

The Effects of Particle Size on Small Angle Neutron Scattering From a Granular Phenolic Resin Char

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Introduction

Porous carbons and chars are important in a wide variety of industrial applications, including the production of activated carbons for use as adsorbents, catalyst supports, gas storage media, electrolytic applications (electrodes, capacitors, batteries, etc.), as well as coal gasification and combustion [1,2]. Accessibility of fluid activating agents to the porosity, and porosity development during activation are critical in the selection of activating agents and conditions, as well as the engineering, and production of many of these materials [2]. The activation process involves a number of different mechanisms, such as widening of accessible porosity, opening of previously inaccessible porosity, and development of new porosity.

One technique that has proven useful in monitoring porosity development in carbons and chars is small angle neutron scattering [3]. The principal “contrast” resulting in scattering of neutrons in porous carbons and chars is that between the solid carbon and the voids or pores. Thus, in its most elementary sense, the greater the scattering intensity the greater the pore density. Accessible (“open”) and inaccessible (“closed”) porosity can be distinguished by using contrast matching small angle neutron scattering (CM-SANS). In its simplest form, this technique consists of performing SANS on “dry” samples where the total scattering is from all the porosity (i.e., both “open” and “closed” pores). The pores accessible from the exterior of the sample are then filled with a liquid (perdeuterated toluene in the current work) that has the same neutron scattering cross section as the solid matrix such that when SANS is performed on the “wet” sample, scattering from the “open” porosity is eliminated, and scattering from the contrast-matched sample yields information about the remaining, inaccessible porosity in these materials. Moreover, the difference in scattering between the corresponding dry and contrast-matched samples provides information about the “open” porosity.

Here we apply CM-SANS techniques to investigate the dependence of scattering intensity and porosity development on char particle size.

Experimental

Char Samples. Phenol-formaldehyde resin was ground and sieved to the following size ranges: SS, < 0.1 mm; S, 0.1 – 0.5 mm; M, 0.5 – 1 mm; and L, 1-2 mm. The sieved samples were heated to 1223 K for 30 min. in flowing helium. The particles were then

re-sieved, even though it was determined that the particle sizes did not change very much during the latter heat treatment. Some of the material was activated in either oxygen (873K) or CO₂ (1173K).

Neutron Scattering. The SANS data were obtained at the Intense Pulsed Neutron Source (IPNS) of the Argonne National Laboratory on the time-of-flight Small-Angle Neutron Diffractometer (SAND). This instrument has a 40 x 40 cm² area detector with a wavevector range $0.035 < Q < 6 \text{ nm}^{-1}$. The sample holders were made of Suprasil with a pathlength of 0.1 cm. The scattering data were corrected for scattering from the sample holder and other instrumental backgrounds. Normalization for the sample thickness and transmission was made, and the data were scaled to yield absolute calibrations. The neutron scattering density of carbon is $5.6 \times 10^{10} \text{ cm}^{-2}$, which is very close to that of perdeuterated toluene that was used for contrast matching in the current experiments. Essentially, granulated char samples were mixed with perdeuterated toluene and allowed to come to equilibrium by immersion in an ultrasonic bath for a minimum of four hours.

Results and Discussion

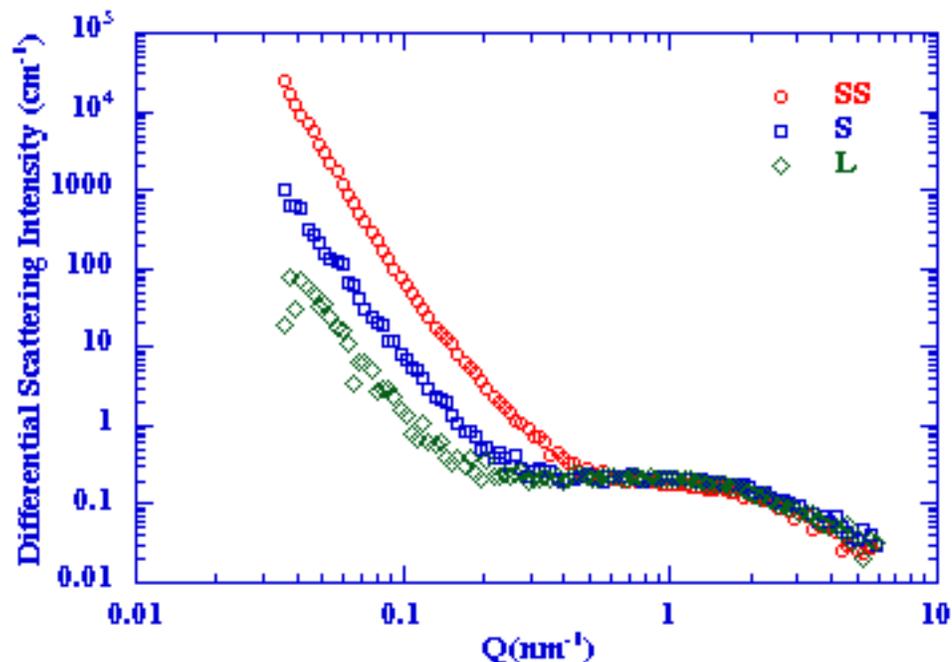


Figure 1. Differential scattering intensities from “dry” samples of unactivated resin char, as a function of particle size.

