POSTER

MONOLITHIC MICROPOROUS CARBON FOR GAS STORAGE

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INTRODUCTION

Many commercial carbons have been evaluated for adsorptive storage of natural gas (ANG) in road vehicles, but most of them have methane volumetric adsorptive capacities (3.5 MPa, 25 °C) less than 100 v/v in units of CH_4 volume (at NTP, 0.1 MPa, 25 °C) per volume of carbon. The volumetric capacity is the critical adsorption parameter, since it is the volumetric energy density of the ANG that limits vehicle driving range. Consequently, monolithic forms of activated carbons should be developed for ANG because the interparticular spaces in a bed of granular activated carbons limit the enhancement of energy density. Parkyns and Quinn [1] suggest that a monolithic carbon with an adsorptive capacity of ~150 v/v at 3.5 MPa is a feasible target for a commercial carbon monolith. Computer simulations [2] of methane adsorption in model micropores suggest that the maximum capacity is 209 v/v at 3.4 MPa in pores of width 11.4 Å. Thus it may be possible to further enhance methane storage capacity by developing monolithic microporous carbons with controlled micropore size from well selected precursors and suitable processing techniques.

EXPERIMENTAL

In this study, AX-21 powdered carbon (Anderson Development Co.) was adopted to form monolithic carbons using a phenolic resin binder, FRD 3656 [Borden (UK) Ltd]. The resin was mixed with AX-21 powder in ratios ranging from 17 to 65 wt.% and the mixture was moulded into discs (∅ 25x5 mm) at 40 MPa and 150 °C. The monoliths were produced by heating at 800 °C for 2 h in N_2. Bulk densities, ρ, of the monoliths were obtained from the weight and geometric volume of the pellet. Adsorption of N_2 at 77 K was measured in a Micromeritics ASAP2000 instrument to calculate BET surface area, S_{BET}, and D-R micropore volume, V_o. Compressive strength, σ_c, was measured on an Instron 1185.

RESULTS AND DISCUSSION

There is a substantial increase in ρ after pelletising AX-21 carbon with 17 wt.% resin, although S_{BET} decreases. With increasing binder content, there is a further, progressive increase in ρ and σ_c accompanied by a progressive decrease in S_{BET} (see Table 1). Assuming that the contribution to S_{BET} from the binder is negligible and that AX-21 carbon is thermally stable after heating to 800 °C, it is possible to estimate the expected value of S_{BET} from the rule-of-mixtures. This shows that the experimental values of S_{BET} for the monoliths are less than the expected values, presumably because of blockage of access to pores in the AX-21 filler by the binder. Therefore, the amount of binder applied should be a balance between adsorptive capacity and mechanical integrity.

Several extensive studies of correlations between S_{BET} values (N_2, 77 K) and methane adsorption at 3.5 MPa and 25 °C allow the methane adsorptive capacities of monoliths to be estimated from S_{BET}.

From a study of 35 commercial activated carbons Mullhaupt *et al.* [3] established the following empirical correlation between maximum gravimetric adsorptive capacity for methane G_{max}, (mmol/g) and S_{BET} (m^2/g):

$$G_{max} = 1.31 + 0.00444\, S_{BET} \quad (1)$$

The maximum volumetric capacity, L_{max} (25 °C, 0.1 MPa) for methane may be estimated from

$$L_{max} = 24.465\, \rho\, G_{max} \quad (2)$$

From a study of 38 commercial carbons Parkyns and Quinn [1] also find that it is possible to estimate the total volumetric capacity for methane, L, from the equation

$$L = L_p + L_g \quad (3)$$

where L_p is the adsorbed methane in micropores given by

$$L_p = (237V_o + 9.2)\rho \quad (4)$$

where V_o is the Dubinin-Radushkevich micropore volume. L_g is the methane adsorbed in non-microporous voids in the monolith given by

