The production of high surface carbons from coal using pre-swelling in solvents to disperse coking catalysts

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Carbons have been produced from Amagá coal using $ZnCl_2$ as a catalyst to increase carbon yields during pyrolysis. It was found that the surface area and micropore volume could be increased by swelling the coal using solvents to create porosity in the coal and increase the dispersion of the catalyst. The highest surface area was achieved using pyridine as the swelling agent and a ratio of 1:1 wt coal:$ZnCl_2$.

1. Introduction

The use of activated carbons in the traditional field of separation processes is continuously increasing [1] and new applications for activated carbons such as in low pressure methane storage [2,3] are being developed. The most desirable characteristics of carbons for use in methane storage are high density, high levels of microporosity and low levels of meso- and macroporosity. A wide range of carbons have been tested after being produced from biomass and polymer precursors [2,3]. The best way of producing such materials is to use a precursor that naturally produces a high char yield and also a high surface area without subsequent activation. The activation of carbons in oxidizing atmospheres, although tending to increase surface areas, also tends to broaden pore size distributions.

Despite problems of ash, sulphur and nitrogen contamination, coal has a number of advantages as a precursor for the production of activated carbons. In particular, compared to biomass precursors, coal is a relatively dense and carbon rich material. This means that following pyrolysis, carbon yields tend to be high and the product relatively dense and microporous.

One method for further increasing carbon yields and levels of microporosity could be to pyrolyse to a coal impregnated with a coking catalyst, such as $ZnCl_2$. The effect of $ZnCl_2$ during pyrolysis is to dehydrogenate hydrocarbons during pyrolysis, promoting increased crosslinkage in the structure, reducing the production of volatile material and hence increasing char yields [4]. One problem in attempting to use a chemical activation with coal is the accessibility of the catalyst to the macromolecular structure. Recent investigations by Larsen *et al.* [5] using liquid uptake data, and by Hall *et al.* [6] using contrast matching small angle neutron scattering, have shown that bituminous coals do not possess a connected pore system. Therefore, in the absence of any agent to transport the catalyst into the structure the effects of $ZnCl_2$ may be mainly limited to the external surface of particles. Possible ways to dispersing the $ZnCl_2$ include the pyrolysis of the coal under high pressure and also dissolving it in a solvent that can diffuse into the coal structure.

It is generally agreed that coals have a three dimensionally crosslinked macromolecular structure [7]. One effect of this is that they increase their volume, or swell, but do not completely dissolve in solvents. Basic solvents such as pyridine tend to swell coals more than non-polar solvents. This is because basic solvents can disrupt hydrogen bonds in coal [8]. During swelling in basic solvents coals undergo a glass to rubber transition [9,10] and, since diffusion in rubbery materials is roughly two orders of magnitude faster than through glassy materials, this may provide an efficient method for catalyst dispersion. Additionally, using small angle neutron scattering, Hall *et al.* [11] have shown that one effect of swelling coals in pyridine is to create microporosity. This may also increase catalyst dispersion.

Therefore, it is of interest to determine whether the influence of pressure or the use of swelling agents can increase the accessibility of $ZnCl_2$ to coals and also whether highly microporous carbons can be produced.

One problem in the production of highly microporous carbons is that a significant amount of the microporosity may be closed to the external surface and therefore unavailable for adsorption. Hall *et al.* [12] have used contrast matching small angle neutron

scattering (CM-SANS) to detect the presence of closed porosity in polymer resins.

2. Experimental procedure

An important Colombian coal, Amagá (76 wt % C, 16.3 wt % O) was ground to less than 100 Tyler mesh in air, dried and stored in a desiccator until required. $ZnCl_2$ was used as the coking catalyst.

