

Enrichment of methane containing gases on carbon molecular sieves

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Five industrial carbon molecular sieves were evaluated with respect to their potential for enrichment of methane containing gases in the equilibrium PSA process. The test simulated the basic stage of the PSA process. Mesopore and micropore structures were determined using nitrogen adsorption/desorption isotherms. Parameters of the Dubinin-Radushkevich equation were calculated, as was the micropore size distribution by the Horvath-Kawazoe method. A correlation between adsorption of methane from gas mixture and texture parameters characterising the adsorbents was established.

1. INTRODUCTION

The industrial introduction of carbon molecular sieves (CMS) opened up a number of new possibilities of using adsorption techniques for the separation of gaseous mixtures. The applications include separation of hydrogen from coke-oven and refinery gases, nitrogen from air and carbon dioxide from its mixtures with nitrogen and carbon monoxide. One of the important technological problems recently addressed is methane extraction in its pure or enriched form (the substitute for natural gas) from gases of low methane content. Such potential methane sources are: mine gases, accompanying coal beds containing 30 to 50 % methane, biogases from the anaerobic decomposition of organic materials or landfill gases, and nitrogenated natural gas. The above mentioned gaseous mixtures may be separated using adsorptive

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techniques, first of all the pressure swing adsorption (PSA) [1]. The basic condition enabling enrichment of the gaseous mixtures in a desired component is the choice of a suitable adsorbent, capable of preferential adsorption of the component on an equilibrium basis.

2. EXPERIMENTAL AND RESULTS

Carbon molecular sieves. Investigations were carried out on five commercially manufactured granulated carbonaceous adsorbents (particle diameters are given in parentheses): Carbotech D55/2 (1.5 mm); Carbotech BF-H2 (1.5 mm); Takeda Inc., Takeda 5A (3mm); Chemviron F30/470A (3mm); Takeda Inc., MSC-5A (5mm).

Texture. Porous structure of carbonaceous adsorbents was studied by an adsorption technique using volumetric apparatus (SORPTOMATIC 1900). Adsorption and desorption isotherms of nitrogen vapours at 77.5K are presented in Figure 1.

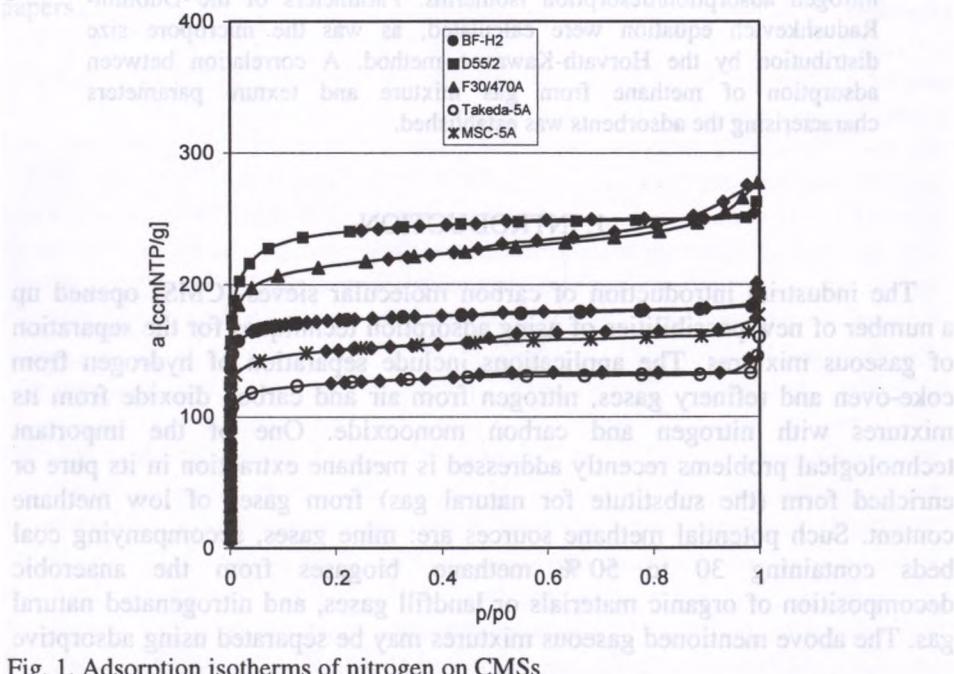


Fig. 1. Adsorption isotherms of nitrogen on CMSs

All the plots have a Langmuir-type shape and some of them a hysteresis loop, which indicates development structures other than the microporous one.

