

THE DEVELOPMENT OF POROSITY IN PITTSBURGH #8 AND WYODAK CHARs AS STUDIED USING CONTRAST MATCHING SMALL ANGLE NEUTRON SCATTERING

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INTRODUCTION

The development of porosity in coal chars is important in both combustion and gasification processes and there have been a large number of investigations and techniques applied to the subject¹. A persistent problem in understanding the development of porosity is the existence of closed porosity, which cannot be accessed from the external surface. Intrusive techniques, such as mercury porosimetry², or adsorptive techniques³ cannot, by definition, give information about such porosity. On the other hand, small angle x-ray scattering (saxs)⁴ and small angle neutron scattering (sans)⁵ techniques monitor scattering from both open and closed porosity and consequently cannot distinguish them. Additionally, saxs data may be complicated by interparticle scattering.

Recently, progress has been made in the understanding of closed and open porosity by using contrast-matching small angle neutron scattering (sans) to investigate the development of porosity^{6,7}. In Hall *et al.*⁶, sans was first performed on dry powdered phenolic resin char (prc). As with saxs, scattering is off open and closed porosity, as well as some interparticle scattering. Sans was then performed on phenolic resin char saturated with deuterated toluene. Following ultrasonication of the toluene/char mixture, the deuterated solvent fills any accessible porosity and interparticle voids. Hall *et al.*⁶ showed that deuterated toluene has the same neutron scattering density as typical polycrystalline carbon ($\sim 5.6 \cdot 10^{10} \text{ cm}^{-2}$) and therefore contrast matches the carbon very closely. With respect to neutrons there is no scattering contrast between the carbon and deuterated toluene in the pores and therefore no coherent scattering. Open porosity is therefore becomes "invisible" to the neutrons. Neutron scattering from the deuterated toluene/char mixture was therefore due to carbon and any porosity that could not be accessed by the deuterated toluene. Hall *et al.*⁶ showed that there was significant residual scattering in the contrast matched sample which was due to a well developed closed pore system. The difference between the dry and contrast matched samples was therefore due to scattering in open pores and interparticle scattering from the external surfaces of the packed prc particles.

Pittsburgh #8 coal is a coking coal and following slow pyrolysis (heating rates $\sim 10 \text{ Kmin}^{-1}$) under nitrogen it goes through a fluid phase⁸ before the onset of significant carbonization. The resulting chars have low surface areas and are highly graphitic⁹. From investigation of the desorption of oxygen complexes, Hall and Calo⁹ have speculated that Pittsburgh #8 char has very low levels of microporosity and that gasification proceeds by the creation of new pores. This thesis has not been explicitly tested.

Conversely, Wyodak is a Subbituminous coal and forms a char of high surface area.

The objective of the present work is to use a technique to investigate the development of Pittsburgh #8 and Wyodak coal chars: contrast matching sans.

EXPERIMENTAL

BET surface areas were obtained from adsorption of nitrogen at 77K using a Quantasorb apparatus over the range $0.01 < P/P_0 < 0.95$.

The sans was performed at the Intense Pulsed Neutron Source (IPNS) at the Argonne National Laboratory at the small angle diffractometer (SAD)¹⁰. The sample holders were made of 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 absolute calibration.

Pittsburgh # 8 and Wyodak coals were selected from the Argonne Premium Coal sample programme. Great care was taken to avoid contact with air during the pyrolysis procedure. The coal was heated under a slight positive pressure of nitrogen at 10 K min^{-1} to 1273K with a heat soak time of 1 hour. The resulting char was ground to between 60 and 100 Tyler mesh. For sans on the contrast matched samples, the chars were mixed with excess deuterated toluene and placed in an ultrasonic bath for 4 hours. Activation of the chars was by air in a tube furnace at 673K.