The high pressure method used in attempts to load the catalyst onto the coal was as follows: 3 g of the dried Amagá were mixed with the same weight of $ZnCl_2$ and placed in a high pressure autoclave. The autoclave was purged with high purity N_2 and pressurized to 1×10^7 Pa. The autoclave was then placed in a heated sand bath at the required reaction temperature (350 or 450 °C) for the required time (15 or 180 min). Following pressure reduction and cooling the products were removed, and the char washed in water to remove the $ZnCl_2$.

The swelling method for catalyst loading was as follows. The required weight of $ZnCl_2$ (0, 50 or 100% of coal weight) was dissolved in either water, ethanol or pyridine and mixed with 3 g of the coal. The mixtures were allowed to come to equilibrium for 12 h. The mixtures were then transferred to a porcelain crucible and the solvent evaporated. The dried coal/catalyst mixtures were then placed in a horizontal tube furnace, purged in a carrier of high purity nitrogen at 120 mL min^{-1}. The reactor was heated to either 600 or 650 °C at 20 °C min^{-1} and left for the required reaction time (15 or 180 min). Following cooling the char was washed with water to remove the $ZnCl_2$.

The surface areas were determined by N_2 adsorption at 77 K using a Micrometitics ASAP instrument. Pore size distributions and tests for the existence of closed porosity in the chars were achieved using contrast-matching small angle neutron scattering. The latter was performed at the intense pulsed neutron source (IPNS) small angle diffraction (SAD) instrument at the Argonne National Laboratory. IPNS is a spallation neutron source in which 450 MeV protons are impacted on a uranium target. For the SAD instrument, the neutrons are moderated using a solid methane block at 22 K. This produces neutrons with a wavelength in the range 0.05–1.4 nm, suitable for small angle scattering. The sample holders were made of a low boron glass, Suprasil with a path length of 0.2 cm. The scattering data were corrected for the scattering from the sample holder and other instrumental backgrounds. Normalization for the sample thickness and transmission were made and the data were scaled to yield an absolute calibration. Deuterated toluene was used as the contrast matching liquid.

Scanning electron microscopy (SEM) was used to observe the morphology of the particles following pyrolysis.

3. Results and discussion

The results of the high pressure, no solvent experiments are shown in Table I. The Brunauer–

1456

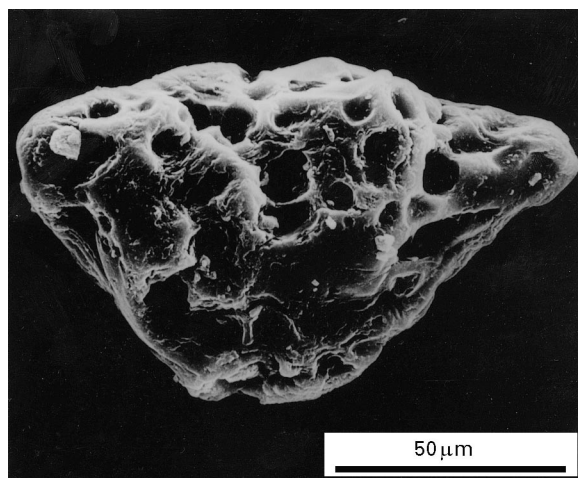| Run	Temperature (°C)	Time (min)	Char yield (%)	BET area (m²g⁻¹)
1	350	15	74	3
2	350	180	nd	2
3	450	15	78	2
4	450	180	59	18

Figure 1 SEM micrograph of char produced from Amagá coal that had been pyrolysed under a 1×10^7 Pa N_2 atmosphere for 15 min at 350 °C.

Emmett–Teller (BET) surface area of the original Amagá was 8 m² g⁻¹. Therefore, most of the samples exhibit a *reduction* in surface area during pyrolysis. The char yields are relatively high for samples 1 and 3 at 74 and 78% respectively. One explanation for the reduction in surface area could be that as tars are emitted from the pyrolysing coal they come in contact with the $ZnCl_2$ at the external surface. Accelerated pyrolysis then takes place here forming an impervious barrier for the emission of further tars. The surface area may therefore be reduced by the blocking of porosity. The SEM micrograph of Fig. 1 shows strong pitting on the surface. This could be caused by localized pressure build up fracturing the external barrier. The only exception to this is the 450 °C, 180 min experiment. The char yield is lower and the surface area higher for this experiment. Apparently, some loss of carbon has taken place. This may be due to gasification by CO_2 formed during pyrolysis opening closed porosity.

