

SYNTHETIC CARBONS DERIVED FROM LIGNOSULPHONATE WASTE AS NEW MATERIALS FOR GAS STORAGE

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Introduction

Natural gas adsorbed on microporous carbons at 34 bar and 298 K is widely believed to be a promising alternative to compressed natural gas (200 bar and 298 K) for natural gas vehicles because of its low capital and operating cost [1]. Methane is used as a model for natural gas and the relevant parameter is the volumetric capacity of methane stored. Molecular simulations [2] suggest that microporous carbon with a pore size of about 1.1 nm is optimum for methane storage. Such a carbon should also have low mesopore, macropore, and void (interparticle) volumes. Parkyns and Quinn [1] have shown the importance of maximising the bulk density of the carbon by minimising the void volume in order to enhance the volumetric methane capacity, e.g. by the development of carbon monoliths. First step assessments of storage assume that the higher the surface area and micropore volume, the higher the adsorption of methane at 298 K. Here, we report the characterisation of materials derived from lignosulphonate waste by using nitrogen adsorption at 77 K, mercury porosimetry, helium pycnometry and scanning electron microscopy (SEM). Initial results concerning methane adsorption at 298 K on the most promising activated carbon will be presented.

Experimental

Microporous carbons were made from cross-linked porous resin, in the form of spherical particles containing up to 70-weight % of sodium lignosulphonate waste from the paper-pulp industry, which was carbonised and then activated in carbon dioxide. Five samples of lignosulphonate derived materials were characterised: M1 (the crude-resin precursor), M2 (the carbonizate), M3 and M4 (two activated materials with 44% and 55% of burn-off respectively), and LF-15 (another resin-based activated carbon with 59% of burn-off). SEM studies showed that the activated materials comprise hollow spheres and solid spheres containing holes. The samples were characterised by nitrogen adsorption at 77 K (ASAP 2010, Micrometrics Instrument Corporation) to measure BET surface areas and pore volumes. The

particle and high-pressure densities of the carbons were measured using a mercury porosimeter (Autopore II 9220, Micrometrics Instrument Corporation). The skeletal carbon densities were measured by a helium pycnometer (AccuPyc 1330 Micrometrics Instrument Corporation). Excess methane adsorption isotherms at 298 K were measured gravimetrically on a Hiden Intelligent Gravimetric Analyser (IGA) up to a pressure of 8 bar.

Results and Discussion

The measured densities, including packing density (ρ_a), skeletal density (ρ_{He}), particle density (ρ_1) and high-pressure density (ρ_2) of M2, M3, M4 are listed in Table 1. The distribution of the relative pore fractions for the activated sample M3 and M4, calculated using equations described elsewhere [1], are illustrated in Figure 1. The two activated samples M3 and M4 show a similar distribution of pore fractions and the main observation is that the non-microporous fraction (voids and macro- and mesopores) represents a large fraction of the total volume (Figure 1).

Table 1. Densities / g cm⁻³ for the carbonised and activated resins.

	ρ_a	ρ_{He}	ρ_1	ρ_2
M2	0.57	1.97	0.90	1.14
M3	0.37	2.20	0.56	0.74
M4	0.33	2.10	0.50	0.67

BET surface areas and micropores volumes can be used as preliminary parameters to compare the activated carbons M3, M4 and LF-15. Some authors have shown that there is a linear relation between methane capacity and BET surface area [3] or micropore volume [1] for a given material. The values of the volumetric methane stored capacities of M3, M4 and LF-15 have been estimated by using the relations presented elsewhere [1, 3] and the results are summarised in Table 2. The BET surface areas, microporous volumes and packing densities of the samples are also listed in Table 2. The two empirical expressions give different values of the volumetric methane stored capacity for the same sample

This can be understood by the fact that these two expressions involve two different parameters, i.e., either the surface area or the micropore volume. Using the Parkyns and Quinn micropore equation, the M4 sample is predicted to have the highest stored methane capacity (95 v/v).