Unactivated Resin Char Samples. Differential scattering intensities from “dry” samples as a function of particle size are presented in Figure 1. Two distinctly different regimes of behavior are apparent in this figure: $Q > 0.5 \text{ nm}^{-1}$, for which there is little or no variation in total scattering with particle size; and $Q < 0.5 \text{ nm}^{-1}$ for which the total scattering *increases* monotonically with *decreasing* particle size. This demarcation corresponds (roughly) to scatterers of about 10 nm in size, such that $Q > 0.5 \text{ nm}^{-1}$

includes the smaller mesoporosity and the microporosity, and $Q < 0.5\text{nm}^{-1}$ includes the larger mesoporosity, macroporosity, etc.

Interpretation of this behavior in terms of differences in char porosity would mean that the smaller particles exhibit a greater proportion of larger scatterers, or porosity, than the larger particles. However, upon grinding, smaller particles are created from larger particles primarily by fracturing of larger particles along large pores, faults, or defects. This process would actually tend to *decrease* the relative amount of larger porosity somewhat with decreasing particle size. Since the scattering form factor is considerably amplified with decreasing Q , this would mean a considerable decrease in the scattering intensity at the lowest Q values for even modest decreases in the population of larger scatterers. This is inconsistent with the behavior of the data in Figure 1. The latter suggest a rather more even *amplification* of the scattering intensity over the entire range of $Q < 0.5\text{nm}^{-1}$ with *decreasing* particle size.

In another SANS study of the behavior of a char produced from a highly cross-linked phenol-formaldehyde resin [4], it was found that the total scattering intensities at low burn-offs from the “dry” samples *decreased* with burn-off, unlike for other carbons where it typically increases due to porosity development [5]. (The BET surface areas of these chars were all quite low: $2.2\text{m}^2/\text{g}$ unactivated to $22.2\text{m}^2/\text{g}$ at 21% burn-off). This behavior was shown to be due to the selective burn-off of disordered carbon material with a broad distribution of sizes up to about 30 nm, with a mean *ca.* 10.2 nm, which originally blocked access to the intrinsic underlying porosity [4]. Initial burn-off of this carbon material occurred *via* progressive removal of the disordered carbon, converting initially inaccessible to accessible porosity. There was no evidence of significant widening or alteration of the intrinsic underlying porosity, nor of the development of new porosity up to almost 21% burn-off [4].

The BET surface areas of the unactivated chars in the current study are also quite low ($<1\text{m}^2/\text{g}$), and thus they are not microporous, at least from a gas adsorption point of view, although a significant amount of scattering in the small pore size range is evident in the scattering data for $Q > 0.5\text{nm}^{-1}$. These samples appear to share qualitative similarities with the chars in reference [4]. The accessible surface area of these chars is dominated by the external surface that scales as some function of $1/r$ (e.g., $3/r$ for perfect, nonporous spheres), where r is the characteristic particle radius. Thus it seems plausible that an explanation of the behavior of the scattering data in Figure 1 is somehow related to the external surfaces of the particles.

It is well known that non-graphitizing carbons are generally composed of a mixture of ordered aromatic regions and disordered regions. It has been observed that during oxidation of carbon blacks and partially graphitized carbons, the disordered regions are the most reactive and are attacked most rapidly [6]. This type of behavior also applies to phenolic resins chars (PRC). It has been reported that the crystallite dimensions of the ordered regions in a 1000°C PRC did not change appreciably up to 10% burn-off; and up to 40% burn-off for a 1400°C PRC [7], which implies that the burn-off must have occurred preferentially in the disordered carbon. It has been hypothesized that the disordered regions in PRC materials arise primarily from the methylene bridge carbons in the phenolic resin precursor, according to studies employing ^{13}C -labeling of the resin via the formaldehyde reagent [8,9]. Larger meso- or macropores usually occur within the amorphous carbon phase at microcrystallite boundaries, for example. Many polymer

