METHANE STORAGE AT COMMERCIALLY ATTRACTIVE LEVELS IN SUPERACTIVATED CARBONS AND COMMERCIAL ACTIVATED CARBON FIBERS

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Introduction

Natural gas storage with an adsorbent has been considered a promising technology for use in natural-gas fueled vehicles [1]. Among adsorbents investigated, carbon materials are the most effective in the storage of natural gas at low pressures (e.g. 4 MPa)[1]. Critical issues in the commercialization of the adsorbed natural gas storage technology include the storage capability of the adsorbent and the facility and cost of its manufacturing.

Previous studies [1,2,3] have shown that there are three important parameters which affect the use of the carbonaceous materials in the storage of natural gas. First of all, the *packing density* is a very important parameter to reach a high volumetric storage capacity of methane. This parameter has nearly equal importance as the micropore volume in determining methane uptake. Secondly, from a practical point of view, the amount of methane that can be *delivered* by the activated carbon is more important than the total uptake capacity. Finally, the third parameter of importance is the *density of adsorbed methane*. Among the different materials analyzed [1-3], activated carbon fibers and chemically activated carbons are attractive due to their special pore size distribution.

Thus, the objective of the present work is to analyze the applicability of both, high capacity carbon adsorbents prepared by a single stage chemical activation proccess and commercial activated carbon fibers, for methane storage.

Experimental

Two activated carbons have been chosen from a series of activated carbons prepared in our laboratory. The raw material used is a Spanish anthracite which has been submitted to a single stage potassium hydroxide activation process. The details of the process have been described elsewhere [4]. Moreover, different commercial activated carbon fiber materials (fiber, felt, and cloth) have been used in this study. Surface area characterization has been accomplished by physical adsorption of gases. Table 1 presents the results of porous texture characterization calculated from the application of the BET equation to N_2 adsorption at 77 K results and Dubinin-Radushkevich (DR) equation to N_2 adsorption at 77 K and CO_2 adsorption at 273 K [2]. The packing density of these materials has been determined by pressing a given amount of carbon material (in the range of 0.5-0.2 g) at a pressure of 1000 kg into a mold with a cross-sectional area of 1.59 cm^2. Methane adsorption isotherms at 298 K and up to 4 MPa have been carried out in a DMT high-pressure microbalance (Sartorius 4406). Further description of the experiments and the corrections for the experimental results have been described elsewhere [2]. Methane isotherms have been measured on all the samples without packing and, for selected samples, after packing the sample in an aluminium DSC container with an opening.

Table 1. Pore characterization results.

Sample	S BET (m^2/g)	V(CO_2) (cm^3/g)	V(N_2) (cm^3/g)
KUA1GC	1788	0.80	0.83
KUA1L26	2949	0.59	1.15
Commercial fiber	2206	0.43	0.79
Commercial felt	1741	0.60	0.81
Commercial cloth	1658	0.58	0.80

Results and discussion

Figure 1 presents the nitrogen adsorption isotherms corresponding to the two activated carbons prepared in our laboratory and the commercial activated carbon fiber materials. It can be observed that all samples have Type I isotherms characteristic of microporous materials. The degree of activation for these carbonaceous materials is high and micropore volumes obtained are large. This is an advantage for their application in methane storage (see Table 1). In this plot it can be observed that the knees of the isotherms present different width, indicating different micropore size distributions. This also can be observed in Table 1 by comparing the differences between the micropore volumes calculated from CO_2 and N_2 adsorption isotherms. These values are similar for the activated carbon with lower adsorption capacity (KUA1GC), which reflect a narrow micropore size distribution.

Figure 2 presents the methane adsorption isotherms obtained for all the samples used in this study. This plot shows a remarkable increase in methane adsorption for the activated carbon with higher adsorption capacity

(KUA1L26). This behaviour is expected according to the correlation, dicussed in previous studies[1,2], between methane adsorption and micropore volume. Methane adsorption for all the commercial samples is similar because they have a similar micropore volume. However, the sample KUA1GC has the same micropore volume as the commercial samples, but presents a higher methane adsorption capacity, since it has a narrower micropore size distribution.
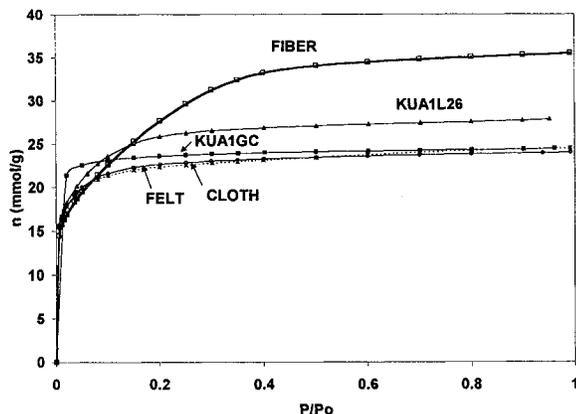

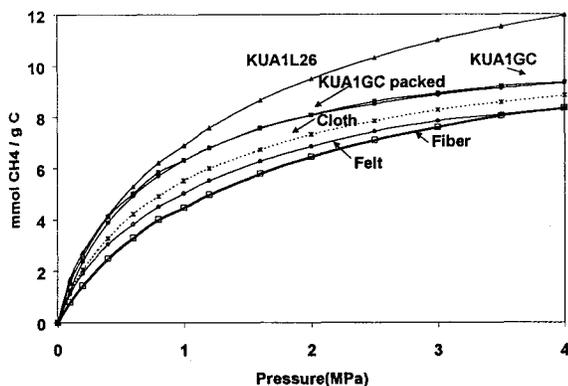**Figure 1.** N_2 adsorption isotherms at 77 K.

Figure 2. Methane adsorption isotherms at 298 K.

Figure 2 also shows the reproducibility of the results without packing and after packing the activated carbon manually up to the packing density in the aluminium DSC container. It can be noted that the acessibility of methane is not affected by the large packing density of these materials.

Table 2 contains the packing density, the volumetric uptake of methane, the methane delivery to atmospheric pressure, and the methane density (calculated as methane uptake divided by V_{micro}).

The values presented in Table 2 clearly show that all the samples used in this study have large volumetric methane

adsorption capacities because of their high micropore volumes and high packing densities. The maximum values reached (184 V/V, 159 V/V) correspond to the chemically activated carbons. Additionally, methane delivery values are also very high, reaching in the best sample 157 V/V which clearly surpass the 150 V/V value considered commercially useful [1]. Regarding the commercial activated carbon fibers, the results are rather interesting and confirm the expectations previously obtained from the study done with activated carbon fibers prepared in our laboratory [2].

Table 2. Methane storage values.

Sample	Packing density (g/cm^3)	Storage capacity (V/V)	Delivered CH$_4$ (V/V)	Methane density (g/cm^3)
KUA1GC	0.69	159	137	0.18
KUA1L26	0.62	184	157	0.17
Com. fiber	0.76	155	140	0.18
Com. felt	0.74	151	131	0.16
Com. cloth	0.67	149	129	0.17

Conclusions

Methane capacities close to 185 V/V and methane deliveries near 160 V/V have been reached using chemically activated carbons derived from a Spanish anthracite. These values clearly surpass the 150 V/V value considered useful from a commercial point of view. The activated carbon fibers, due to their special pore size distribution are also interesting for this application.

Acknowledgments

References

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