used as Nitrogen generators, as Oxygen concentration in the desorbed gas (enriched Oxygen) is of only 30-45 % vol, due to the high partial pressure of Nitrogen in the air ($P_{N_2} = 0,78$ as compared to $P_{O_2} = 0,21$).[12-19]

The achievement of this procedure of selective adsorbents made of deposit coal (Petrila pitcoal) with features of molecular sieves CMS-HP and the change of their internal structure to increase their selectivity allowed the performance of the experiments to enrich Nitrogen in the air by Oxygen selective adsorption within a laboratory PSA system.

This paper presents the data obtained for air Nitrogen enrichment by Oxygen selective adsorption in a PSA column loaded with carbon molecular sieve, CMS-HP (O_2).

The paper also show the data obtained when air Nitrogen is enriched by using experimental PSA system in one enriched variant, by recycling between adsorbers.

RESULTS

General properties of CMS-HP(O_2) were measured using the pycnometric method.

Separation specific parameters of O_2 by selective adsorption on CMS-HP (O_2) at elevated pressure ($2 \div 10$ bar) are presented in Table 1.

Summary of the optimized N_2 - PSA experiments are presented in Table 2.

The gas flow velocity through the CMS - HP (O_2) bed determines the remaining O_2 concentration in the N_2 produced. By changing this velocity, the O_2 concentration can be adjusted between $0,03 \div 5,20$ vol.%.

In Table 3 are presented experimental data for N_2- PSA plant with additional deoxo system.

The N_2 concentration after N_2 - PSA plant decrease from 96,95 vol. % at 94,56 vol. % when gas exit flow increases from 10 L/h at 100 L/h. After deoxo system for all gas exit flow range, the N_2 is obtained with a purity of better then 99,45 vol.%. The flexibility of N_2 - PSA system with regard to flow rate and purity makes it easy to meet the requirements on the consumer's side.

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Table 1

Separation specific features of O_2

Adsorption pressure (bar)	Dynamic adsorption capacity, a (cm^3/g)	O_2 adsorption efficiency, η (%)	The breakthrough time, t (s)	Concentration up to breakthrough at adsorber exit (vol. %)	
				(O_2 + Ar)	N_2
2	0,20	80,50	80	3,20 ÷ 4,80	95,80 ÷ 94,22
4	0,47	82,38			
6	0,61	80,90			
8	0,82	80,90			
10	1,02	80,47			

Table 2

O_2/N_2 separation from air (optimized)

Exp. no.	Q (L/h)	v (m/s·10^{-2})	Concentration in product (vol. %)			O_2 adsorption efficiency (%)	N_2, recovery (%)	Productivity ($cm^3 N_2/cm^3$ CMS · h)
			O_2 + Ar	O_2	N_2			
1.	10	0,14	0,96	0,03	99,03	99,76	26,96	7,07
2.	20	0,28	1,07	0,14	98,93	98,93	26,82	14,13
3.	30	0,42	1,15	0,22	98,84	98,30	26,71	21,18
4.	40	0,56	1,24	0,31	98,75	97,62	26,65	28,24
5.	50	0,69	1,13	0,20	98,86	98,46	26,74	35,31
6.	60	5,43	1,50	0.57	98,49	95,61	26,26	42,21
7.	70	0,97	1,62	0,63	98,37	95,15	26,11	49,18
8.	80	1,10	2,05	1,12	97,94	91,38	25,56	55,96
9.	90	1,30	3,89	2,96	96,70	77,23	23,94	62,16
10.	100	1,40	6,14	5,21	93,85	59,92	20,32	66,78

Table 3

Experimental data for the N_2- PSA + Deoxo system

Exp. No.	Q (L/h)	v (m/s·10^{-2})	O_2 concentration in product (vol. %)		N_2 concentration in product (vol. %)	
			PSA exit	Deoxo exit	PSA exit	Deoxo exit
1.	10	0,14	3,04	0,45	96,95	99,54
2.	20	0,28	3,15	0,50	96,84	99,49
3.	30	0,42	3,26	0,55	96,73	99,44
4.	40	0,56	3,40	0,47	96,59	99,52
5.	50	0,69	3,48	0,54	96,51	99,45
6.	60	5,43	3,86	0,50	96,13	99,49
7.	70	0,97	3,93	0,52	96,06	99,47
8.	80	1,10	4,44	0,54	95,55	99,45
9.	90	1,30	4,57	0,42	95,42	99,57
10.	100	1,40	5,43	0,47	94,59	99,52

DISCUSSION

Experimental data were processed obtained within ICSI in laboratory PSA system, with adsorbents obtained by our own procedure from deposit coal.