carbons are also glassy with the openings of the micropores in the microcrystallites initially blocked by amorphous carbon material. Such carbons appear to be non-microporous to N_2 adsorption at 77K, but have considerable underlying microporosity in the inaccessible microcrystallites. In the case of PRC, the amorphous carbon material has been reported to appear as "globular particles" on the external surface with characteristic sizes in the range of 30 nm [10]. This material appears to be deposited primarily on the surface of larger pores or faults and comprises much of the material that "blocks" the underlying microporosity in the microcrystallites. It is noted that 30 nm lies roughly in the middle of the characteristic size range where the significant variation in scattering intensity is observed to occur in Figure 1. In another study, it was found that during carbonization of phenolic resins at 723K and 1023K, the destruction of crosslinks leads to the formation of clusters of aromatic units [11]. The latter are probably related to the globular structures observed in reference [10]. Gupta and Harrison [11] also found that their char was conductive, suggesting the presence of large ordered graphitic planes as well. These observations are completely consistent with the hypothesis formulated above that the PRC consists of both disordered (i.e., globular structures) and ordered (i.e., large graphitic layers), and that the burn-off of the larger disordered carbon structures opens up the underlying blind porosity which they originally "block."

Upon grinding, amorphous material residing on the walls of larger pores will be increasingly exposed to the external surface of the particles as the larger features (pores/faults) are destroyed. Thus the zeroth order approximation is that upon grinding, the amount of amorphous material on a particle would scale roughly as its surface area (since the surface area of the smaller porosity is inaccessible). Consequently, small particles effectively *concentrate* the amorphous material on their external surface. When these particles are sieved from a ground sample, then it would be expected that the smallest particles would have the largest concentration of amorphous carbon, and thus the greatest concentration of larger scatterers, just as observed. However, grinding should not affect the microcrystallites where the bulk of the smaller porosity lies, and thus their contribution to scattering would remain constant with respect to particle size, just as observed.

Contrast-matching (i.e., filling the accessible pore volume of the samples with perdeuterated toluene) would reduce both the contributions from the larger, accessible pores as well as that from amorphous surface carbon, since it would lie primarily in the larger, accessible porosity, and thus be "matched." Figure 2 shows that this hypothesis is also consistent with the data. The CM scattering at low q is considerably reduced by matching from that in Figure 1, and is very similar for the "L" and "S" particles, and, although a little greater (possibly due to some micropore coalescence – see below), not very much different for the "SS" particles either. The relatively small variations observed could be due to statistical differences in the samples measured.

The data in Figure 2 show a significant decrease in the CM-microporosity for the "SS" particles. The dry sample scattering data in Figure 1 also show a much more modest decrease at high Q for the "SS" particles. This behavior can be interpreted to mean that some of the smallest microporosity has become accessible in the "SS" particles, and a much smaller amount was lost to pore coalescence. In the smallest particles, it would be expected that the external surface area eventually reduces to the

order of that of the exteriors of the microcrystallites themselves. Without data on the microcrystallite sizes in these chars, however, it is not possible to say that this occurs for the < 0.1 mm particles or not. But, when the exterior surfaces of the microcrystallites become a significant fraction of the exterior surface of the particles themselves, disturbance of the amorphous carbon at the exterior of the microcrystallites *via* the grinding/fracturing process would tend to expose pore mouths at microcrystallite surfaces. For similar reasons, but apparently to a much lesser extent, mechanical action on microcrystallite surfaces in the smallest particles could cause a small fraction of the original micropore population to coalesce into somewhat larger pores, as suggested by the data in Figures 1 and 2.

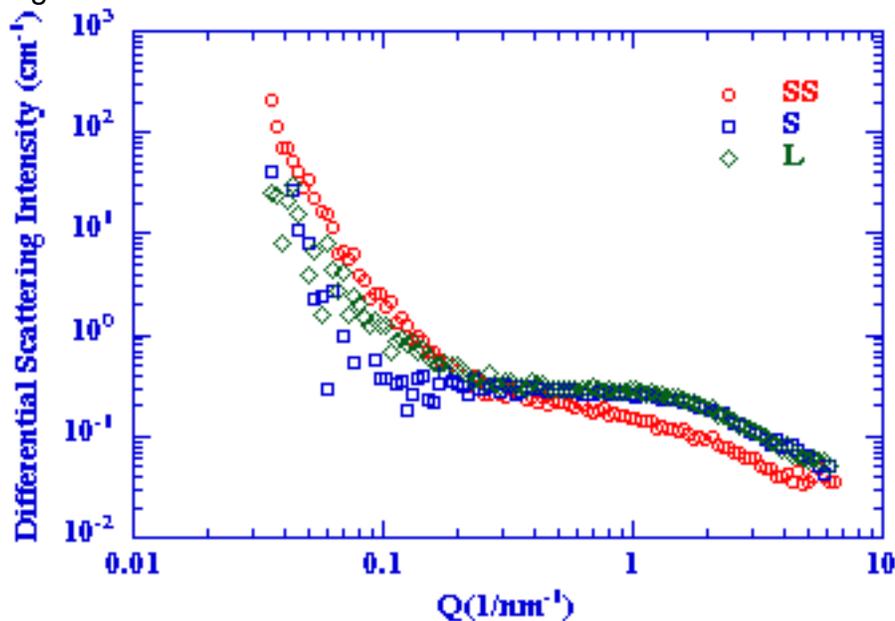


Figure. 2. Differential scattering intensities of the samples contrast-matched with perdeuterated toluene.

