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CHARACTERIZATION OF POROSITY *VIA* SECONDARY REACTIONS

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SUMMARY

The following was accomplished during the reporting period:

- Contrast matching, small angle neutron (SANS) scattering data obtained for resin char has been analyzed in detail.
- Conclusions derived from this analysis include:
  - Contrast matching SANS has been demonstrated to be a useful technique for monitoring the activation/gasification process.
  - It is demonstrated how this technique can be used to address such important issues as the role of "closed" *vs* "open" porosity, and interparticle scattering.
  - It has been used here to establish that the development of porosity in phenolic resin char upon gasification in air proceeds primarily by "opening up" of originally "closed" porosity. This is quite different than the behavior of Pittsburgh #8 coal char, for example, as presented in a previous quarterly report (DE-FG22-91PC91305-14).

Plans for the next reporting period:

Plans for the next reporting period include additional work on the random pore model which is being used in conjunction with CO and CO_2 TPD spectra to interpret porosity development in chars. Work will also include an initiation of the final analysis of all the data in preparation for formulating the final report for the project.

1.0. PROJECT BACKGROUND

1.1. Overview.

Specific surface area, as well as its accessibility to gaseous reactants, are of paramount importance for all heterogeneous interactions occurring at coal char surfaces. Accessibility of this surface area is governed by the pore structure morphology of the char; i.e., pore size distribution, tortuosity, intersections, shape, etc. The porosity morphology of coal chars varies over a considerable range and is determined by a large number of factors including the nature of the porosity of the precursor material prior to carbonization, the carbonization process, and extent and method of any subsequent activation or gasification. A persistent problem in this area has been the reliable, quantitative measurement and characterization of the resultant porosity, especially the micropores. For example, electron microscopy tends to be qualitative; small angle X-ray or small angle neutron scattering (SAXS/SANS) can suffer from sensitivity to interpretive models, and the inability to distinguish porosity that communicates with the surface from that which does not; and gas adsorption techniques also have several well known drawbacks. The latter, however, are perhaps the most reliable in general, but yield pore size distributions indirectly *via* surface area and pore volume measurements, and can also be laborious and time-consuming. Therefore, there is still a critical need for practical and facile techniques to characterize the porosity of coal chars.

1.2. The Current Project.

The current project is directed at the development of a new approach to this very old problem. During the course of recent work applying temperature programmed desorption (TPD) to the determination of energetic distributions of oxygen complexes on the surfaces of oxidized coal chars (Calo *et al.*, 1989, 1991), we discovered that secondary interactions occurring within the char structure during TPD produce characteristic features in the resultant spectra that appear to be quite sensitive to char porosity. The relative and absolute extents of these secondary interactions form the basis of a potential characterization technique. The use of such a method to characterize coal char porosity is potentially attractive because the requisite spectra can be obtained in a single TPD experiment -- a very facile experimental procedure. However, the unambiguous and quantitative interpretation of such data in terms of parameters that can be used to characterize coal char porosity still requires development and an improved understanding of the controlling phenomena. These issues define the primary focus of the current work.

The background and general approach of the secondary interaction method for the characterization of porosity was outlined in the first quarterly technical progress report on this grant (DE-FG22-91PC91305-1), and, therefore, it will not be repeated here. Here we report on the progress that has been made in the construction, development and testing of a new TPD-MS/TGA system being developed in our laboratory for the purpose of conducting the temperature programmed desorption experiments for obtaining the secondary interaction data.

The project plan also includes the use of other techniques to characterize porosity in addition to the secondary interaction approach for the purposes of comparison, quantification, and validation. It is noted that at least two other more well established methods will be used in such a manner. Specifically, gas adsorption techniques in our own laboratory, and small angle scattering (SAS) (X-ray (SAXS) and neutron (SANS)). The latter will be accomplished in conjunction with Dr. Peter J. Hall of the Department of Pure and Applied Chemistry of the University of Strathclyde, Glasgow, Scotland. The data will be analyzed using models and computational techniques being developed in our laboratory.

2.0. PROJECT WORK

Porosity Evolution in a Phenolic Resin Char *Via* Contrast-Matching Small Angle Neutron Scattering

2.1. Background.

A large number of techniques have been applied to porosity investigation in carbons and chars such as gas adsorption (Grimes, 1982; Mahajan, 1982; Mahajan and Walker, 1978), mercury intrusion porosimetry (Hall, 1986) and small angle scattering techniques (Kostortz, 1979; Porod, 1982). The latter are potentially very powerful techniques in this context and, although there have been a large number of investigations using Small Angle X-ray Scattering (SAXS), these investigations have not attained their full potential, partly due to inadequate theoretical analysis and partly due to the inherent limitations of the technique itself.

One feature of SAXS is that scattering is from porosity that is accessible to the external surface (referred to as "open" porosity) as well as porosity that is not accessible to the external surface (referred to as "closed" porosity). (Porod, 1982). Gas adsorption and mercury intrusion techniques are only sensitive to open porosity. By itself, SAXS techniques cannot decouple open from closed porosity, which is a serious limitation to its application since pores developed by gasification may have a different form and size distribution to closed pores formed during precursor pyrolysis.

To compound further the problems of SAXS, a number of SAXS investigations show that the scattering intensity increases monotonically, even at the smallest scattering wave vectors, q. This suggests that the size of the largest scattering entities cannot be resolved by SAXS techniques. One explanation for this could be that the largest scattering entities are due to interparticle scattering from the generally granular samples. This possible explanation has not yet been tested.