In any case, the surface areas of these chars are too low to be of interest, at least without further activation. Although there may be significant closed porosity in these samples, it was decided not to investigate these chars further with CM-SANS because our objective was to produce high surface area chars without further activation. The principal conclusion from runs 1–4 is that pressure loading of the $ZnCl_2$ is ineffective in producing high surface area carbons without subsequent activation.

TABLE II Experiments with water and ethanol, 100% $ZnCl_2$, Amagá coal with atmospheric pressure N_2 flow

Run	Solvent	Temperature (°C)	Time (min)	Char yield (%)	BET area (m^2g^{-1})
5	Water	500	15	79	186
6	Water	600	15	nd	239
7	Ethanol	500	180	70	546
8	Ethanol	600	15	77	696
9	Ethanol	600	180	60	647

Table II shows the results of using water and ethanol to disperse the $ZnCl_2$ in the coal prior to pyrolysis. Water was determined to have a swelling ratio of $1:12$ and ethanol a swelling ratio of $1:44$. The surface areas are much greater than for the pressure produced samples but the char yields are broadly the same. Since both liquids swell coal to some extent it is reasonable to assume that during the soaking period some $ZnCl_2$ has diffused into the coal structure. Furthermore, since ethanol swells the coal more than water the dispersion of $ZnCl_2$ in the ethanol swollen coal would be expected to be greater.

Comparing runs 6 and 8 it can be seen that the ethanol treated sample has a greater surface area. A possible explanation is as follows. During the swelling stage porosity is created in the coal allowing $ZnCl_2$ to diffuse into the structure. The higher swelling ethanol allows more catalyst to diffuse into the coal. When the solvent is removed from the coal, the structure collapses, trapping the $ZnCl_2$. During the pyrolysis phase the catalyst promotes crosslinking by promoting dehydrogenation reactions, as described in the Introduction, producing carbon–carbon bonding in the structure. A relationship between crosslink density in precursors, char yields and carbon surface area has been established by Hall et al. [13] for oxidized cellulose.

The effect of increasing the pyrolysis temperature for both the water (runs 5 and 6) and the ethanol (runs 7 and 9) is to increase the surface areas. This may be due to the fact that crosslinking reactions have not been fully completed at 500 °C. However, the maximum surface area of this set was for run 8, at 600 °C for 15 min. Increasing the time of pyrolysis (run 8 and run 9) decreases the char yield and the surface area. The reasons for this are unclear. It is unlikely to be due to gasification reactions as in runs 2 and 3 because runs 8 and 9 were performed in a flowing nitrogen atmosphere, which would remove any CO_2 and H_2O from the sample. The decrease in char yield and surface area may be due to the fact that devolatilization is not fully completed after 15 min of pyrolysis.

The results of Table II suggest that use of a higher swelling solvent may further increase catalyst dispersion and therefore surface area. Therefore, it was decided to use pyridine, a basic solvent and well known as a good swelling agent. Apart from the swelling properties of pyridine there is one other important difference between it and the solvents in Table II. Pyridine extracts a large amount of material from coals. In a complete soxhlet extraction $\sim 30\%$ of most bituminous coals can be dissolved. As such, apart from the porosity created in swollen coals, extra porosity may be
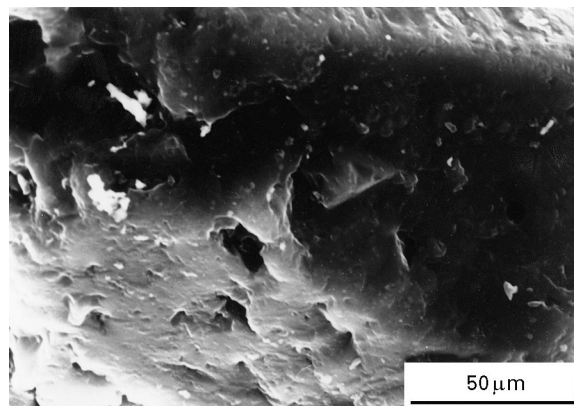