Activated Resin Char Samples. One test of the preceding hypothesis is to compare scattering from different-sized particles activated to the same extent. Since amorphous carbon is preferentially removed with increasing burn-off, the scattering should eventually be reflective of just the porosity, which should be similar for different-sized particles burned off to the same extent. In Figure 3 is presented just such a comparison for the S and M-sized particles for 25% burn-off in at 1173K. As shown, the total scattering curves are essentially the same, as expected. That is, the large differences at low Q , evident in Figure 1, have disappeared.

The results of a comparable set of experiments with oxygen at 873K, presented in Figure 4, are somewhat different. As shown, although the differences between the scattering curves for the two particle sizes at low Q have largely disappeared, just as in Figure 3, here there are significant differences in the small porosity that were not apparent in either Figure 1 or 3. As shown, the smaller S particles have developed significantly more “open” porosity at the very smallest pore sizes, whereas the larger M particles have developed most of their open porosity at larger pore sizes (i.e., the larger micropores up to the smaller mesopores). Thus, particle size has a significant effect on porosity development. It is apparently more facile to develop small porosity in the

smaller particles than in the larger ones. Since activation is a reaction-diffusion process, the shorter mean diffusion path length in the smaller particles would tend to favor more new porosity development than pore-widening for the more reactive O_2 activating agent (at the selected temperatures).

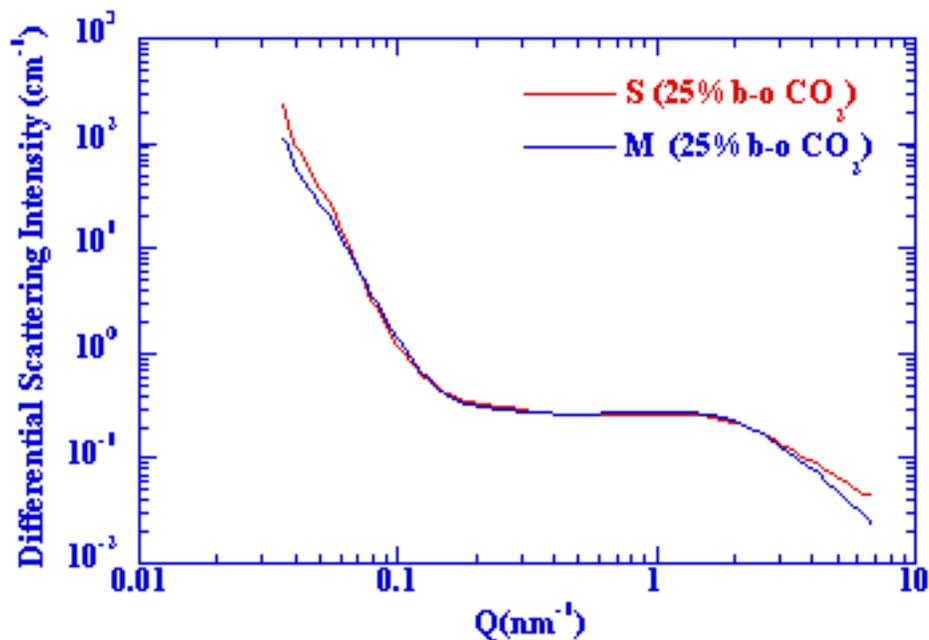


Figure. 3. Differential total scattering intensities from two different particle size samples, burned-off to 25% in CO_2 at 1173K.