Small angle neutron scattering (SANS) has received less attention than SAXS in the investigation of porous carbons even though in a variety of circumstances it is a more powerful and flexible technique. In particular, there has been no major investigation using SANS contrast matching techniques.

In related studies Gethner (1986) has performed contrast matching experiments on coal using H_2O/D_2O and C_6H_{12}/C_6D_{12} mixtures. Coals are essentially complex porous organic glasses and Gethner (1986) was able to demonstrate how appropriate isotope mixtures reduced the coal/solvent mixtures to pseudo- two phase scattering systems and proceeded to analyze the SANS data using Guinier, Porod and Debye models. Another study of note was performed by Winans and Thiyagarajan (1988) who performed SANS on Pittsburgh #8 coal swollen with C_6D_6 and pyridine-d_5. They used modified Guinier analyses to demonstrate the existence of elongated pores in the pyridine swollen coal of approximate size 9Å.

As already mentioned, despite their utility, contrast matching techniques have not been applied to porous carbons. Using contrast matching techniques it should be possible to decouple open porosity and interparticle scattering from closed porosity scattering by performing the following experimental sequence. Initially, SANS would be performed on a dry sample. As mentioned, scattering is from open and closed porosity as well as any contribution from interparticle scattering. If SANS were to be performed on a carbon sample soaked with a liquid that contrast matches the carbon exactly then the liquid would fill the voids between the particles (thus eliminating interparticle effects) and fill open porosity (thus eliminating open porosity scattering). Scattering in this case would only be from closed porosity. The difference between the two scattering curves would then represent open pore and interparticle scattering. In turn, these data could be corrected to yield information concerning open porosity if information about the magnitude of interparticle scattering could be determined.

As indicated above and in previous quarterly reports, small angle scattering is being used in this project as an auxiliary porosity characterization technique. In the previous quarterly report (DE-FG22-91PC91305-14), we presented an analysis of SANS data obtained for Pittsburgh #8 coal char. These samples exhibited considerable scattering. However, when the voids between the particles were filled with a liquid that had the same neutron scattering density as the carbon, the amount of scattering was reduced by more than two orders of magnitude. Analysis of the scattering invariant in terms of surface area showed that the char had very little porosity. To date this has been the only contrast matching SANS study of carbon and the first recognition that interparticle scattering effects are important.

In the current report, we focus on SANS data obtained for a very different char -- a phenolic resin char (PRC). Some of the scattering data for this char sample were briefly presented in a previous quarterly report (DE-FG22-91PC91305-10); here we present a more detailed analysis.

Upon slow pyrolysis, phenol-formaldehyde resin forms a low density and highly microporous char. Since this material is a "glassy" carbon, the apparent surface area of the unactivated char is very low (generally < 2 m^2/g), indicating that most of the porosity is initially inaccessible to gas adsorption probes. However, it is well known that small amounts of burn-off disproportionately increase the BET surface area, due to the "opening up" of "closed" porosity. Therefore, unlike the nonporous Pittsburgh #8 coal char, contrast-matched phenolic resin char would be expected to exhibit considerable scattering in SANS experiments.

From high pressure mercury intrusion porosimetry experiments on a highly activated sample of PRC (i.e., with low levels of closed porosity), the density of this particular char was determined to be 1.67 g/cm^3, which is close to the true "skeletal" density of carbon. This density corresponds to a neutron scattering density of 5.6×10^{10} cm^{-2}. Perdeuterated toluene also has a scattering density of 5.6×10^{10} cm^{-2}, which, therefore, makes it suitable as a contrast-matching material for neutrons for PRC.

With the preceding in mind, SANS was performed on unactivated PRC and PRC activated to 21% weight loss on both dry samples and samples activated to 21% weight loss.

2.2. Experimental.

The scattering experiments were performed at the Intense Pulsed Neutron Source (IPNS) at the Argonne National Laboratory using the small angle diffractometer (SAD) (Epperson *et al.*). A 64 x 64, position-sensitive multidetector was used to detect scattered neutrons; the wavelength of the neutrons was determined by time-of-flight. The sample holders were made of Suprasil with a pathlength 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. The intensity, I(q), was expressed as a function of the scattering wave vector, $q = 4\pi \sin(\theta)/\lambda$, where θ is half the scattering angle and λ is the wavelength of the neutrons. The entire q range ($0.005 < q < 0.35$ Å) of the small angle diffractometer was used.

For the contrast matching experiments the PRC samples were mixed with deuterated toluene and allowed to come to equilibrium by immersion in an ultrasonic bath and standing for four hours.

Phenolic resin was produced by a method described in detail by Sandler and Karo (1977). PRC was produced from the phenolic resin by pyrolysis under nitrogen at 900°C for one hour. Activation took place in oxygen at 470°C for varying times. The surface areas of the chars were determined using nitrogen adsorption at 77K in a Quantachrome Quantasorb apparatus.

2.3. Results and Discussion.

Figure 1 presents the scattering data for unactivated PRC. As discussed above, the "dry" curve results from scattering from the entire sample; that is, from all the PRC porosity as well as any interparticle scattering. Conversely, the scattering from the PRC char and deuterated toluene mixture (referred to as the "contrast matched" sample) should arise only from the "closed" porosity present in the char without the complication of interparticle scattering, because the deuterated toluene contrast matches the carbon very closely. Consequently, the scattering from the contrast matched sample is less than that from the "dry" sample, as shown in Figure 1.