Figure 2 SEM micrograph of char produced from Amagá coal that had been swollen with pyridine and loaded with 100 wt % $ZnCl_2$, dried then pyrolysed under atmospheric pressure N_2 at 600 °C for 15 min.

TABLE III Experiments with pyridine, variable $ZnCl_2$, Amagá coal with atmospheric pressure N_2 flow

Run	$ZnCl_2$ (wt %)	Char yield (wt % daf)	BET area (m^2g^{-1})	Micropore area (m^2g^{-1})	Micropore volume (cm^3g^{-1})
10	0	65	8	6	0.002
11	50	71	670	nd	nd
12	100	71	1106	937	0.368

formed due to extraction of soluble material. This may further enhance the catalyst dispersion.

An SEM micrograph for the char created using pyridine swelling is shown in Fig. 2. Comparison of Figs 1 and 2 highlights radical differences in the pyrolysis of the chars. The extreme surface pitting of the pressure formed char is absent for the pyridine treated char. This suggests that the impermeable layer is absent from the pyridine produced char and that most of the $ZnCl_2$ has diffused into the structure.

Table III shows the results of the pyridine treated coal chars and the effect of varying the amount of $ZnCl_2$. The pyrolysis time was 15 min and the pyrolysis temperature was 600 °C. Run 10, a blank experiment, shows that the presence of $ZnCl_2$ is important to the creation of open porosity during pyrolysis. The surface area of the chars increases with increasing weight of $ZnCl_2$ even though there is not much change in the char yield. The objective of producing high surface area carbons without a subsequent activation step has finally been achieved for the run 11 and run
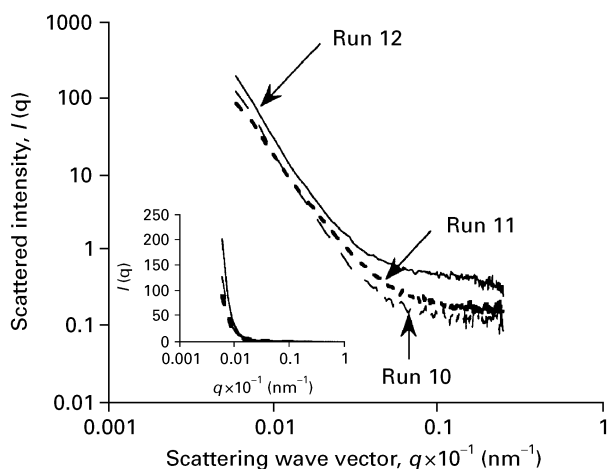
Figure 3 Small angle neutron scattering on chars produced from Amagá coal that had been swollen with pyridine, loaded with 0, 50 and 100 wt % $ZnCl_2$, dried then pyrolysed under atmospheric pressure N_2 at 600 °C for 15 min.

Figure 4 Small angle neutron scattering on char produced from Amagá coal that had been swollen in pyridine, dried then pyrolysed under atmospheric pressure N_2 at 600 °C for 15 min. Both the dry sample and the char contrast matched by mixing with d-toluene are shown.

12 carbons, and the surface areas are sufficiently high to be of interest for practical applications. It was therefore decided to further investigate the porosity of these carbons using contrast matching small angle neutron scattering (CM-SANS).