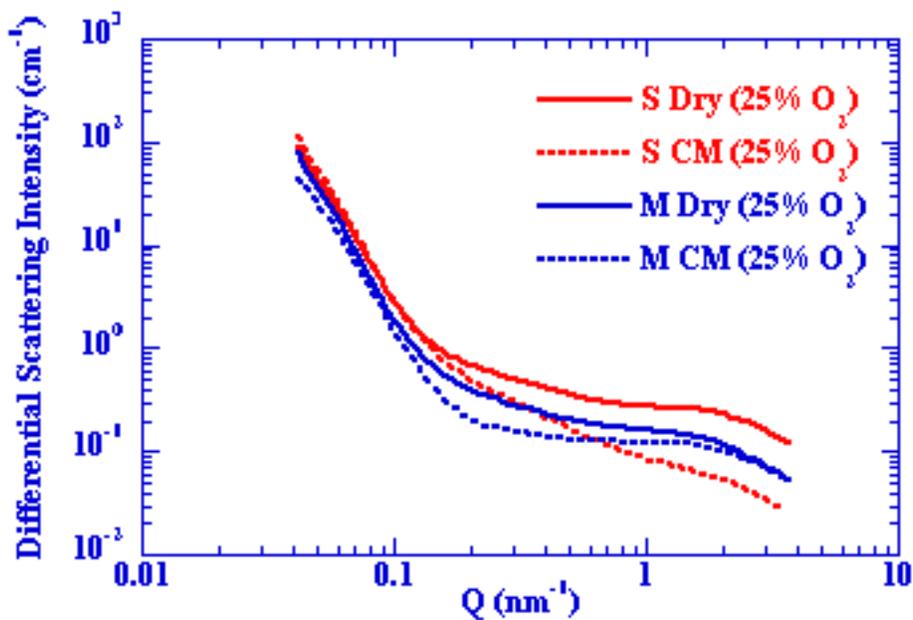


Figure. 4. "Dry" and contrast-matched (CM) differential scattering intensities from two different particle size samples, burned-off to 25% in O_2 at 873K.

From Figures 3 and 4, it might be anticipated that CO₂ and O₂ develop porosity differently. However, the total scattering data in Figure 5 suggest that CO₂ and O₂ (at least under the current experimental conditions) produce somewhat similar results at low burn-offs. But the contrast matching data show that O₂ produces significantly more “open” porosity than does CO₂. It is noted that at these low burn-offs, the development of new porosity is still not very important, which is why the total scattering data (which does not distinguish between “open” and “closed” porosity) from the samples activated with the two gases are still somewhat similar. However, it appears that O₂ is more efficient at removing amorphous carbon blocking the underlying small porosity, which is consistent with O₂ being more reactive under the current experimental conditions.

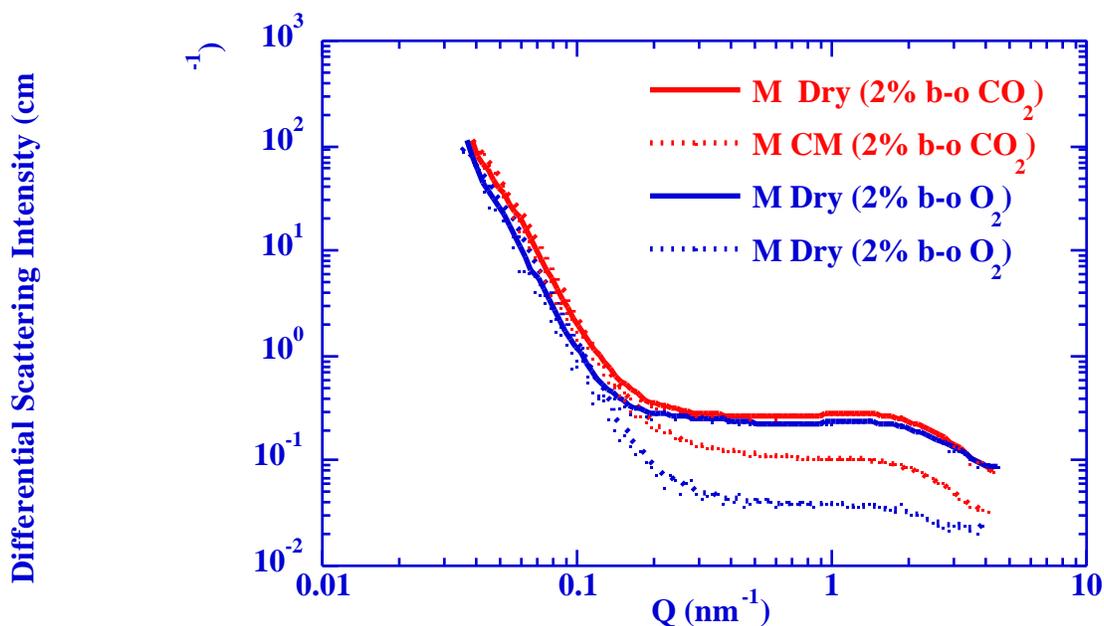


Figure 5. “Dry” and contrast-matched (CM) differential scattering intensities from the M-size particles, burned-off to 2% in either CO₂ at 1173K or O₂ at 873K.

Conclusions

Simplified schematics of the hypothesized behavior of “small” and “large” particles are depicted in Figures 6-8 with respect to activation and contrast-matching processes for “unactivated” and “activated” particles. For unactivated phenol-formaldehyde resin char, the significant increase in scattering with decreasing particle size has been attributed to amorphous carbon structures that initially “block” underlying smaller porosity in more ordered microcrystallite regions.

It has also been shown that char activation and porosity development can be sensitive to char particle size, as well as activating agent and conditions. It may be possible to exploit these results to develop desirable pore structures for particular applications. CM-SANS is demonstrated to be a useful technique for monitoring such processes.

