METHANE STORAGE IN ACTIVATED CARBON FIBERS

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INTRODUCTION

Natural gas (NG) has a considerable advantage over conventional fuels both from natural abundance and from an environmental point of view. However, as it is well known, its great disadvantage is its lower heat of combustion per unit of volume [1]. Compressed natural gas (CNG) may be a solution but high pressures are needed (up to 25 MPa) for natural-fuelled vehicles.

Alternatively, adsorbed natural gas (ANG) offers a very high potential for exploitation (both transport and large-scale applications). However, because its actual equivalent storage, in comparison with CNG, is quite low (8-10 MPa), suitable development of adsorbent manufacture to maximise methane uptake per unit of volume of adsorbent is needed. Among the available adsorbents, activated carbons have shown the greatest promise [1,2]. Because the methane storage (at room temperature and pressures up to 4 MPa) is exclusively restricted to the micropore volume, activated carbons with meso and macropore volumes have to be avoided. Besides the considerable work carried out with activated carbons [1,2] further investigations would be desirable to completely avoid these types of pores and larger inter-particles voids.

Selected precursors and processing techniques, including monolithic forms of activated carbons, are being investigated to improve the volumetric adsorptive capacity for methane storage [1]. However, a perusal of the literature reveals that activated carbon fibers (ACF) have been very little exploited for methane storage. The present paper analyses the potential use of two series of ACF. The results show that they are quite suitable and promising for that purpose.

EXPERIMENTAL

Two series of activated carbon fibers derived form isotropic petroleum pitch have been used. Details of the preparation of the carbon fibre and of the activation process have been reported elsewhere [3]. Basically, the fibre carbonized in N_2 for 1/2 hour at 1273 K, was used as the starting carbon material. The activation process used was carried out at 1160 K either in a CO_2 atmosphere (CFC series) or in a steam/N_2 mixture, 1/1 by volume, (CFS series). Porous texture analysis of the activated carbon samples, carried out by N_2 and CO_2 adsorption (77 and 273 K, respectively), was completed with methane and CO_2 high pressure adsorption at 298 K. A DMT high pressure microbalance (Sartorius 4406) connected to a PC, for data acquisition, was used. The balance is equipped with a pressure indicator and a thermocouple mounted in the sample housing, as well as with a rotary pump. The maximum working pressure used in this study, with a precision of 0.1%, was 4 MPa.

RESULTS AND DISCUSSION.

The effects of the activating gas and of the burn-off on methane storage have been studied. The petroleum pitch-based activated carbon fibers used exhibit different porous texture evolution with burn-off depending on the activating gas used (3). Figure 1 shows the volume of N_2, CO_2 and methane adsorbed, using liquid density values of 0.80, 1.02 for N_2 and CO_2 and 0.14 g/cc for CH_4 (deduced from experimental data), respectively. It can be observed that CO_2 activation produces a higher methane uptake at higher burn-off levels. These results agree with a previous one in which it was reported that CO_2 develops essentially microporous ACF(without any significant contribution of larger pores) contrary to steam (see Fig 1).

It is well recognized that experimental correlations between high pressure methane uptake and N_2 adsorption at 77 K exist [1,2]. However, because in our ACF with low burn-off slow diffusion of N_2 at 77K is expected (see Fig.1), both low and high pressure adsorption of CO_2 have been determined. Figure 2 shows the correlation obtained between methane adsorption and the micropore volumes, deduced combining N_2 and CO_2 adsorption data (DR), the latter used for samples

with N_2 activated diffusion problems. The good linearity and the absence of a significant intercept at the origin confirms the relationship between these two parameters. High pressure adsorption of CO_2 also confirm this correlation. From Figure 2 the 0.14 g/cc density used in Fig.1 has been deduced for the adsorbed methane. This density value, almost constant and independent of the degree of activation, indicates that higher degree of activation, specially for the CFC series, should be exploited because methane uptake would improve.

From a practical point of view, volumetric capacity has more interest than adsorption per unit of mass. Therefore, bulk density has been determined for most of the samples. Interestingly, the values obtained are quite high. As expected, the bulk density decreases with the degree of activation from 1.1 g/ml (0% BO) to 0.8 g/ml (54% BO). Two important characteristics of these ACF, specially in the CFC series, should be pointed out: 1) they have a high micropore volume that develops very well upon activation, without forming larger pores (see Fig 1) and 2) they have a quite high bulk density. Therefore, the volumetric capacity for these ACF are positively high. It is worth noting that the adsorptive capacity of 150 v/v, suggested for monolithic carbon [1] has been reached with the CFC 54 sample. Furthermore, for the reason above commented, it is expected that using CO_2 activation and higher burn-off degrees a larger adsorptive capacity can be obtained.
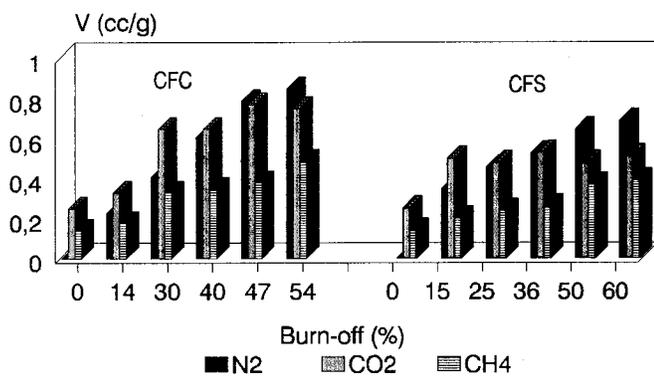
Complementary work which is now under progress seems to confirm it. Thus, a sample with a 73 % BO, with and N_2 surface area of 2400 m^2/g, will reach, assuming a bulk density of 0.7 g/cc, a methane uptake value (deduced from extrapolation of Figure 3) of 171 v/v.

Finally, reversibility of the methane adsorption process has been studied and similarities in both the adsorption and desorption isotherms have been found. The amount of methane retained at 0.1MPa, which is also an important parameter from a practical point of view, is of about 12% for sample CFC 54.

REFERENCES

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2.   J.T. Mullhaupt et al, "Carbon '92", 367, 1992.
3.   J. Alcañiz, D. Cazorla, A. Linares, S. Yoshida and A. Oya, *Carbon*, 32, 1277, (1994).

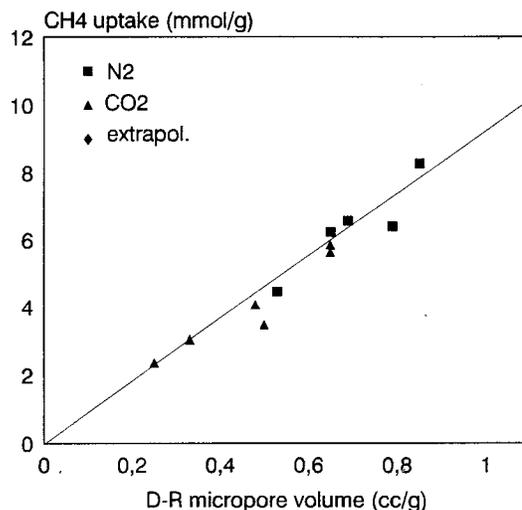Figure 1. D-R micropore volume from N_2 and CO_2 adsorption and CH_4 uptake at 298 K.

Figure 2. CH_4 uptake versus D-R micropore volume