Figure 2 shows a typical 298 K methane isotherm for activated carbon M4. Also shown in Figure 2 is a best fit to the data using the Tóth equation [4], a three-parameter variant of the Langmuir isotherm.

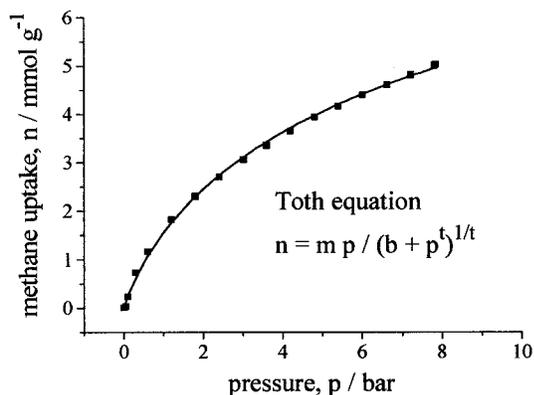


Figure 2. Methane isotherm at 298 K for activated carbon M4 plus best fit to Tóth equation.

It has been found that all measured methane isotherms (to 8 bar) can be accurately fitted by the Tóth equation. Methane uptake at 34 bar of M4 has been calculated by extrapolation of the Tóth equation. The methane stored capacity and delivered capacity (stored capacity at 34 bar minus capacity at 1 bar) of M4 have been calculated as ~94 v/v and 53 v/v respectively. This stored methane capacity is in good agreement with that estimated from

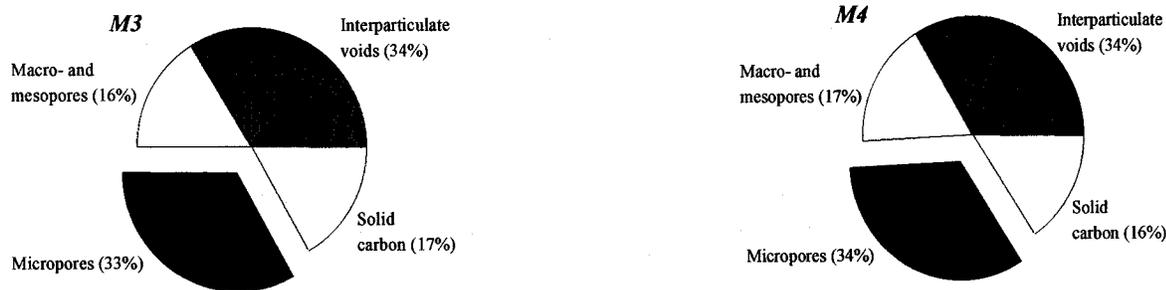


Figure 1. Pore volume fractions in activated materials M3 and M4.

Table 2. Estimated methane stored capacities at 34 bar and 298 K on M3, M4 and LF-15 activated carbons calculated from packing densities and surface areas [3] or pore volumes [1].

	S_{BET} $\text{m}^2 \text{g}^{-1}$	$V_{\text{micropore}}$ $\text{cm}^3 \text{g}^{-1}$	ρ_a g cm^{-3}	Mullhaupt <i>et al.</i> [3]	Parkyns and Quinn [1] $V_{\text{stored}}(2)$ v/v
M3	1202	0.595	0.37	60	78
M4	1610	0.915	0.33	68	95
LF-15	1235	0.552	0.47	78	88

the micropore volume using the empirical expression of Parkyns and Quinn [1] (Table 2).

Conclusions

Further studies are necessary on monoliths manufactured from the activated samples because of the low packing density and therefore the low delivered capacities (~53 v/v). The Tóth equation seems to be a good way to estimate stored and delivered methane capacities from measurements over a limited range of pressure.

References

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Acknowledgements

Research sponsored by the EU under TMR contract ERBFMBICT972773 and INTAS contract INTAS -96-1023.