Acknowledgement

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References

- [1] Patrick, JW. Porosity in carbons: characterization and applications. New York NY: Wiley. 1995.
- [2] Rodríguez-Reinoso, F. Activated carbon: Structure, characterization, preparation and applications. Marsh, H, Heintz, E, and F. Rodríguez-Reinoso, F, editors. Introduction to carbon technologies. Alicante, Spain: University of Alicante 1997: 35-101.
- [3] Calo, JM, Hall, PJ, and Antxustegi, M. Carbon porosity characterization *via* small angle neutron scattering. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2001; 187-188: 219-232.
- [4] Antxustegi, MM, Hall, PJ, Calo, JM.. The use of contrast-matching small-angle scattering techniques to monitor closed porosity in carbons. J. Colloid Interface Sci 1998; 202: 490-498.
- [5] Foster, MD, and Jensen, KF. SAXS investigation of a model carbon pore structure and its change with gasification. Carbon. 1991; 29(2): 271-282.
- [6] Donnet, JB. Structure and reactivity of carbons: From carbon black to carbon composites. Carbon. 1982; 20(4), 267-282.
- [7] Chang, HW, and Rhee, SK. Oxidation of carbon derived from phenolic resin. Carbon. 1978; 16(1): 17-20.
- [8] Yamashita, Y, and Ouchi, K. A study on carbonization of phenol-formaldehyde resin labelled with deuterium and ^{13}C Carbon. 1981; 19(2): 89-94.
- [9] Antxustegi, MM, and Calo, JM. The Reactivity behavior of ^{13}C -labelled phenol-formaldehyde resin char. Proc. Carbon '97, 23rd Biennial Conf. Carbon, Pennsylvania State University, 1997; 404-405.
- [10] Román-Martínez, MC, Cazorla-Amorós, D, Linares-Solano, A, Salinas-Martínez de Lecea, C, and Atamny, F. Structural study of a phenol formaldehyde char. Carbon. 1996; 34(6): 719-727.
- [11] Gupta, A, and Harrison, IR. Small-Angle X-ray Scattering (SAXS) in carbonized phenolic resins. Carbon. 1994; 32(5): 953-960.