The results demonstrate that Carbon Molecular Sieves for O_2/N_2 separation from air 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. The separation specific parameters of O_2 by selective adsorption on CMS - HP (O_2) indicate their suitability for packing N_2-PSA columns, to produce purity N_2 can be used a N_2-PSA plant with additional after - cleaning using deoxo process.

Our results are as competitive as those on the world market.[17-19]

EXPERIMENTAL

1. Experimental part of air Nitrogen enrichment process

PSA process of air Nitrogen enrichment includes the following phases: air pressurization; O_2 adsorption under pressure and getting N_2 as a product; depressurization; O_2 traces removal by vacuum use.

Adsorption features at O_2/ N_2 separation from air for CMS-HP (O_2) were experimentally established by laboratory PSA system fit with an adsorption column (fig. 1).
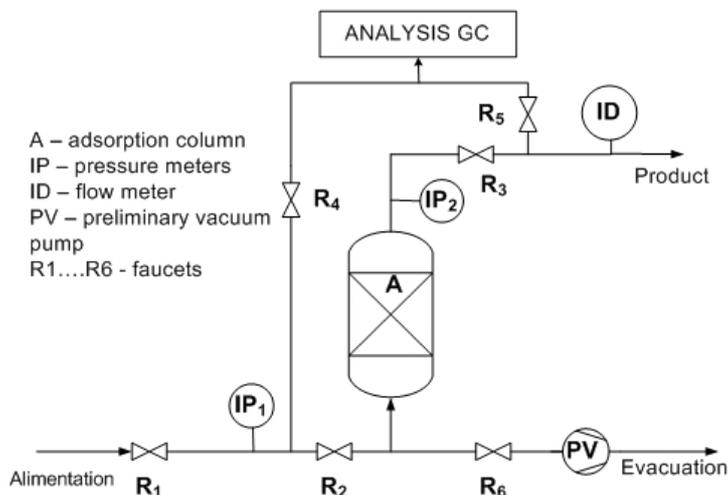

Fig. 1 – Experimental testing scheme of selective adsorbents:
A-adsorber; ID-flow rate meter; R1...R6 - tabs; IP-pressure meter; PV- vacuum pump.

The experimental system was dynamically operated and its monitoring was done by gas-chromatographic analysis.

Adsorption column is 0.700 m high with an inner diameter of 0.05 m.

Experimental conditions were the following: gaps fraction of the adsorbent layer, $\varepsilon_g = 0.67$; adsorption column feeding gas: air, with 21% vol; O_2 - component which is adsorbed selectively and 78% vol. N_2 - component which is not adsorbed; operation temperature: 23°C; pressure on adsorption: 4 and 6 bar; gas flow rate through adsorber: 25 and 40 L/h; length of selective adsorption: 80 s.

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

The pitcoal which was used as carbon precursor for the preparation of CMS was procured from Petrila mine - Hunedoara County, Romania. The experimental procedure followed for the production of CMS is represented by the flow chart shown in Figure 2.

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 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 at 700 ÷ 750°C in N_2 flow for 30 min in the reactor (350 mm length and 50 mm i.d.) with one pre-heater.

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

3. Coke deposition by organic polymer cracking

In order to reduce the pore size of Initial CMS - HP (carbonaceous substrate), a solution of organic polymer was used as the cracking agent for coke deposition. The aim of coke deposition is to reduce the pore opening to the required molecular range. The sieve character of the initial CMS- HP was desired improved by impregnation with a 4 wt% solution of polystyrene in benzene. The amount of polymeric impregnator used to block the substrate macropores will vary with the desired gas selectivity. The optional dosage may by determined by varying the dosage and identifying the impregnated sieve with the optional sieving properties. The experimental procedure followed for the modification of Initial CMS-HP by impregnation with a solution of polystyrene in benzene is represented by the flow chart shown in Figure 3.

