

Biochar Characterization in Complex Soil Mixtures - High Resolution Nitrogen Pore Distribution Analysis (HRPDA)

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Abstract

Complex mixtures of porous materials have been the subject of intense study for the past seventy years in heterogeneous catalysis due to their utility in converting petroleum fractions to useful products including, most notably, gasoline. A technique which emerged almost 30 years ago, based on controlled pulses of volumetric doses of nitrogen gas to porous solids at liquid nitrogen temperature, produced details of the pore distribution and the pore volume of these different components of complex mixtures that was not possible from previous instruments. Thus, this method is described as a high resolution pore distribution analysis (HRPDA) technique. This technique provides an accuracy of 1-2 Å, and was successfully used to measure the thickness of a single molecular layer of tungsten oxide bound to the surface of a transitional alumina. In this paper we have applied this HRPDA method to the characterization of mixtures of a state-of-the-art, and apparently unique, Cabot carbon black (developed for fuel cell application), mixed with Mississippi loess to prove that the HRPDA approach would be applicable for biochar amended soils *at low contents of biochar mixed with soil*. This particular Cabot carbon black, Black Pearl (BP) 2000, is probably at the pinnacle of potential biochar-like materials with a surface area of 1500 square-meters per gram (m²/g) and a pore volume of over 3 cubic centimeters per gram (cc/g). It is demonstrated by the characterization work from Micromeritics Analytical Services that quite accurate information can be obtain for the individual components as well as mixtures of the carbon black with the loess soil in concentrations of 1-5 wt%. This work was intended to provide the foundation for characterization of real biochar materials in soil, and to provide details of the transformations of biochar materials in soil over time. We also utilized a combination of Hg porosimetry and HRPDA to the characterization of a charcoal on the opposite end of the spectrum of BP 2000, a typical charcoal used for briquettes which had a low surface area. Despite this low surface area there was considerable pore volume at > 1 micrometer size range in this particular charcoal of about 2 cc/g water uptake based on the un-ground briquettes. This material was characterized and demonstrated to have a quite low surface area of about 2-3 m²/g. This low surface area charcoal had the pores filled with water, and was subjected to eight cycles of freeze-thaw-freeze (FTF) conditions to simulate conditions in soils subjected to freezing conditions. The modification of the carbon structure after these limited FTF-cycles was substantial, and suggests great care must be exercised in translation of biochar materials developed in the Amazon Basin to colder climates where the soil is subject to FTF-cycles. In subsequent experiments BP 2000 was found to undergo major changes when subjected to FTF-cycles, also. This work suggests that there may be an opportunity for nano-technologists to approach biochar synthesis that can tolerate soils subjected to FTF-conditions.

Introduction

Heterogeneous catalysis is based almost exclusively on oxide support materials that are made of primary particles that have nano-dimensions for the particle diameter, e.g., 200Å or 20 nm diameter (1). The packing spaces between the primary, non-porous particles provide the diffusion path for gas or liquid phase reactants to interact with catalyst particles that are, in turn, attached to the surface of the primary oxide particles. An analogy would be sand-size particles attached, or glued, to the surface of a close-packed arrangement of ping pong balls. It is essential in heterogeneous catalysis to know the amount of the void spaces in an aggregate of these particles, and to have a way to measure the sizes of these void spaces formed between these particles, which are, in the main, non-porous and are termed primary particles. In practical terms, it would be impossible to prepare the small metal or metal oxide catalyst particles themselves attached to the supporting oxide surface without knowing precisely the pore volume provided by these primary particles. Sophisticated characterization methods have been developed over the years that can measure accurately not only the pore volume but the sizes of the spaces formed in aggregates of these primary, non-porous solids (2). For over 50 years Cabot Corporation has made a wide variety of carbon blacks and activated carbons that have pore volumes and internal void spaces that can closely parallel to those of oxide materials used predominantly in catalysis. In fact, there are examples where carbon-based catalyst supports provide unique characteristics where they excel for particular applications, and where they are the preferred support material eclipsing oxide supports. One example is selective hydrogenation of unsaturated hydrocarbons where metals such as Pd, Rh, Ru, or Pt are dispersed on the surface of carbon supports. Usually these precious metals are present in the material as very small metal clusters, or particles, on the order of 1-3 nm diameter in size that are attached to the carbon surface. So, there is a history of application of porous carbon materials in the area of heterogeneous catalysis that provides a reference frame for biochar soil-amending materials.