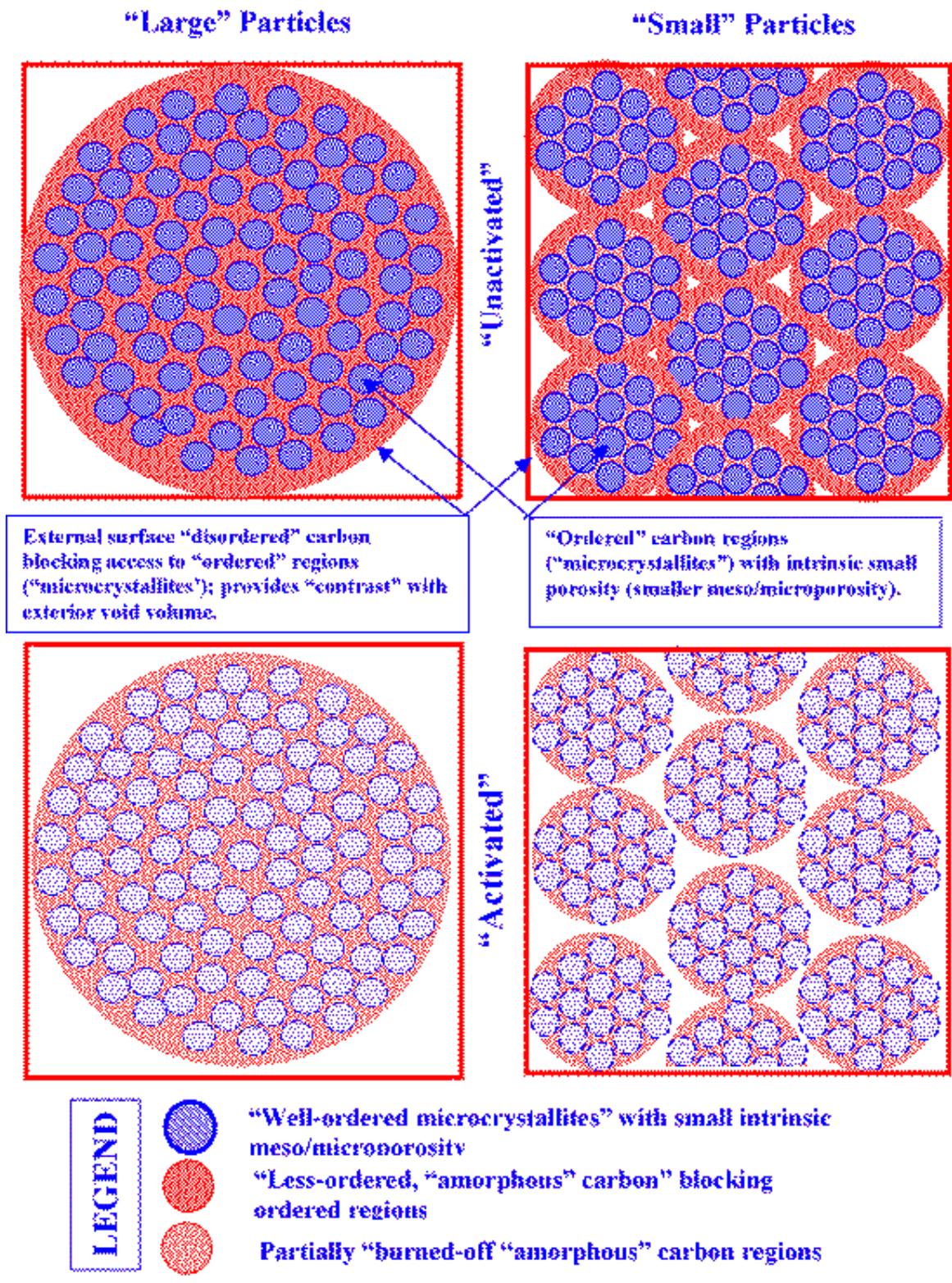
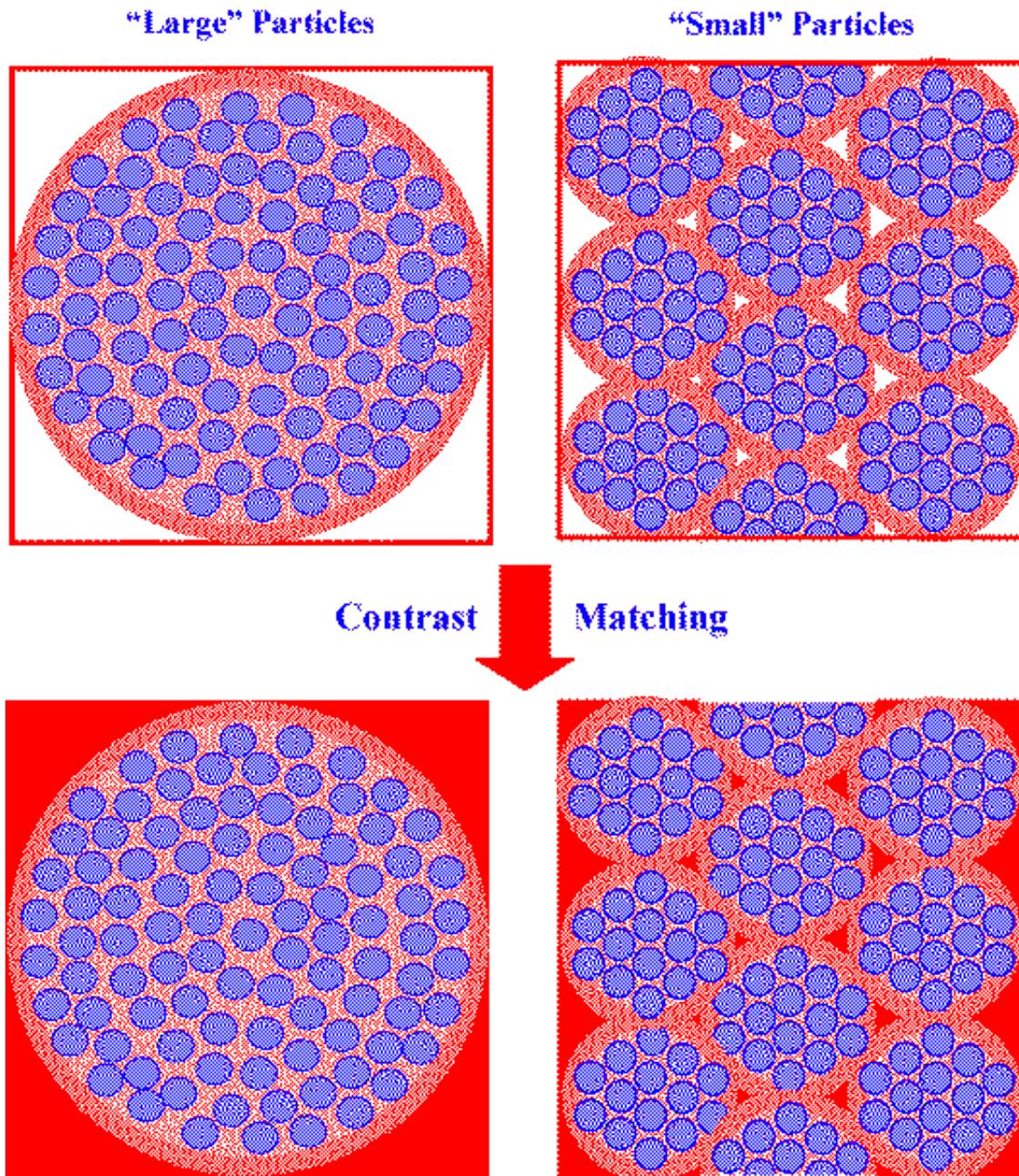


Figure 6. Schematic of phenol formaldehyde char activation.