The difference between the "dry" and contrast matched samples is also shown in Figure 1. This "difference" curve should represent primarily the effects of interparticle scattering, as a result of the following arguments. The 77K N_2 BET surface area of the unactivated PRC was determined to be 2.5 m^2/g, which indicates that most of the surface area is external; this is a typical observation for "glassy" carbons. The relatively intense scattering in Figure 1 from both the "dry" and deuterated toluene-soaked samples supports the thesis that most of the surface area is internal. The integral under the dry scattering curve is 1.169 (arbitrary units) and the integral under the contrast-matched sample is 0.701. Therefore for the 0% burn-off sample, 60% of the total scattering is due to "closed" porosity. In contrast, scattering from "closed" porosity for Pittsburgh No. 8 coal char was less than 5% of the.total dry sample scattering intensity. This coal undergoes a fluid phase on pyrolysis and loses practically all its porosity.

In summary then, the dry scattering curve is due to interparticle scattering and and internal porosity, while the contrast matched scattering curve is due to scattering from pores that cannot be accessed by the deuterated toluene. The difference scattering curve represents interparticle scattering and any pores that can be accessed by the deuterated toluene.

Activation to 21% burn-off increases the nitrogen BET surface area to 21 m^2/g. This is still not a very large surface area in the context of activated carbons (Lowell and Shields, 1984). Figure 2 presents the corresponding dry, contrast-matched, and difference scattering curves for PRC activated to 21% burn-off. As with Figure 1, the scattering from the contrast matched sample is less than for the dry sample, due to the contrast matching. However, there is a difference in the relative intensities of the scattering curves in comparison to Figure 1. For the unactivated carbon, the ordering of the scattering intensities was dry > contrast matched > difference; while for the 21% burn-off sample the order is dry > difference > contrast matched. The integral under the dry scattering curve is 0.920 (arbitrary units) and the integral under the contrast matched curve is 0.301. Therefore, 32.7% of the total scattering is from closed porosity, which represents a decrease of 27.2% from the unactivated sample. This decrease in intensity of the contrast matched sample at 21% burn-off clearly indicates that the activation process is "opening up" previously inaccessible, "closed" porosity.

The contrast matched scattering curves for the unactivated and 21% burn-off samples are compared in Figure 3. As just indicated, the decrease in scattering intensity evident for the 21% burn-off sample is due to the reduction in "closed" porosity that cannot be accessed by the deuterated toluene. The ratio of these two curves is shown in Figure 4. As can be seen, this ratio is practically invariant over the range $0.05\ \text{Å}^{-1} < q < 0.2\ \text{Å}^{-1}$. This is consistent with the fact that the pore size distribution of the "closed" porosity does not change with activation, which is exactly what would be expected. This is further corroboration that the contrast matched scattering curves represent scattering solely from "closed" porosity.

Figure 5 compares the difference scattering curves between the unactivated and 21% burn-off samples. As shown, there is a marked enhancement in scattering intensity for the 21% burn-off sample for $q>0.025\ \text{Å}^{-1}$. This is emphasized in the plot of the ratios of the two difference curves presented in

Figure 6. This behavior is attributed to the formation of open pores of size <240Å during gasification. However, there is very little change in the scattering curves for $q<0.025$ $Å^{-1}$, indicating no significant changes in interparticle scattering or the development of the larger porosity during gasification. The slope of the line over the linear portion of the curve is -3.84, which is close to the ideal Porod scattering value of -4; i.e, $I(q) \alpha q^{-4}$. The difference between these two values could be due to the fractal roughness of the external surface. The corresponding fractal dimension is 2.16. This suggests that this part of the curve is due to scattering off large, relatively smooth objects. As shown, the nature of these scatterers does not change with activation.

The utility of the contrast matching SANS technique for characterizing porosity development is exemplified by Figure 7 in which the scattering data from the "dry" unactivated and 21% burn-off samples. It can be seen that there is very little difference between the two curves which, without further information, would suggest that no significant changes were induced by activation. These are the type of curves that would be expected from small angle X-ray scattering for example. In addition, the "dry" curve for the unactivated sample yields an apparent fractal dimension of 2.0 for the linear portion of the curve. This would be indicative of scattering by smooth surfaces. Also, this curve suggests the presence of accessible pores below 40 Å. However, as amply demonstrated above, such pores do not exist for the unactivated char sample..

2.4. Conclusions.

Contrast matching SANS has been demonstrated to be a very useful technique for monitoring the activation/gasification process. It can be used to address such issues as the role of "closed" porosity and interparticle scattering. It has been used here to establish that the development of porosity in phenolic resin char proceeds primarily by "opening up" of originally "closed" porosity. This is quite different than the behavior of Pittsburgh #8 coal char, for example, as presented in a previous quarterly report (DE-FG22-91PC91305-14).

3.0. PLANS FOR NEXT REPORTING PERIOD

Plans for the next reporting period include additional work on the random pore model which is being used in conjunction with CO and CO_2 TPD spectra to interpret porosity development in chars. Work will also include an initiation of the final analysis of all the data in preparation for formulating the final report for the project.