Texture parameters: specific surface area S_{BET} (calculated from BET method), micropore volume W_0 and energetic parameters B , E_0 (determined from Dubinin-Radushkevich equation)[2] and mesopore surface S_{me} (obtained according Dollimore-Heal's method)[3] for the CMS's are compared in Table 1.

Tab. 1. Parameters of porous structure calculated from adsorption isotherms of nitrogen

Adsorbent	W_0 [cm ³ /g]	$B \cdot 10^6$ [K ⁻²]	E_0 [kJ/mol]	S_{BET} [m ² /g]	S_{me} [m ² /g]	D_{HK} [nm]
D-55/2	0.374	1.031	18.9	825	22	0.58
BF-H2	0.271	0.681	23.2	607	16	0.71
Takeda-5A	0.190	0.421	29.5	428	21	0.50
F30/470A	0.336	0.902	20.2	780	56	0.63
MSC-5A	0.230	0.544	26.0	508	34	0.52

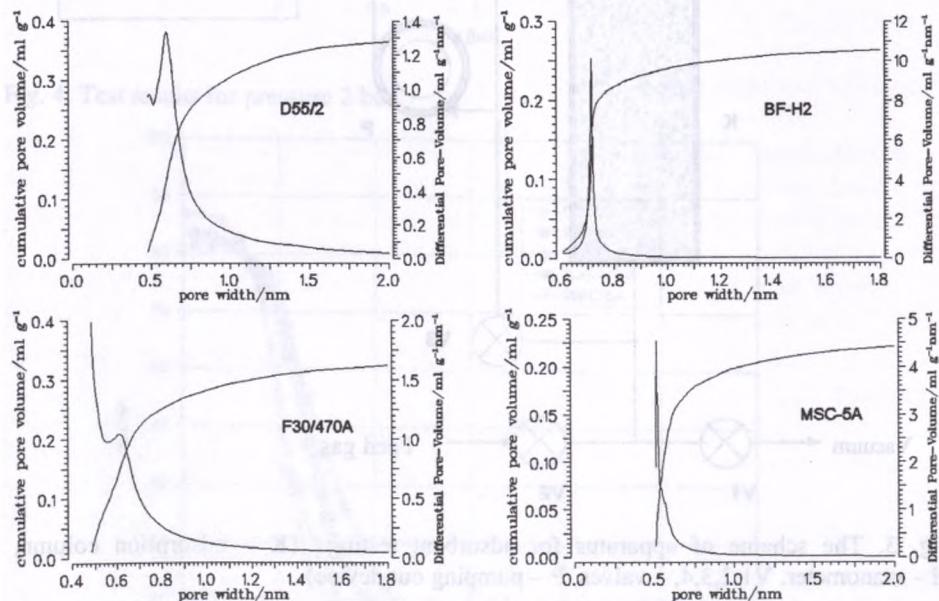


Fig. 2. Pore size distribution in micropores range according to Horvath-Kawazoe method

To better understand the character of microporous structure of CMS's, pore size distributions were calculated using method of Horvath and Kawazoe[4]. The size distribution of micropores was analysed in terms slit width pores.

The distribution curves for selected adsorbents are presented in Figure 2, while the pore slit widths d_{HK} are listed in Table 1. The distributions are nearly symmetrical and rather narrow, with the most frequently occurring pore widths between 0.4 and 1.0 nm.

Testing of adsorbents in the PSA process conditions. The selection methodology requires that it simulates the two basic stages of equilibrium PSA process. First of these is the pressure increase due to feed gas and the second, the concurrent desorption[5]. Methane is more strongly adsorbed than nitrogen or oxygen on the carbonaceous adsorbents. It can be recovered at the stage of concurrent desorption when vacuum is used. The carbon molecular sieves were tested for the separation of methane from nitrogen mixture containing 50% vol. of methane. A diagram of the experimental equipment is shown on Figure 3.