Carbonaceous substrate (≈ 500 g) was impregnated for 2 hours with a solution containing 4 wt% polystyrene in 1000 g of benzene. Excess solution was decanted and the substrate was dried in air flow (40 ÷ 60L/h) for 12 ÷ 16 hours. After drying, the impregnated substrate was heated for 30 min. at 150°C in the reactor 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 heaters were switched off and the reactor was allowed to cool in N_2 flow. The product, CMS - HP(O_2) was removed at room temperature (25 ÷ 30°C).
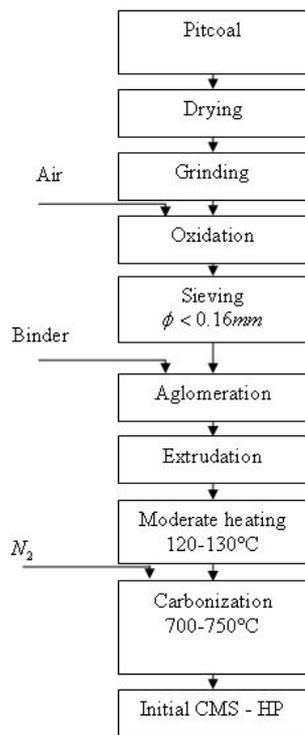
Fig. 2 – Procedure for the Initial CMS-HP preparation.

Fig. 3 – Procedure for the CMS-HP(O_2) Preparation.

4. Adsorption measurement

Performance tests for separation of O_2/N_2 from air on CMS - HP (O_2) were carried out by using a PSA single adsorber with 200 mm length and 50 mm i.d.

The complete cycle of a laboratory PSA consists of the following steps: pressurization of the adsorber with feed gas (air); adsorption and production of N_2; counter - current depressurization; evacuation by vacuum pump.
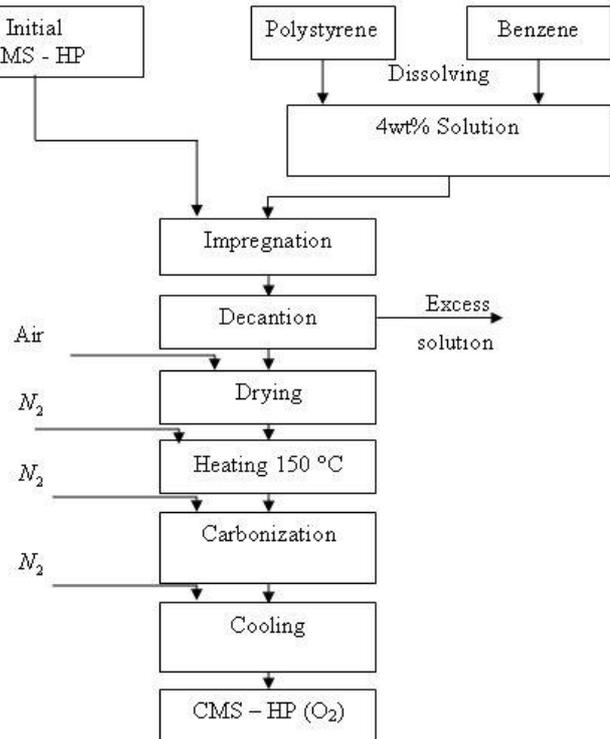
The initial gas (air) and the samples collected were analyzed by GC with thermal conductivity detector (TCD) using Molecular Sieve column at oven and detector temperatures of 100°C and 120°C respectively. The influence of the operating parameters (pressure and flow rate) on the breakthrough curves was investigated. Dynamic adsorption capacity for O_2 was measured in the pressure range $2 \div 10$ bar and calculated with the formula:

$$a = \frac{Q \cdot p(C_i - \overline{C_e}) \cdot t}{m} \qquad (1),$$

where: a - adsorption capacity, expressed in cm^3(gas O_2)/g of CMS at the working pressure and ambient temperature; Q - gas exit flow rate (cm^3/s); p - adsorption pressure (bar); C_i - O_2 feed concentration (fraction %); $\overline{C_e}$ - mean O_2 concentration up to breakthrough 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 O_2 adsorbed (vol.%); C_i - O_2 feed concentration (vol.%).

5. Nitrogen recovery from air

After previous laboratory tests the N_2 - PSA process was run in an experimental plant. The flow diagram of the optimized plant is shown in Figure 4.

Two adsorbers (700 mm length and 72 mm i.d.) are filled with CMS - HP (O_2) and equipped with incoming air pipes and outgoing nitrogen pipes and valves. Air compressed to 4 bar enters the CMS -HP(O_2) bed in one adsorber. On passing over the CMS - HP (O_2), O_2 is adsorbed and nitrogen leaves the adsorber.

Operating conditions of experimental plant was: adsorption pressure: 4 bar; temperature: ambient; gas exit flow rate: $10 \div 100$ L/h; adsorption time: 1 min.; desorption pressure: $6 \div 8 \cdot 10^{-2}$ bar.