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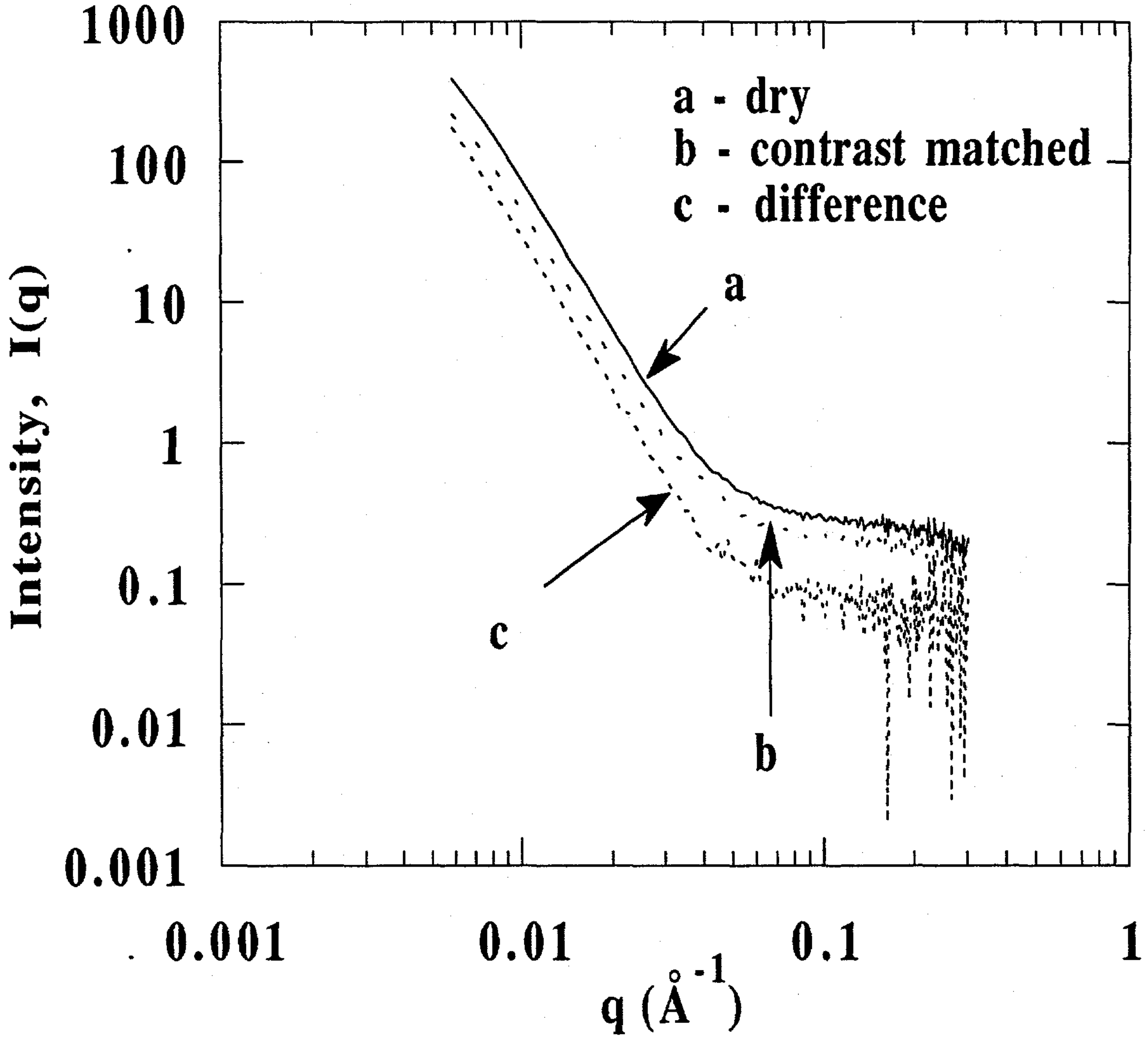

Figure 1. Small angle neutron scattering from unactivated phenolic resin char: (a) dry; (b) contrast matched by mixing with deuterated toluene; and (c) the difference between the scattering curves.