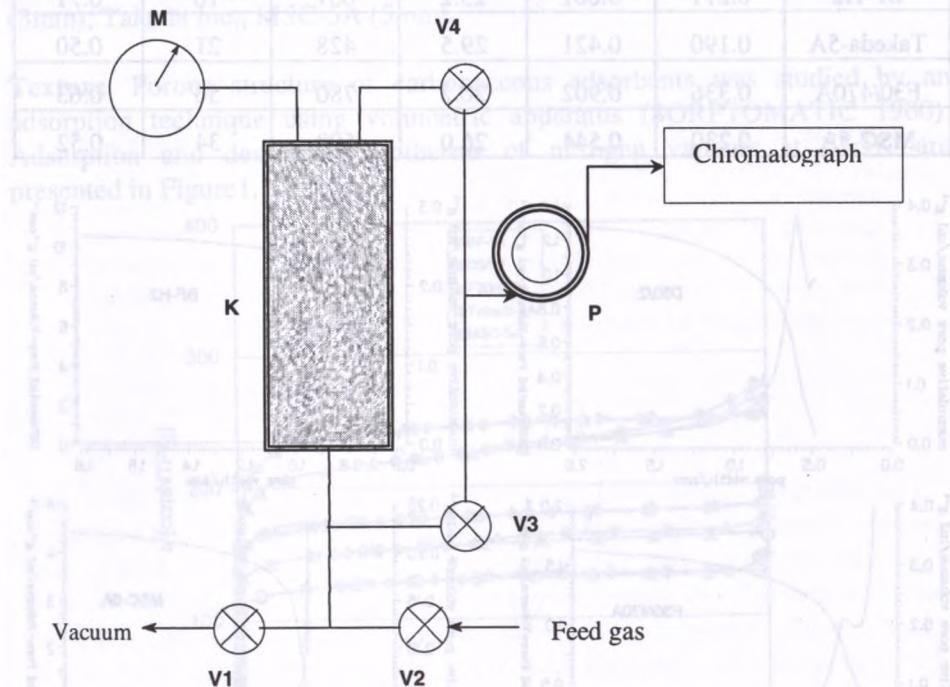


Fig. 3. The scheme of apparatus for adsorbent testing (K – adsorption column, M – manometer, V1,2,3,4, – valves, P – pumping out device)

The measurement consisted of three steps: i. sample degassing in the test column under pressure of a few mm Hg during 30 minutes, ii. pressure rise in the column by means of the feed gas up to 2, 3 or 4 bar, iii. concurrent desorption from the column with the simultaneous analysis of outflowing gas. The curves in Figures 4-6 illustrate the change in methane concentration at the outlet as a function of starting pressure in the column.