SANS of the dry samples for runs 10, 11 and 12 is shown in Fig. 3. The overall intensity of scattering increases with increasing $ZnCl_2$ content in the pyrolysis. This is consistent with the increase of porosity as monitored by nitrogen adsorption. Run 12 differs from runs 10 and 11 in the scattering over the region $0.04 < q < 0.29$ (where q is the scattering wave vector) in that there is an upward deviation in the scattering curve. This has been previously observed by Foster and Jensen [14] and is caused by scattering of micropores. CO_2 adsorption has also shown that this carbon contains considerable microporosity. At the highest q value available on the IPNS instrument, 0.029 nm^{-1} the curve deviates downward, suggesting that the size of the smallest micropores cannot be resolved by the instrument. At the low q end of the scattering curves the scattering intensity is increasing, suggesting that the size of the largest scattering entities cannot be resolved by the instrument. Hall *et al.* [12] have shown that small angle scattering from the dry samples comes from three sources, open porosity, closed porosity and interparticle scattering. Contrast matching by mixing the sample with deuterated toluene eliminates interparticle scattering and also scattering from open porosity. The contrast matching results are shown in Figs 3–5.

The effects of contrast matching for run 10 are shown in Fig. 4. There is no significant change in scattering intensity for any q value. The surface area of this char is very small, suggesting very low levels of open porosity. Therefore, the scattering from both the dry and contrast matched curves probably comes from porosity that is closed to the external surface. Neither of the curves linearize on Guinier plots which suggests that there is a broad range of scattering objects, in fact the point that the curve is linear on
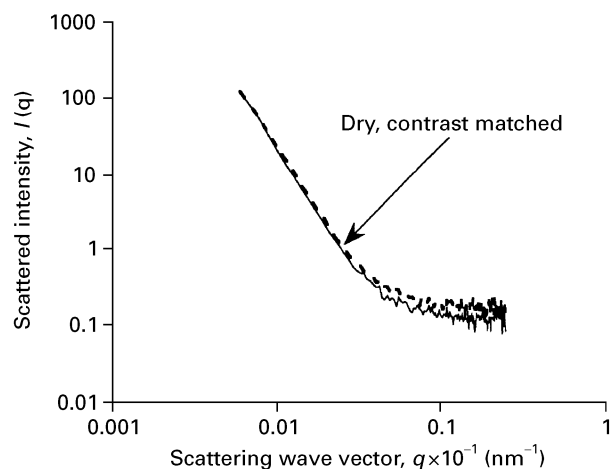

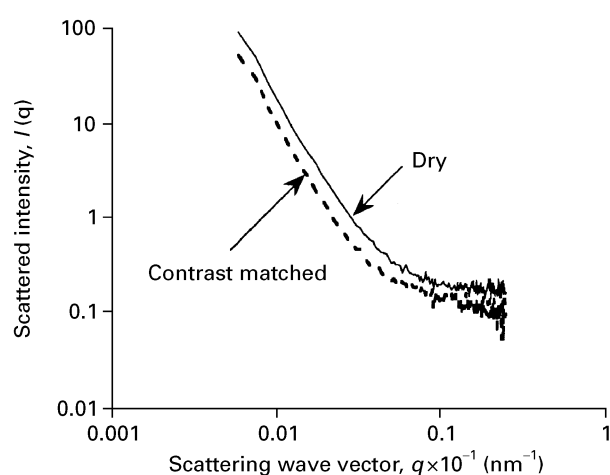*Figure 5* Small angle neutron scattering on char produced from Amagá coal that had been swollen in pyridine, loaded with 50 wt % $ZnCl_2$, dried then pyrolysed under atmospheric pressure N_2 at 600 °C for 15 min. Both the dry sample and the char contrast matched by mixing with d-toulene are shown.

a log–log plot over the range $0.00058 < q < 0.003$ nm^{-1}, suggests scattering from a fractal surface. The fractal dimension is 3 ± 0.005 which suggests that the scattering is from a very rough surface.