A powerful technique in determining the sizes of void spaces in catalyst supports and the amount of pore volume is based on adding volumetric doses of nitrogen gas at liquid nitrogen temperatures. This technique, albeit an indirect method, provides a virtual “blue-print” of the interior void spaces in porous materials with great accuracy and detail. This characterization method became known as a high resolution pore distribution analysis (HRPDA), and was so powerful that all of the analytical groups of the major oil companies and chemical companies relied heavily on the information from these techniques. The techniques were so widely used that dedicated instruments were employed in the majority of these companies. HRPDA has been widely used in the characterization of support materials, and Micromeritics has been one of the industry leaders in characterization of such materials (3). As the technique evolved over time it was often employed to characterize catalyst materials that involved a complex mixture of different components with very different pore sizes and pore volumes. One of the standard materials used as a check of these instruments’ reliability and reproducibility at Exxon Research and Engineering Company was regular evaluation of weighed-mixtures of three different controlled-pore-size PQ Corporation silica gels. By observing how reproducible the characterization of these weighed mixtures of controlled pore glasses were to accurately measure the pore volume of each component, the technique was put to good use in the characterization of other complex mixtures of different porous components. One such mixture was various micro-porous zeolite materials at low

concentration when mixed with clay or silica-alumina diluents. These materials were employed in Fluid Catalytic Cracking processes, and provided the majority of the gasoline used in our transportation network.

HRPDA was found to be a powerful technique to determine the precise amount of zeolite in a complex mixture of lower surface area clay and/or silica-alumina supports. These complex mixtures of oxide materials had very different pore distributions for the different components. Nevertheless, these differences among the materials allowed HRPDA to provide a complete blueprint of the pore distribution in these complex mixtures, and even to provide a very accurate measure of the amount of the microporous zeolite component in the complex mixture. We will see that this same approach was successfully extended to the case where Black Pearl 2000 was mixed with a Mississippi loess soil at low carbon contents of 1-5 wt.%. Black Pearl 2000 has also been characterized recently (4) and reported to have a small pore volume of 0.08 cc/g with 8.2 Å diameter pores. This work was initiated to provide the foundation for the characterization of biochar samples in soil as a function of aging in the soil over time, and, perhaps, even add important information about the intrinsic structure of biochar itself in aged soil environments. If this approach were to prove successful and more widely employed there is every reason to expect that it could contribute to establishing the structure-function relationships of many biochars in soil samples. One of the main objectives in heterogeneous catalysis is to determine the structure-function relationship of the catalyst particles to their catalytic effectiveness, and, also, the stability of the catalyst to convert reactants to valuable products over time. So there is a natural bridge in the goals that soil scientists have in getting a handle on the importance of biochar structures to soil productivity in real world conditions, and those goal in the field of catalysis to determine the structure-function relationships of catalysts to their volumetric productivity of catalyst-derived products.

One way we used to demonstrate the power of HRPDA was a study of a commercial charcoal briquette, and then to investigate the changes in the structure after repetitive freeze-thaw-freeze (FTF) conditions. This procedure is considered a first step toward understanding how the structure of biochar materials might respond in soils where repetitive FTF-conditions occur. This characterization work suggested that major transformations have occurred in this carbon structure by the cyclic freezing treatment. In this case, Hg porosimetry was combined with HRPDA to track the transformation that had taken place to better understand the information obtained from the volumetric dosing procedure. Based on this work it seemed prudent to experimentally establish structural-stability of biochar materials used in environments where the soil is subjected to FTF-conditions. We recently completed parallel studies of the very hard, spherical particles of BP 2000, and determined after two cycles of FTF-treatment that the BP spheres had been reduced dramatically in size. Before this work was started to investigate the impact of FTF-cycles of biochar materials very high pore volume zeolite materials, exclusively with micro-pores in the size range of 0.5-0.6 nm diameter, when subject to FTF-treatment were completely destroyed when the void spaces were filled with water. The expanding volume of the ice in the interior void space of porous solids exerts a tensile stress within the structure that may have considerable impact on the structural integrity of many classes of porous solids, especially when subjected to repeated cycling conditions. On the other hand, it has been established that there are certain zeolite structures that are immune to transformation when ice is formed within their structure, chabazite (5). In recent

work an approach to prepare FTF-tolerant materials has been successful, and will be the subject of future communication to the biochar community.