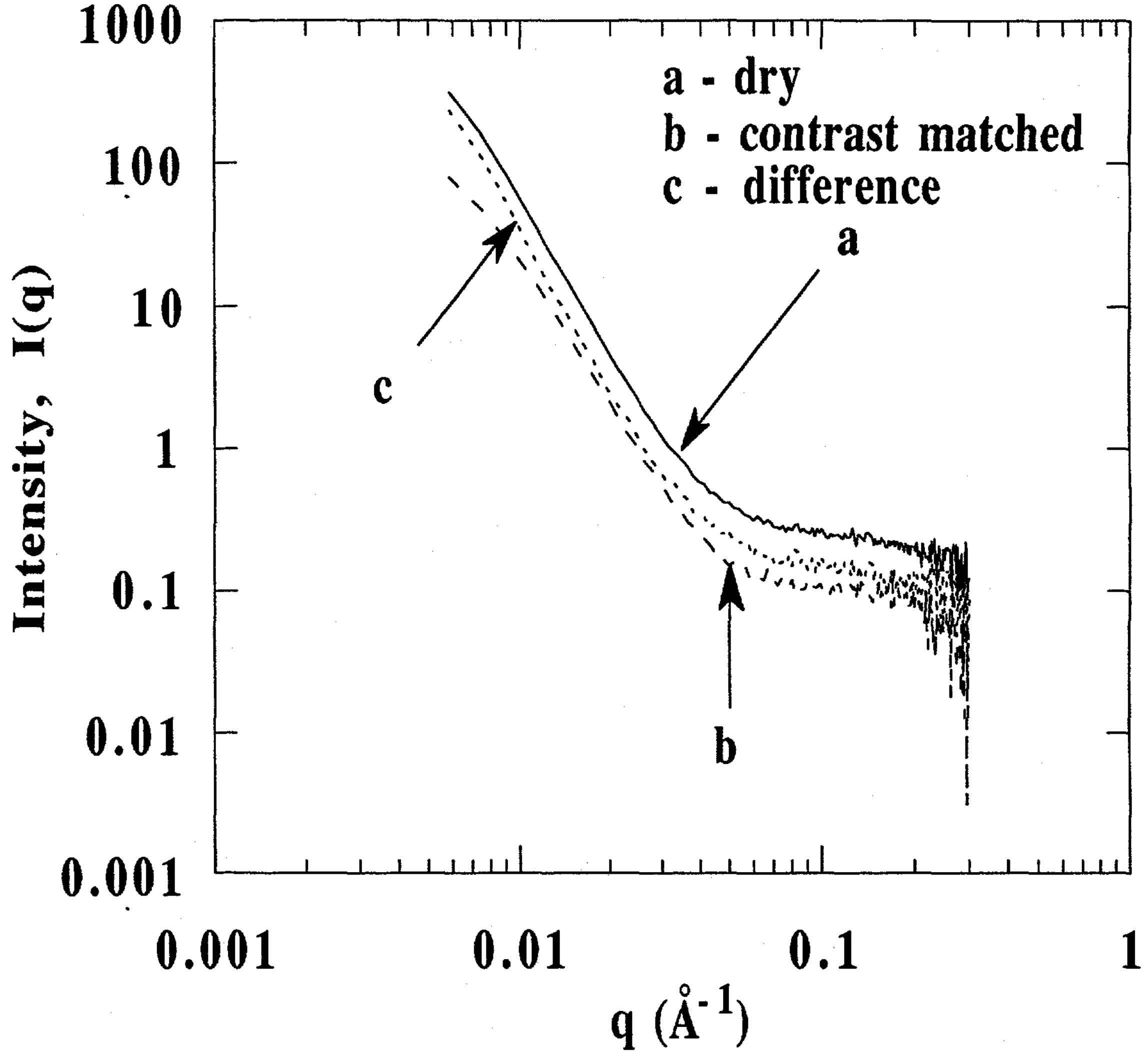

Figure 2. Small angle neutron scattering from phenolic resin char activated in air to 21% burn-off: (a) dry; (b) contrast matched by mixing with deuterated toluene; and (c) the difference between the scattering curves.

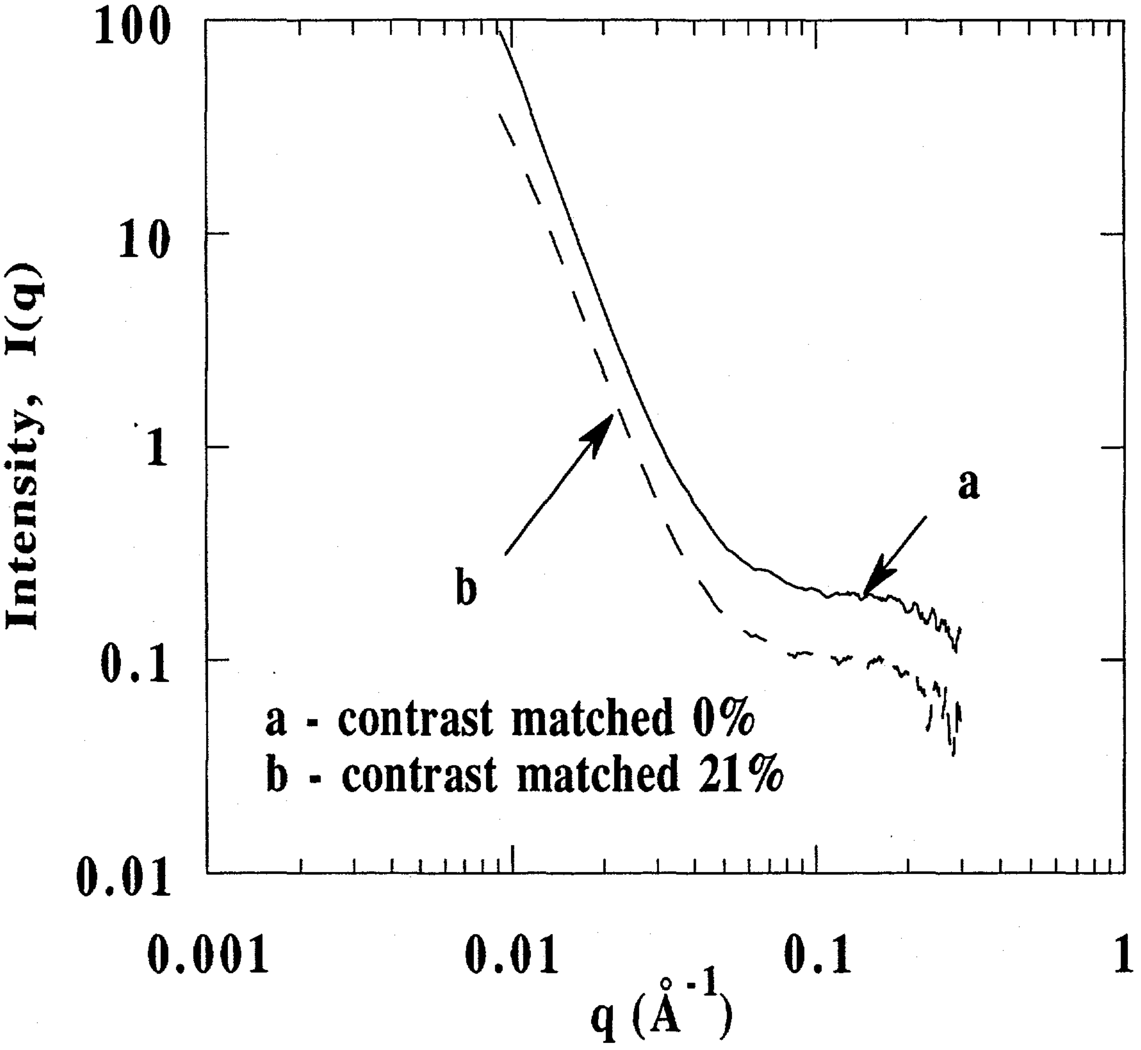

Figure 3. Comparison of the scattering from the unactivated and activated (in air to 21% burn-off) phenolic resin char samples that have been contrast matched by mixing with deuterated toluene.