RESULTS AND DISCUSSION

Pittsburgh #8 char: 77K nitrogen adsorption isotherms were made for Pittsburgh #8. The surface area of the ungasified char was $8 \text{ m}^2 \text{ g}^{-1}$, which suggests no significant open porosity. This has been previously observed by Hall and Calo and is typical of chars from coking coals. The isotherm is of Type 2 according to the BDDT¹¹ classification, which is typical for non-porous materials or materials which have pore systems with significant amounts of meso- or macro- porosity. As discussed, the gas adsorption gives no indication as to the possible existence of closed porosity or whether porosity development proceeds by opening porosity or developing new porosity.

Small angle neutron scattering for the ungasified char is shown in Figure 1. To summarize, the dry curve represents coherent scattering from open and closed porosity as well as interparticle scattering. The contrast matched curve represents scattering from closed porosity and the difference curve represents scattering from open porosity and interparticle scattering.

From the dry curve it can be seen that there is no significant scattering for $q > 0.15 \text{ \AA}^{-1}$. This suggests the absence of scatterers of size less than $\sim 40 \text{ \AA}$ and the absence of well developed microporosity. There is therefore consistency between the isotherm and sans data. The scattering data increases monotonically over the q range studied which suggests that the size of the largest scatterer cannot be resolved. This may be either due to interparticle scattering or scattering from a small number of large pores.

From Figure 1 it can be seen that the effect of contrast matching by the addition of deuterated toluene reduced significantly the scattered intensity at all q -values. To illustrate this more graphically, the scattering is shown on a linear scale as an insert in Figure 1. The integral under the "dry" scattering curve is 2.19 (arbitrary units) and the integral under the contrast matched curve is 0.10 (arbitrary units). Therefore scattering has been reduced by a factor of 22. Therefore, 4.8% of the total scattering is due to closed porosity. This compares to 59.9% for the ungasified phenolic resin char of Hall *et al.*⁶ and shows clear differences between the pore structures of prc and Pittsburgh #8 coal char. Figure 1 also shows that there is no significant scattering for $q > 0.078 \text{ \AA}^{-1}$, for the contrast matched sample, which suggests the absence of porosity less than $\sim 75 \text{ \AA}$. It is probable therefore that scattering is due to a small number of large pores.

Gasification to 0.8% burn-off increases the surface area to $80 \text{ m}^2 \text{ g}^{-1}$, which suggests the development of porosity. Analysis of the BET isotherm curve shows a BDDT Type 2 adsorption isotherm for this char although the knee is more clearly defined than for the ungasified char. This may suggest the development of significant levels of microporosity. The sans data for the 0.8% burn-off char are shown in Figure 2. The results are qualitatively the same as for the ungasified char. Contrast matching reduces the scattered intensity very significantly, which

suggests that there is very little porosity. The scattering integral for the dry sample is 3.33 (arbitrary units) and this reduces to 0.15 for the contrast matched sample. Therefore 4.8% of the total scattering is due to closed porosity, which is similar to the ungasified char. The scattering data suggests that deuterated toluene can access all of the porosity developed during gasification.

Comparison of the scattering from the contrast matched samples in Figures 2 and 3 (shown as an insert in Figure 2) shows that they are very similar. Invariance of scattering from contrast matched samples has previously been observed by Hall *et al.*⁶ for phenolic resin. This constitutes evidence that the scattering is indeed from closed porosity which is unaffected by gasification. The scattering data from the 0% and 0.8% samples therefore show that gasification proceeds by the creation of new porosity, rather than the opening of closed porosity as is the case for phenolic resin char⁶.