Experimental

The surface area and porosity characteristics of the sample materials were determined by the physical adsorption technique and porosity also was determined by high pressure mercury intrusion porosimetry (MIP).

Physical adsorption is a surface phenomenon by which gas molecules (the adsorptive) are weakly bound to the surface of the solid (the adsorbent) by van der Waals forces and occurs on all surfaces provided temperature and pressure conditions are favorable. Physical adsorption does not affect the structure or texture of the solid material, and desorption takes place readily when conditions are reversed. Beginning at very low pressure, say 10^{-5} mmHg, and slowly increasing the pressure stepwise, the adsorption process proceeds with the accumulation of layers of molecules (the adsorbate) on the surface and within pores. The number of molecules that condense on the solid with each step in pressure is not only dependent on the pressure, but also on surface features. Therefore, a plot of the cumulative quantity of gas adsorbed as a function of pressure can assume various shapes. This plot is called an isotherm and its shape contains information about the surface of the solid.

There are numerous theories of the adsorption and desorption processes that account for the shape of the isotherm. The most widely employed model in the determination of surface area from a physical adsorption isotherm is the Brunauer, Emmett and Teller (BET) theory (6). The theory describes the progression of surface coverage by gas molecules and is used to determine the point in the process at which the surface is covered with a single layer of molecules. This point in the adsorption process is termed *monolayer coverage* and the quantity of molecules required to form the monolayer is called the *monolayer capacity*. The theory takes into account that a second and higher layers begin building prior to the completion of the first layer.

The instrument, having measured the quantity of gas adsorbed by the sample at each pressure (the isotherm) and BET theory providing the point on the isotherm when monolayer coverage is achieved, allows one to determine the monolayer capacity. With knowledge of the surface area occupied by a single molecule at the experimental temperature from sources such as McClellan and Harnsberger (7), the product of this and the monolayer capacity yields the surface area of the solid.

Mathematically, the BET theory expresses the amount of gas adsorbed by the sample at each pressure step. Pressure (P) is expressed relative to the saturation pressure (P^0) of the gas at the experimental temperature, yielding the relationship,

$$V_{STP} = \frac{v_m C P}{(P^0 - P) \left[1 + (C - 1) \frac{P}{P^0} \right]} \quad (x)$$

where V_{STP} is the quantity of gas expressed as a gas volume under conditions of standard temperature and pressure, v_m the monolayer capacity also expressed in *standard volume* terms, and C is a constant related to the heat of adsorption, which is the energy liberated when a molecule adsorbs.

Rearranging Equation x into linear form gives

$$\frac{P}{V_{STP}(P^o - P)} = \frac{1}{v_m C} + \left(\frac{C-1}{v_m C}\right) \frac{P}{P^o} \quad (\text{x1})$$

If the adsorption process conforms to the BET model, a plot of

$$\frac{P}{V_{STP}(P^o - P)} \text{ vs } \frac{P}{P^o} \quad (\text{x2})$$

will yield a straight line approximately between 0.05 and 0.30 P/P^o and referred to as the BET range. The slope of the line will be

$$\left(\frac{C-1}{v_m C}\right) \quad (\text{x3})$$

and the intercept

$$\frac{1}{v_m C} \quad (\text{x4})$$

permitting the values of v_m and C to be determined.

Porosity information also can be extracted from the shape of the isotherm. Macropores and mesopores fill by capillary condensation, building up layers of condensate on the pore walls until the size of the remaining open space and the relative pressure achieve a critical relationship at which time the remaining “core” of the pore fills. All macro- and mesopores will be filled with condensed adsorbate (capillary condensation) at pressures somewhat below the prevailing

saturation vapor pressure of the adsorptive. Micropores, however, spontaneously fill at very low pressures governed by a completely different process.