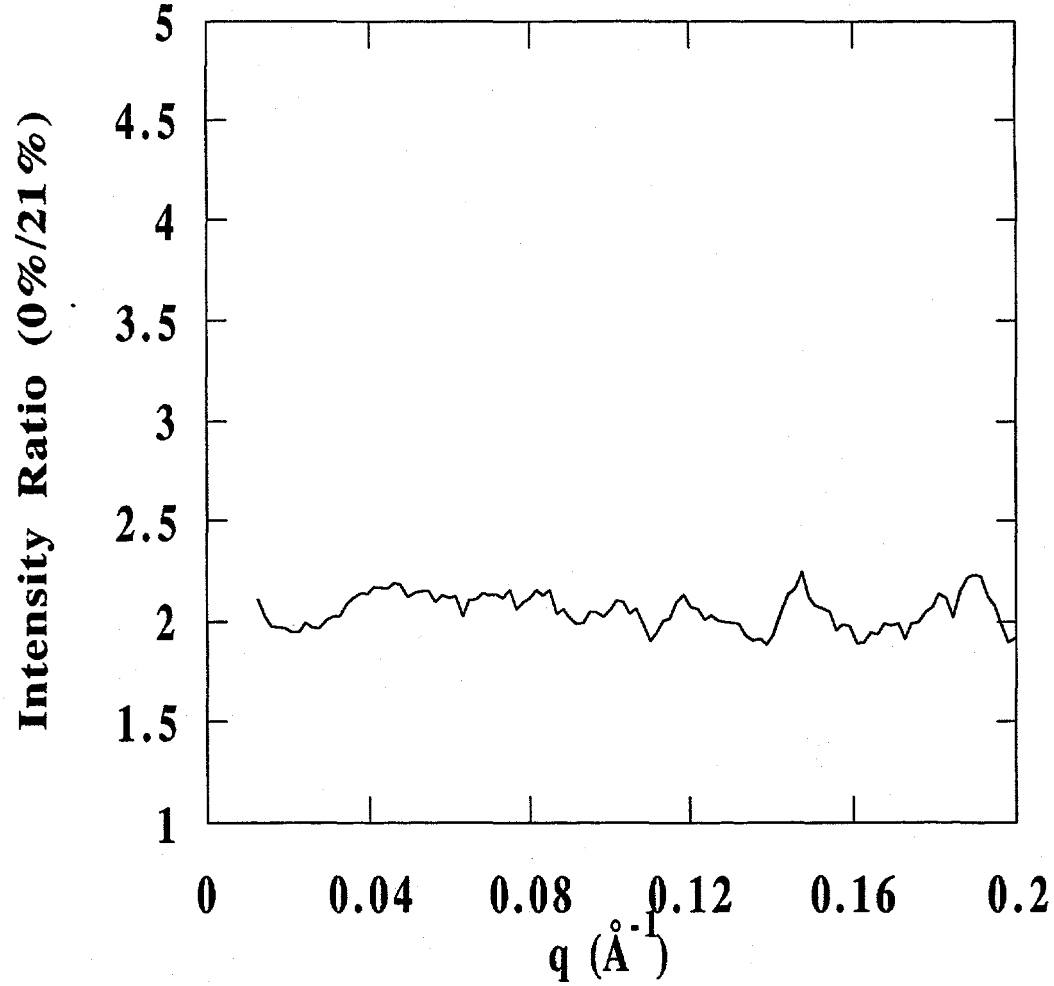

Figure 4. Ratio of the scattering intensities of the unactivated and activated (in air to 21% burn-off) phenolic resin char samples that have been contrast matched by mixing with deuterated toluene.