The dry scattering curve in Figure 2 is typical for a material with a well developed micropore system. For convenience, the scattering behaviour for Porod type of behaviour is also shown in Figure 2. The upward deviation from this is due to the presence of micropores formed during gasification. Since the ungasified char has a low surface area, and the adsorption isotherm for the ungasified char is typical for a non-porous material, the scattering in the "difference" curve of Figure 1 is therefore dominated by interparticle effects, i.e. scattering determined by the external surface of the particles and the packing of the char particles. Again, this effect has been observed by Hall *et al.*⁶ for phenolic resin char. The form of the scattering curve for the ungasified sample approximates to Porod behaviour, which suggests that it is due to the presence of relatively large scale scatterers. Since the surface area of the 0.8% gasified char suggests the development of open porosity then the difference curve of Figure 2 must therefore contain information about interparticle scattering as well as the additional porosity. The difference curves are compared in Figure 3. The curves converge at low- q , which suggests that the nature of the background scattering has not changed significantly. The difference between the two difference curves (0.8%_{diff}-0%_{diff} in Figure 3) is therefore due to scattering from any additional pores created during the gasification process. Using the technique of subtracting interparticle scattering effects, the development of porosity in Pittsburgh #8 coal char can be studied in detail.

BET surface areas increase with gasification. The surface area at 13.5% burn-off is 252 m²g⁻¹. The isotherms are all of type 2, although the "knee" seems to be more clearly defined for the 0.8% and 4.5% gasified chars. SANS for the gasified chars are shown in Figure 4. The data are difference scattering curves that have been corrected for interparticle scattering by further subtraction of the "difference" scattering curve of Figure 1. The scattering curves therefore give information about pores that have been developed during gasification. The Guinier analysis⁽¹²⁾ for the 0.8% gasified char shows a linear section with a radius of gyration, $R_g = 16.3 \text{ \AA}$. Therefore, the early stage of gasification appears to produce microporosity. The scattering curve for the 4.5% gasified char in Figure 4 is also typical for a microporous network and the Guinier plot is also linear with $R_g = 13.5 \text{ \AA}$. The conclusion is that further microporosity is being produced. In contrast, the scattering curve for the 13.5% gasified char is typical for a pore system with a wide range of pore sizes. The Guinier plot confirms this by showing curvature over the entire q -range. The log-log plot is linear over the range $0.0058 \text{ \AA} < q < 0.054 \text{ \AA}$ and the slope of the line is -3.8. This deviates slightly from the Porod ideal and is probably due to fractal roughening of the pore surfaces. The fractal dimension is 2.2, which agrees with other fractal investigations of the surfaces of gasified carbon surfaces. Therefore in the burn-off range 4.5%-13.5% micropores appear to be opened to produce a pore system with a wide size range.

Wyodak Char: In this case, the picture is quite different. It is not possible to define the amount of interparticle scattering as in the case of Pittsburgh #8 because in the case of ungasified wyodak char, there is some initial opened and closed porosity. As before, the extent of scattering due to closed porosity can be obtained by examining the scattering from the contrast matched sample. But after subtracting the scattering due to closed porosity, the difference curve will tell about the interparticle scattering at the same time as the open porosity. Another input in the scattering curve could be scattering of the mineral matter in the coal char. This may have much more importance than in the case of Pittsburgh #8 because in the results presented here the

gasification is taken to much later stages. At 70% weight loss, the ash content of the sample is high. It is observed that there is a bump in the scattering curve between $0.03\text{\AA}^{-1} < q < 0.09\text{\AA}^{-1}$ that remains invariant with gasification. The origin of this feature could be scattering from ash particles, but further work is needed to test this.

The contrast matched curve for the ungasified Wyodak char in Figure 5 shows considerable scattering. This suggests the presence of closed porosity in the sample. Other experiments show that the extent of closed porosity diminishes as gasification increases to 58% weight loss where it can be seen that the scattering from the closed pore is almost nil (Figure 6). After this stage, around 68% weight loss, the extent of closed porosity seems to increase. The explanation for this could be associated with the scattering of ash particles. The BET surface area decreases from $397\text{m}^2\text{g}^{-1}$ for 58% weight loss char to $267\text{m}^2\text{g}^{-1}$ for 68% weight loss char.