Perhaps the most frequently used classical theory for determining pore volume distribution by pore size in the meso- and macropore ranges is described by Barrett, Joyner and Halenda (9), hence, it is called the BJH method. Since the BJH method does not apply in the micropore range, classical models such as those of Dubinin-Radushkevich (10), Dubinin-Astakhov (11), and Horvath, and Kawazoe (12) are used to characterize micropores.

A more modern approach to extracting surface features from the isotherm is to use a molecular-based statistical thermodynamic theory that allows relating the adsorption isotherm to the microscopic properties of the system. Adsorption equilibrium at any relative pressure results in the space near the surface having acquired a greater average density of gas molecules than regions farther removed. Describing the equilibrium distribution of the gas molecules near the surface as a function of system pressure and the molecular properties of the components of the system, a model can be constructed for the adsorption isotherm for the system. Modern physical chemistry provides several ways to calculate this distribution based on the fundamental thermodynamic law that a configuration of minimum free energy exists at equilibrium.

For the work reported here, density functional theory (DFT) was used for reducing the adsorption isotherm because it provides an accurate method of describing inhomogeneous systems yet requires fewer calculations than other mathematical techniques such as molecular dynamics and the Monte Carol method. A significant feature of DFT is that it applies over the complete range of the isotherm and is not restricted to a confined range of relative pressures or pore sizes as are the classical models.

Mercury intrusion porosimetry was employed in this study to provide porosity information complimentary to that of gas adsorption. Mercury is a non-wetting liquid for most solids and, due to surface tension, will span a pore opening rather than enter the pore provided the relationship between the external pressure on the mercury and the size of the pore opening exceeds a certain set of equilibrium conditions. Washburn (13) in 1921 derived an equation describing the equilibrium of the internal and external forces in terms of the surface tension of the liquid, the contact angle between the liquid and solid, and the cross-sectional shape of the capillary. The equation states simply that the pressure required to force a non-wetting liquid to enter a capillary of circular cross-section is inversely proportional to the diameter of the capillary and directly proportional to the surface tension of the liquid and the angle of contact with the solid surface.

To derive the relationship between external pressure and the size of the pore affected, consider mercury in contact with a pore opening of circular cross-section and diameter D . The surface tension of the mercury acts along the circle of contact over a length equal to the perimeter of the circle, πD . Thus the force opposing the entry of mercury into the pore equals $-\pi D\gamma \cos\theta$, where γ is the surface tension of mercury and θ the contact angle between the mercury and solid. An external pressure must be applied to overcome the resistive force and cause intrusion of the mercury into the pore. Since pressure is defined as force per unit area ($P = F/A$), it follows that the force produced by an external pressure acting over the area of the circular pore opening which the mercury bridges is $(\pi D^2/4)P$. At equilibrium, the force promoting intrusion and the force opposing intrusion are equal; thus

$$-\pi D \gamma \cos \theta = \frac{\pi D^2 P}{4} \quad (\text{x6})$$

or, simplified

$$D = \frac{-4\gamma \cos \theta}{P} \quad (\text{x7})$$

which is the Washburn equation and the working equation for determining the sizes of pores affected by a step in pressure.

Upon an increasing pressure step, mercury will be forced into pores smaller than those already filled, the smallest size being determined by Eq. x7. Mercury that enters pores during an increasing pressure step comes from a reservoir in which any change in the volume of mercury contained is detected in microliter quantities. For each pressure step, the equilibration pressure, P , and the mercury volume V removed from the reservoir over that step are recorded. A series of pressure steps from P_1 to P_n provides a set of experimental data points, (P_i, V_i) , from which the size range of pores affected, D_i to D_{i-1} and the total volume of those pores, V_i , can be calculated for each pressure step, 1 to n . A plot of these points is called an intrusion curve. If the pressure is decreased in a step-wise manner, mercury is returned to the reservoir with each decreasing pressure step. A plot of these data produces an extrusion curve. When examining the two curves, it will be noted that the extrusion curve did not retrace the intrusion curve, the difference between the two curves (the hysteresis) is indicative of pore shape.