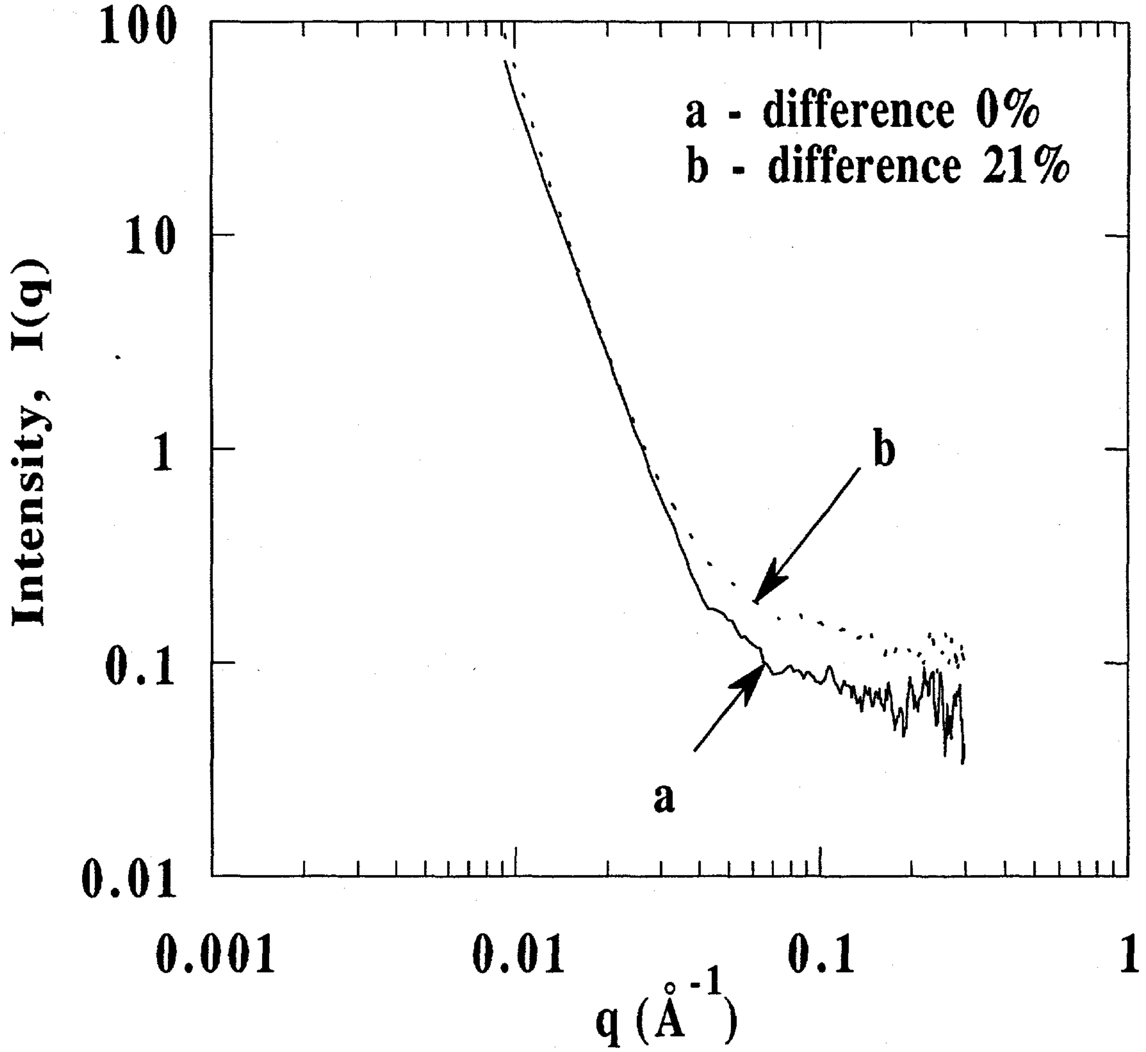

Figure 5. A comparison of the "difference" scattering curves for unactivated phenolic resin char and resin char activated to 21% burn-off from Figures 1 and 2. The curves have been smoothed for clarity.