External surface (amorphous carbon) structures “matched,” but intraparticle features remain invariant.

- “total” (dry) scattering differs in larger scatterer region, but not in region of smallest scatterers
- “contrast-matched” scattering almost independent of particle size

Figure 7. Schematic of contrast-matching unactivated phenol formaldehyde char particles.

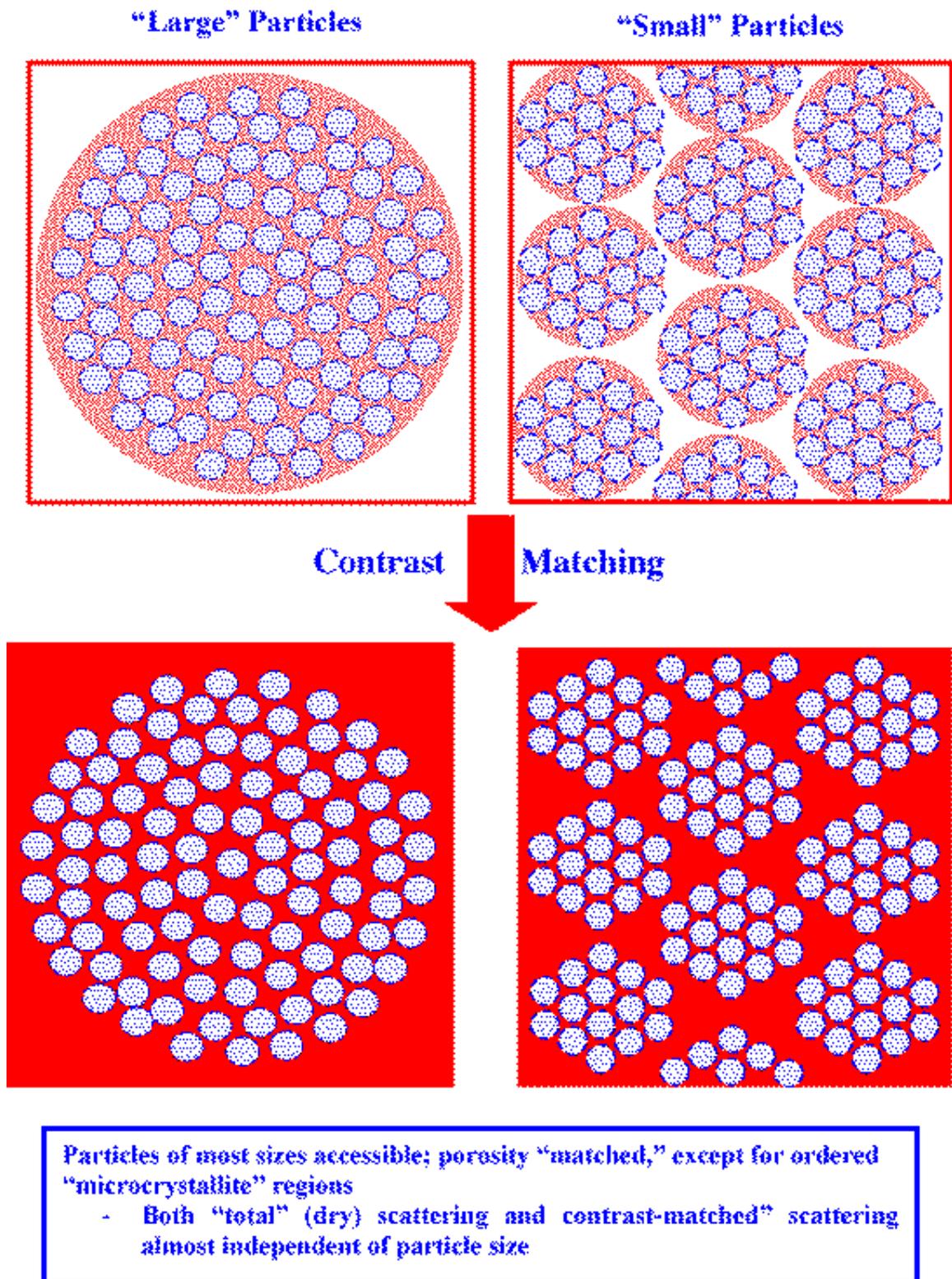


Figure 8. Schematic of contrast-matching activated phenol formaldehyde char particles.