$$L_g = 36(1 - V_o\,\rho - 0.345\,\rho) \quad (5)$$

Values of L and L_{max} are in reasonable agreement. Figure 1 shows that G_{max} decreases progressively with decreasing AX-21 carbon content in the monoliths. However, the value of L_{max} increases to a maximum of 151 v/v for the monolith with a phenolic resin content of 31 wt.%. From equation (2) the maximum in the volumetric capacity results from the opposing trends of a reduction in G_{max} and increase in bulk density with increasing resin carbon content. Chahine and Bose [4] report a volumetric capacity of 144 v/v for a monolith made from AX-21 carbon with 2 wt.% of an unspecified binder. Quinn [5] has studied the formation of a series of monoliths made from AX-21 carbon and PVDC latexes. Figure 2 compares the estimated L_{max} values for the AX-21-phenolic resin monoliths with measured values for AX-21-Saran159 monolith. Figure 2 shows that the volumetric capacities of the AX-21-phenolic resin carbons are higher than those of the AX-21-Saran159 carbons at low binder contents, but the reverse is true at high binder contents.

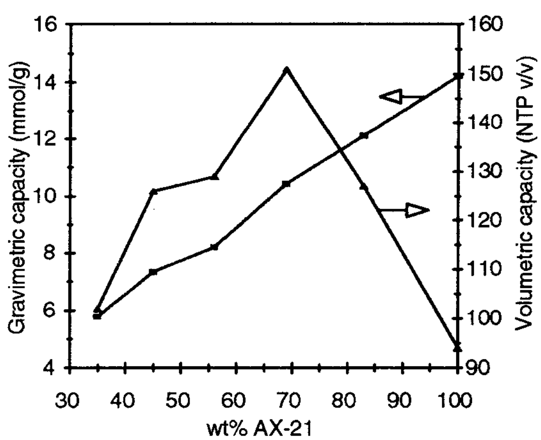

Figure 1 Volumetric and gravimetric capacities of methane in AX-21/resin monoliths

CONCLUSIONS

Monolithic carbons can be prepared from AX-21 carbon by a simple process using phenolic resin as a binder. A resin content of ~30 wt.% yields a monolith with adequate strength and an estimated volumetric capacity for methane of ~150 v/v, which is in the target range for commercial carbon monoliths.

REFERENCES

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2. K.R. Matranga, A.L. Myers, and E.D. Glandt, Chem. Eng. Science, 47, 1569, 1992.
3. J. T. Mullhaupt *et al.*, "Carbon'92", p367, 1992.
4. R. Chahine and T. K. Bose, "20th Biennial Conference on Carbon", p638, 1991.
5. D. Quinn, "Gas Utilisation Research Forum", London, 1990.

Table 1 Properties of AX-21-resin monoliths

AX-21 (wt%)	ρ (g/cm^3)	S_{BET} (m^2/g)	V_o (cm^3/g)	σ_c (MPa)
100	0.27	2909	1.22	—
83	0.43	2432	1.19	—
69	0.59	2054	0.86	10.09
56	0.64	1553	0.66	10.29
45	0.70	1357	0.62	28.72
35	0.72	1007	0.44	35.26

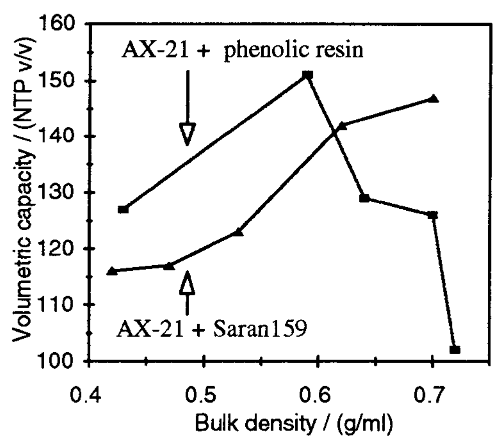

Figure 2 Comparison of volumetric capacities of AX-21 carbon monoliths