During adsorption in one adsorber, a second adsorber is regenerated by reducing the pressure to ambient pressure and vacuum application. After a certain adsorption time ($1 \div 2$ min.), the O_2 starts to breakthrough the CMS bed at the top of the adsorption vessel. At this stage the adsorption step is stopped. Nitrogen is recovered during the adsorption phase, while an O_2 - enriched waste gas ($30 \div 35$ vol.% O_2) is produced in the desorption phase (depressurization).

Because of the pressure differences between adsorption and desorption, significant pressure losses at desorption and the relatively short cycle times, precise requirements are imposed on the technical design of N_2 - PSA. Therefore, before starting the adsorption step in the second adsorber, a pressure equalization step of both, adsorbers to pre-pressure the second adsorber.
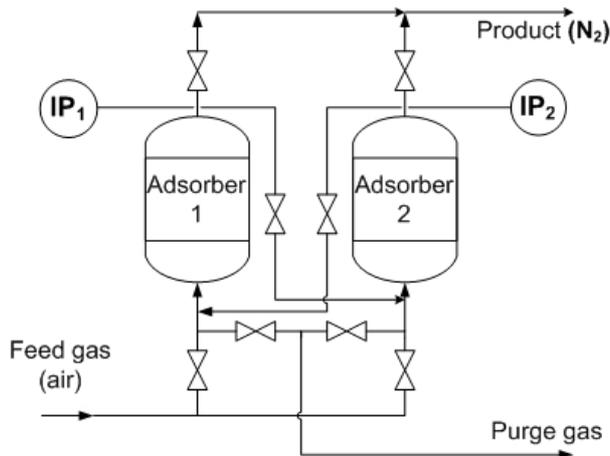
Fig. 4 – Flow sheet of the experimental optimized N_2 -PSA plant.

The samples collected were analyzed by GC with TCD. Using the concentration values were calculated:

Separation efficiency (η) by formula (2);

Nitrogen recovery, by

$$R_{N_2} = \frac{\overline{C_{e(N_2)}} - C_{i(N_2)}}{C_{i(N_2)}} \cdot 100 \qquad (3),$$

where: R_{N_2} - Nitrogen recovery, %; $C_{i(N_2)}$ - N_2 feed concentration, fraction %; $\overline{C_{e(N_2)}}$ - mean N_2 concentration up to breakthrough at adsorber exit, fraction %.

Productivity, cm^3 N_2/cm^3 CMS-HP (O$_2$) · h which was calculated for every gas exit flow rate. Productivity shows the relative decrease of the adsorbed elements concentration. It is computed as follows: the exit gas (N$_2$) debit flow compared to CMS- HP (O$_2$) volume used.

To produce purity N_2 was used a N_2-PSA plant with additional after -cleaning using copper as an O$_2$-reducing reactant, (Figure 5).

The deoxo unit needs one external heated reactor filled with copper for the endothermic reaction:

$$O_2 + 2Cu \xrightarrow{\ 550^\circ C\ } 2CuO$$

The loaded cooper can be regenerated by adding H$_2$ during the regeneration step. For this two - step process (deoxidation and regeneration), two reactors are necessary to achieve a continuously operating deoxo system. The N_2 from the PSA plant with the remaining O$_2$ passes the heated reactor without adding hydrogen. On passing through the reactor, the O$_2$ is removed by reacting with the copper surface. The remaining heat can be reduced by a standard after - cooler to the required level. The advantage of the deoxo unit based on cooper in comparison with the deoxo unit using palladium on platinum as a catalyst is that the purity N_2 leaves the unit dry and without any remaining hydrogen.
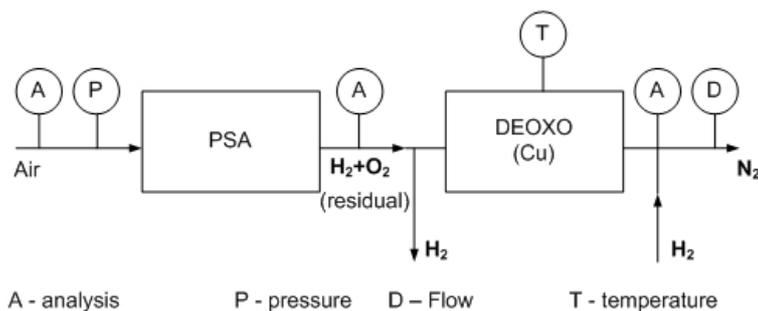

Fig. 5 – Scheme for a N_2-PSA+ DEOXO system.

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