Fig. 5 shows the corresponding data for run 11. Contrast matching (cm) gives a reduction in the scattering intensity over all q values. The BET surface area of the char is $670 \text{ m}^2\text{g}^{-1}$, which indicates the presence of a well developed pore system. The reduction in scattering intensity for the contrast matched sample is therefore due to deuterated toluene filling the open porosity and eliminating scattering from open porosity. If the toluene were to enter all of the porosity then the scattering would be reduced to almost zero, as has been previously observed by Hall *et al.* [12] for a char produced from Pittsburgh No. 8 coal. As is the case for the run 10 carbon, there is not much evidence of scattering from micropores and the form of the scattering curves is that from a fractal surface with
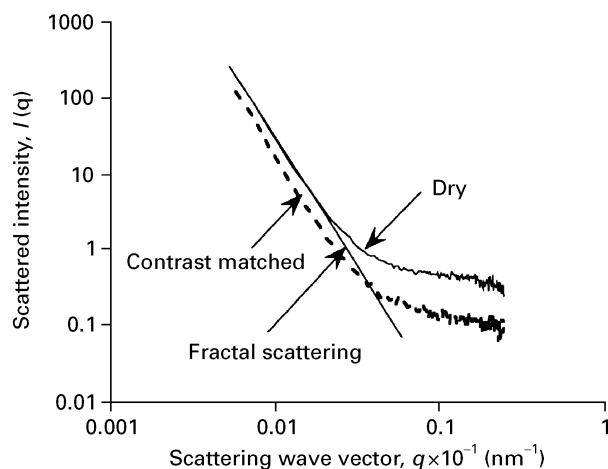
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Figure 6 Small angle neutron scattering on char produced from Amagá coal that had been swollen in pyridine, loaded with 100 wt % $ZnCl_2$, dried then pyrolysed under atmospheric pressure N_2 at 600 °C for 15 min. Both the dry sample and the char contrast matched by mixing with d-toulene are shown.

a fractal dimension of 2.95 ± 0.05. Although it is not possible to calculate the Porod scattering invariants, $\int q^2 I(q) \, dq$, (where $I(q)$ is the scattered intensity) absolutely they give a useful indication of the extent to which the scattering interface has been reduced by contrast matching. The porod invariant for the dry sample is 1×10^{-3} and this reduces to 6.6×10^{-3} for the CM sample. Therefore, it may be concluded that although there is significant open porosity, as shown by the surface area, there is also considerable closed porosity.

Fig. 6 shows the SANS result for run 12. It can be deconvoluted into two parts, fractal scattering for $q < 0.0022 \, \text{nm}^{-1}$ and scattering from microporosity which is manifested as an upward deviation from the fractal line. As previously mentioned, it is the only sample which exhibits this behaviour which is caused by the highly microporous nature of this sample, the surface area value of $1100 \, \text{m}^2 \, \text{g}^{-1}$ is also very high. The Porod invariants are 2.1×10^{-2} for the dry sample and 6.5×10^{-3} for the CM sample. This shows that there is still some closed porosity in the sample. Nevertheless the objective of producing a high surface area carbon without activation has finally been achieved.

4. Conclusions

Coals have an interesting potential use in the production of new, high surface area adsorbents, especially if a coking catalyst such as $ZnCl_2$ is used to increase carbon yields. However, to be effective the catalyst must be well dispersed through the coal. This can only be achieved by pre-swelling the coal in a solvent. A series of solvents with different swelling ratios were investigated. It was found that the highest swelling solvent, pyridine was most effective at dispersing the catalyst to produce a highly microporous carbon with a surface area of $1100 \, \text{m}^2 \text{g}^{-1}$. The surface area of the resulting carbons was found to depend upon the amount of catalyst used. Contrast matching small angle neutron scattering experiments show high levels of closed porosity when no catalyst or small amounts of catalyst were used. These results also suggested that there was some closed porosity in the highest surface area sample. The surface area could therefore be further increased by activation although these experiments were not performed.

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