# LIGNITE DERIVED MONOLITHIC CARBONS FOR METHANE STORAGE

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## Introduction

Adsorbed natural gas (ANG) storage has attracted interest as an alternative to high pressure compressed natural gas (CNG) storage for applications such as natural gas vehicle (NGV) fuel storage systems. Most previous work has focussed on the use of active carbon powders[1] where the volume occupied by interparticular void space, macropores (diameter > 50 nm) and mesopores (50 nm > diameter > 2 nm) may amount for more than 50% of the total storage vessel volume. This project aimed to minimize this 'wasted' volume through the development of carbon monoliths which possess minimal void, macropore and mesopore volume and, at the same time, the maximum possible volume of. Work focussed on the use of Victorian lignite as a relatively cheap precursor material. Three different approaches to monolith production were trialled, namely: binderless extrusion, binderless briquetting and high pressure briquetting (with binder).

## Experimental

Gravimetric methane adsorption capacities were determined at ambient temperature (20±2°C) and 4 MPa (gauge) using a Sartorius high pressure microbalance. Corrections were made for systemic (balance) and sample buoyancy effects. Methane storage capacities were also determined directly in a purpose-built adsorption/desorption apparatus. This unit used calibrated (Brooks) mass flow controllers to measure the volume of gas flowing into and out of an adsorbent filled pressure vessel (maintained at 25°C). Density measurements and pore size distributions were derived from the combination of mercury porosimetry and helium pycnometry data.

## Results and Discussion

Loy Yang lignite possesses very low levels of inorganic impurities (Table 1), is very soft and has high concentrations of oxygen which provide good ion-exchange sites for alkali salts (eg, KOH). These factors help to facilitate good dispersion of activating salt throughout the lignite matrix during blending in a laboratory kneader. Monoliths were formed prior to activation, as briefly described in Table 2. Care was required to maintain monolith integrity during handling and activation.

Differences in storage capacity can be partly attributed to differences in the relative abundance of macro and mesopores (figure 1). Since methane adsorption occurs predominantly in the micropore region, the presence of larger pores is unfavorable. The micropore size distributions for the two better performing samples exhibit distinct maxima at about 0.74 nm (figure 2). Interestingly, this correlates well with the optimal pore size predicted from modeling studies[1,2].

Figure 3 illustrates that there is no deterioration in the performance of a monolith (10cm x 1.3cm diameter) after 20 cycles fill-empty cycles, when using pure methane.

## Conclusions

The high pressure briquetting method proved to be the best approach to monolith production (Table 3). The binderless extrusion method was the least successful. The best monolith prepared from Loy Yang lignite adsorbed 127 g methane/L carbon or 194 $V_{STP}/V_C$ (25°C, 4MPa). Pore size characterisation determined that optimised carbons for methane storage posses micropore size distributions exhibiting maxima at about 0.74 nm, together with minimal void and macropore volume.

## References

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2. Cracknell R F and Gubbins K E: A Monte Carlo study of methane adsorption in aluminophosphates and porous carbons. J Molecular Liquids 1992; 54: 261-272.
3. Bosé T K, Chaine R and St Arnaud J. US Patent 1991: 4,999,330.

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Table 1 Analytical data for Loy Yang Run-of-Mine Coal (-8mm)

| Identifier | % |
|---|---|
| Moisture | 62.2 |
| *Proximate Analysis* | |
| Volatile Matter | 52.0 |
| Ash | 1.0 |
| Fixed Carbon | 47.0 |
| *Ultimate Analysis* | |
| Carbon | 68.0 |
| Hydrogen | 4.9 |
| Nitrogen | 0.66 |
| Sulfur | 0.3 |
| Oxygen (by difference) | 26.1 |