The results show that scattering from open porosity increases faster than the decrease of scattering from closed porosity. This may suggest that during the gasification process, both pore opening and pore creation take place simultaneously.

CONCLUSIONS

Contrast matching has been shown to be a very powerful technique for investigating the development of porosity in carbons both in terms of understanding the effects of closed porosity and the elimination of interparticle scattering. Contrast matching shows that Pittsburgh #8 char has very little closed porosity and consequently that pore development during gasification proceeds by the creation of new pores. In the early stages of gasification (<4.5% burn-off) a pore system with significant microporosity is produced. In later stages of gasification (4.5%-13.5% burn-off) the tendency is to open these micropores, producing a pore system with a broad size distribution. Ungasified Wyodak coal char has a significant amount of closed porosity that opens as gasification proceeds, giving a minimum of closed porosity around 58% weight loss. It is also shown that the increase of surface area during gasification is due to pore opening and creation.

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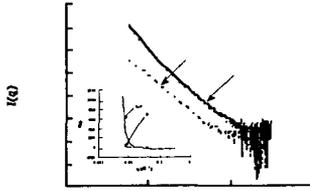


Figure 1. Small angle neutron scattering from unactivated Pittsburgh #8 coal char dry (a), contrast matched by mixing with deuterated toluene (b) and the difference (c) between scattering curves (a) and (b).

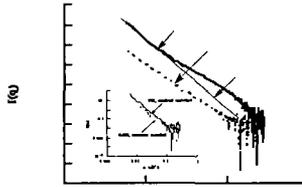


Figure 2. Small angle neutron scattering from Pittsburgh #8 coal char gasified to 0.8% weight loss in air at 673K dry (a), contrast matched by mixing with deuterated toluene (b) and the difference between scattering curves (a) and (b). A comparison of the scattering from the contrast matched ungasified and 0.8% gasified Pittsburgh #8 coal chars is shown as an insert.

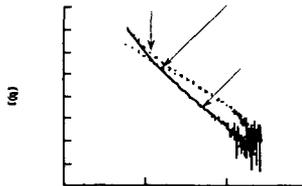


Figure 3. The method for correcting the "difference" scattering curve (curve (c) in Figure 3) by subtraction of the interparticle scattering (curve (c) in Figure 1) to show scattering from pores produced during gasification (0.8%_{diff}-0%_{diff}) for Pittsburgh #8 coal char gasified to 0.8% burn-off in air at 673K.

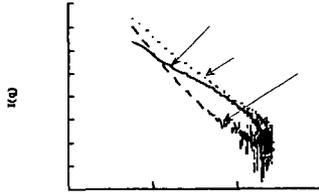


Figure 4. "Difference" scattering curves corrected for interparticle scattering to show small angle neutron scattering from pores produced during gasification for Pittsburgh #8 coal char gasified to different levels of burn-off in air at 673K.

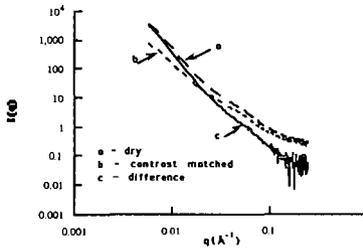


Figure 5: Small angle neutron scattering from ungasified Wyodak coal char dry (a), contrast matched by mixing with deuterated toluene(b) and the difference (c) between scattering curves (a) and (b).

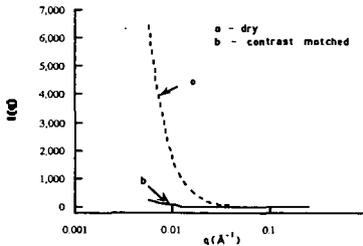


Figure 6: Small angle neutron scattering from Wyodak coal char gasified to 58% weight loss dry (a) and contrastmatched by mixing with deuterated toluene (b). The intensity is shown in linear scale to show how the scattering of the contrast matched almost disappears.