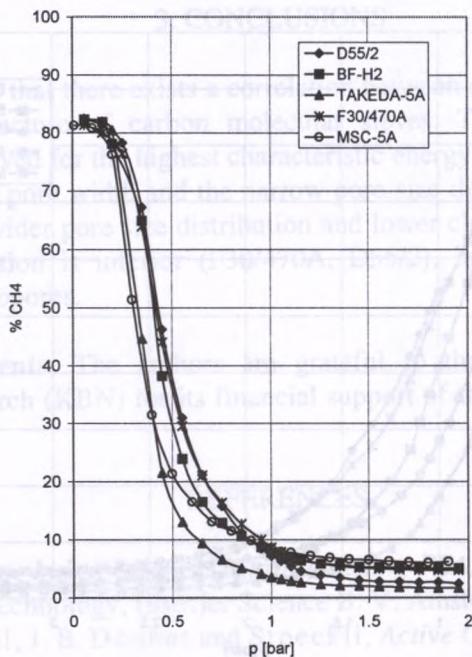


Fig. 4. Test results for pressure 2 bar

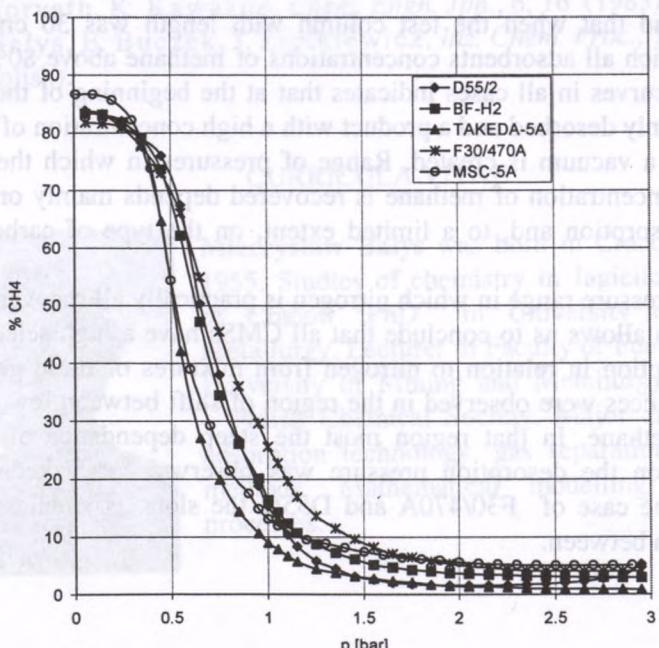


Fig. 5. Test results for pressure 3 bar

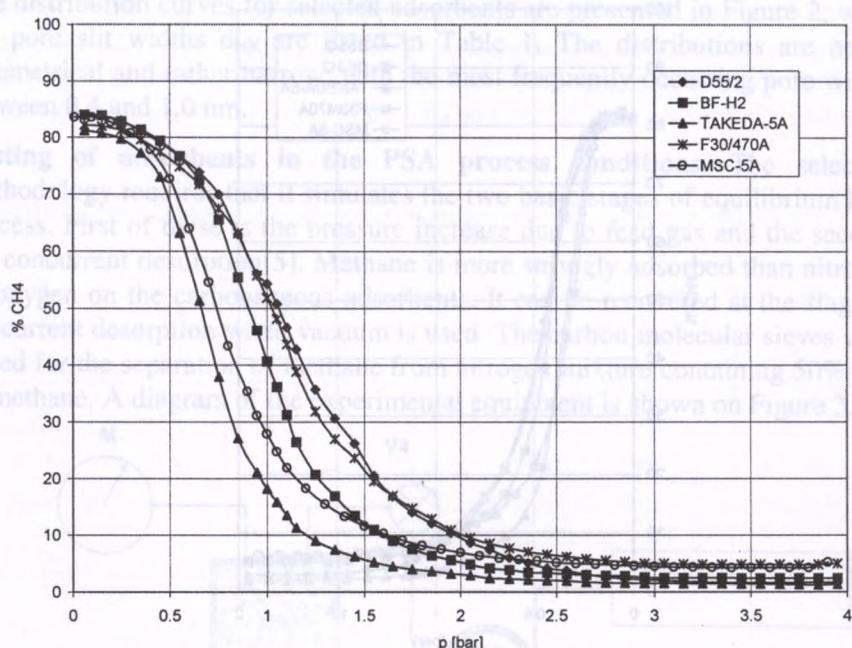


Fig. 6. Test results for pressure 4 bar

It was found that when the test column with length was 30 cm, it was possible to enrich all adsorbents concentrations of methane above 80%. Shape of desorption curves in all cases indicates that at the beginning of the process nitrogen is mainly desorbed and a product with a high concentration of methane is obtained as a vacuum is created. Range of pressures in which the product with a high concentration of methane is recovered depends mainly on starting pressure of desorption and, to a limited extent, on the type of carbonaceous adsorbent.

The wide pressure range in which nitrogen is practically all recovered in the desorption step allows us to conclude that all CMSs have a high selectivity of methane adsorption in relation to nitrogen from mixtures of these gases. The greatest differences were observed in the region of shift between low and high contents of methane. In that region most the steep dependence of methane concentration on the desorption pressure was observed for Takeda-5A and MSC-5A, in the case of F30/470A and D55/2 the slope is smallest and for BF-H2 it lies in between.

3. CONCLUSIONS

It can be seen that there exists a correlation between separation abilities and microporous structure of carbon molecular sieves. The highest separation property is observed for the highest characteristic energy E_0 i.e. adsorbents with lowest dominant pore width and the narrow pore size distribution (Takeda-5A, MSC-5A). For wider pore size distribution and lower characteristic energy, E_0 , effect of separation is inferior (F30/470A, D55/2), in spite of their higher volumes of micropores.

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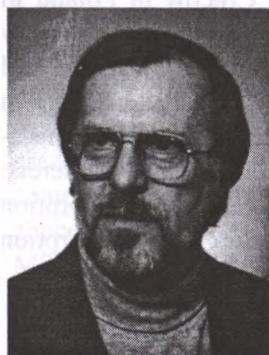
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