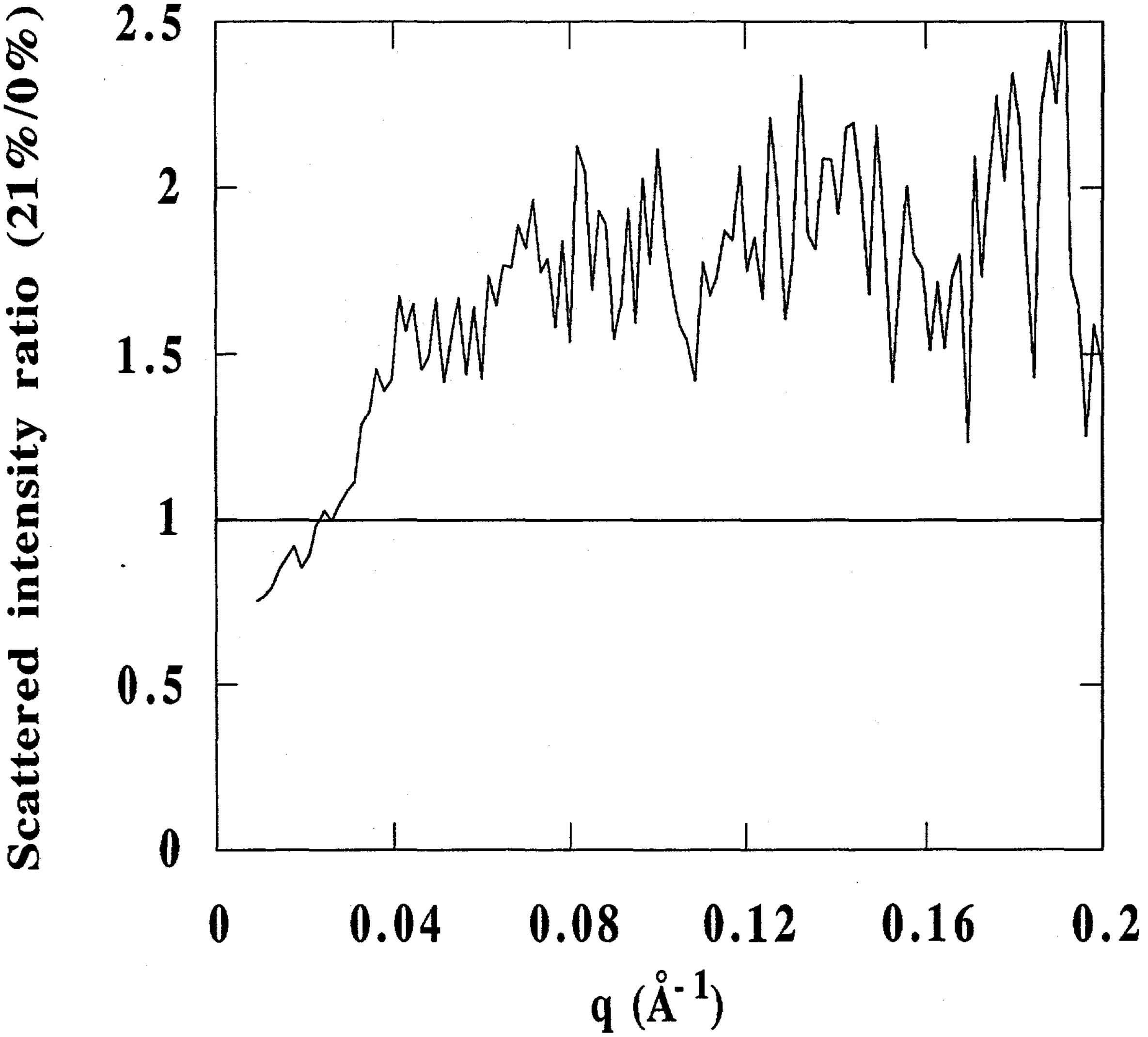

Figure 6. Ratio of the difference scattering intensities of the unactivated and activated (in air to 21% burn-off) phenolic resin char samples.

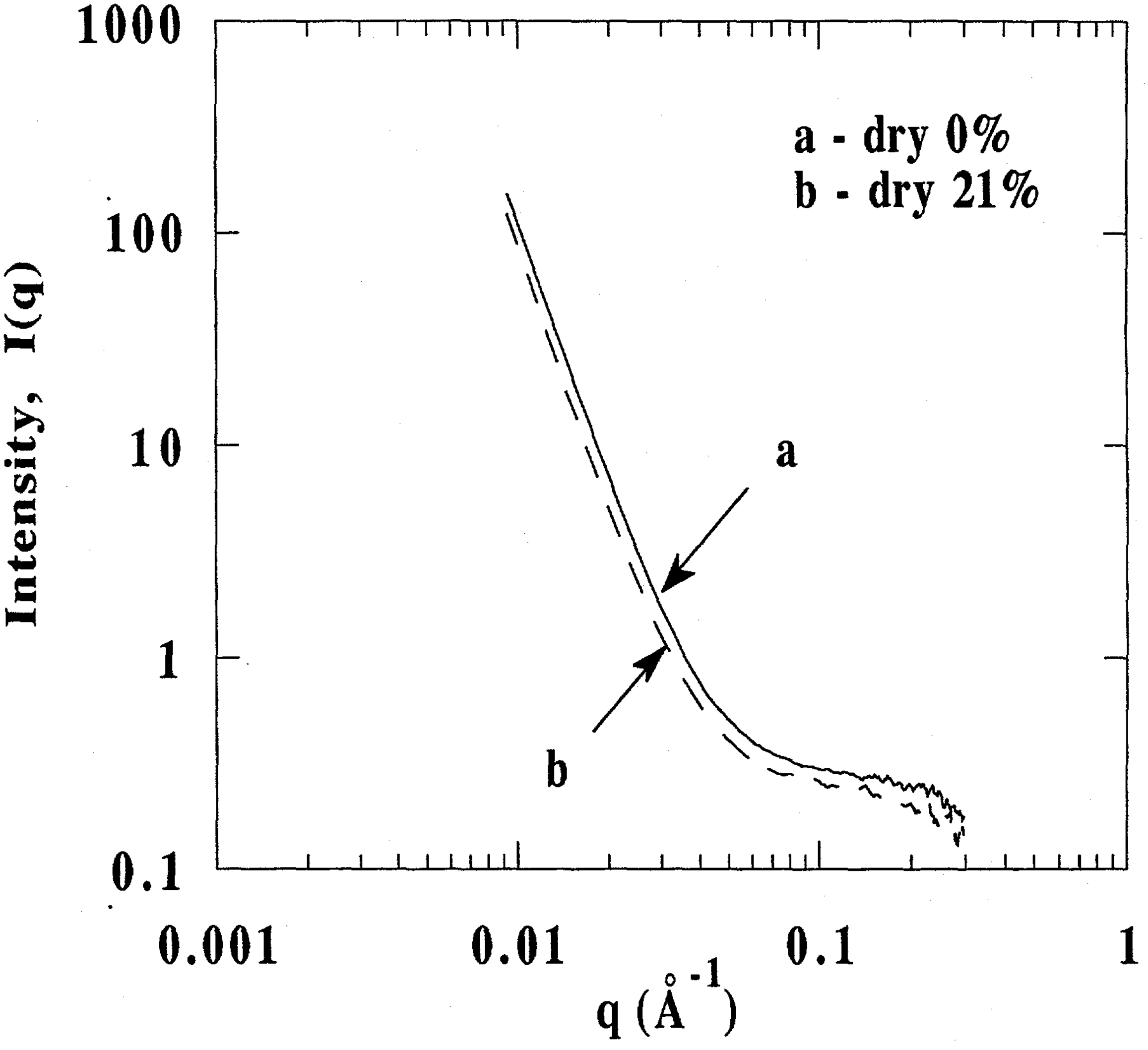

Figure 7. Comparison of the “dry” scattering curves for unactivated and activated (in air to 21% burn-off) phenolic resin char samples.