Table 2 Brief Description of Preparative Methods

| |
|---|
| Binderless Extrusion<br>Lignite and predissolved alkali salt (KOH) were homogenized in a duplex kneader, then discharged through a screw feeder fitted with an extrusion nozzle. Extrudates (20mm diameter) were collected in pellet form, then dried under controlled conditions in a fan forced oven. Preformed pellets were carbonized and activated in nitrogen under temperature programmed conditions extending to 900°C. |
| Binderless Briquetting<br>The homogenization procedure outlined above was followed. Alkali loaded lignite was ground to -212 µm, then briquetted (typically at 15 MPa) in a 30mm die. Carbonization and activation followed the procedure outlined above |
| High Pressure Briquetting (with binder)<br>Lignite char (450°C), mixed with KOH (1/2) ratio, was activated under nitrogen at temperatures up to 900°C, then briquetted in an approach similar to that reported by Bosé[3]. Pre-wetted char was mixed with a solution of PVA (or other binder) in water. Typical briquetting conditions were 500 MPa and 200°C. |

Table 3. Optimum results obtained for each of the three methodologies.

| Method | Methane adsorbed (%w/w) | Methane adsorbed (%g/L) | Methane Stored $V_{STP}/V_C$ |
|---|---|---|---|
| Binderless Briquetting | 13.4 | 74.7 | 114 |
| Binderless Extrusion | 12.9 | 91.6 | 140 |
| High Pressure Briquetting | 12.2 | 126.9 | 194 |

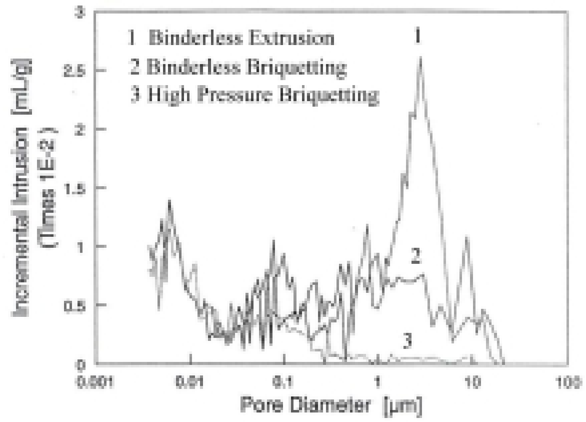


**Figure 1.** Mercury intrusion profiles for samples prepared by the three briquetting methods.

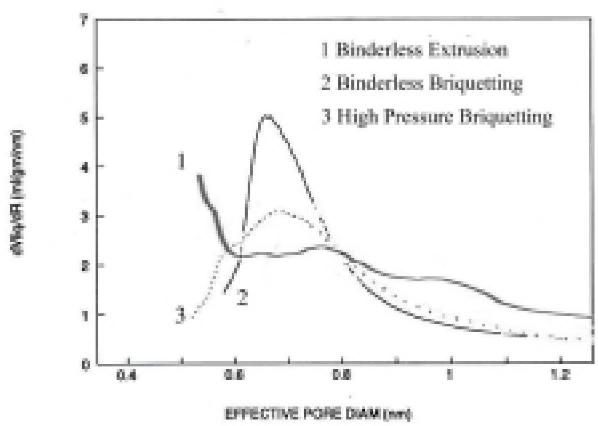


**Figure 2.** Horvath-Kawazoe micropore size distributions determined by Ar adsorption (at liquid Ar temperature).

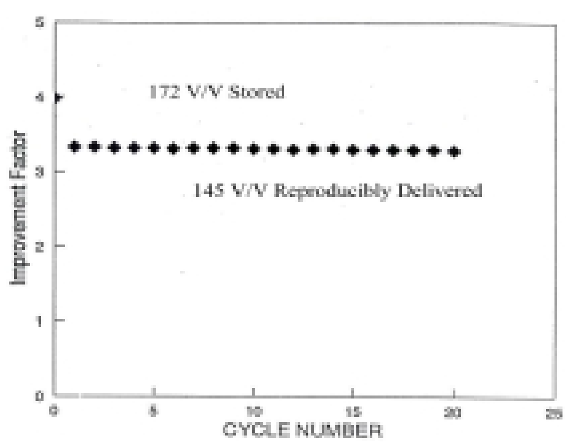


**Figure 3.** Cycling behaviour of monolithic carbon prepared by high pressure briquetting. Cycled between 0.1 and 4 MPa at ambient temperature using pure methane.