Results and Discussion

Our approach was to concentrate primarily on using materials made by a leading manufacture of carbon supports, Cabot Corporation. Early in this work we decided to concentrate on investigating one of the best possible carbon materials made by Cabot, and to concentrate our characterization work on mixtures of this material with a Mississippi loess soil sample at low concentrations at precise addition levels. We were drawn to approach the topic of biochar characterization due to the analogy of characterization work of zeolite materials in complex mixtures already described. Our goal was to characterize these mixtures with Micromeritics advanced gas adsorption characterization methods to prove that such methods would be applicable for biochar materials when mixed with soil at dilute levels. Cabot Corporation provided samples of carbon blacks that spanned as wide a range in physical properties as anticipated to be present in a majority of biochar materials. A recent paper, using techniques analogous to those employed in this work (14), provided the detailed characterization for a biochar made from spruce wood that had a surface area of $10 \text{ m}^2/\text{g}$. Interestingly the pore diameter of this biochar increased by both chemical, KOH, and physical, steam, activation processes where the pore diameter was increased to 13-26 Å and 13-15 Å,

respectively. Cabot's BP 120 had a surface area of 25 m²/g, whereas BP 2000 had a surface area of 1500 m²/g. The latter material was developed for application in fuel cells, and exhibited all of the characteristics deemed important for materials used in heterogeneous catalysis, see Table 1. We did some limited evaluations of various Cabot materials: BP 120, BP 460, BP 480, BP 2000, and Monarch 1100 as a grass amendment material. For a grass lawn, unfertilized for twenty years in a residential neighborhood in New Jersey, the BP 120 sample had a biomass yield after five weeks of 630 grams per sq. meter compared to 1430 grams per sq. meter for the BP 2000 sample measured for a five week growing period. All of the other Cabot carbon black materials had biomass productivities above 985 grams per sq. meter. All of the square meter plots had 1 liter of carbon black added to each in a uniform manner with all plots then "watered in" for five minutes. This more than doubling of the biomass for the BP 2000 compared to BP 120 was a clear indication that the surface area of carbon black does impact the soil productivity even for these short term tests.

Mixtures of BP 2000 with loess soil were chosen to focus our attention on for the characterization work in this paper because of a combination of distinctive characteristics of this carbon black sample, see Table 1 and Figure 1. We will return to a discussion of the complex pattern of pores exhibited in Figure 1, and what is the explanation for a periodic spacing in the pore size of 11–14 nm pore diameter exhibited in Figure 1. We prepared mixtures of 1, 3, and 5 wt.% BP 2000 with a Mississippi loess soil sample (Natchez, Mississippi) and used these samples for HRPDA, see Table 2. Table 2 shows the detailed results for the 1 and 3 wt.% BP 2000 mixed with the loess soil. In addition, the BP 2000 and the Mississippi loess materials were also characterized using the analogous techniques used for the mixture of these samples. One of the key characteristics of BP 2000, which is judged to be important for materials employed in catalysis, is to have a wide range of both meso- and macropore sizes in the material. Macropores are defined as being larger than 500 Å, or 50 nm diameter; mesopores are defined as being between 20 and 500 Å, or 2 and 50 nm, diameter; and micropores are defined as being below 20 Å, or 2 nm, diameter. In BP 2000 mixed with Mississippi loess soil it was possible to establish that considerable contribution to the total pore volume, about 0.2 cc/g, is present between 10 nm and 100 nm diameter. Note that this sample only contains 5 % of the Black Pearl 2000 material. For BP 2000 itself there is about 1 cc/g of pores in this critical size region, see Figure 2. Also, note for BP 2000 that the total pore volume is dominated by the pore distribution in this region. These range-of-pore-sizes, 10-100 nm, are those of importance for almost any catalyst support, as a rule-of-thumb. These pore sizes are deemed critical for effective transport processes in catalyst applications allowing high access to the catalyst's active sites to reactant molecules. The majority of the surface area in BP 2000 is provided by pores below 20 Å, or 2 nm, diameter, see Table 1. Note that there is 1123 m²/g surface area from a total of 1500 m²/g in pores that are < 2 nm diameter based on the t-plot analysis. In this Cabot material it is interesting to note that this high surface area is not due to the typical "slit pores" that are supposed to be the main contributor to the surface area in biochar or charcoal materials. This conclusion is supported by the recent characterization of BP 2000 using analogous techniques, see reference 4. Rather, in BP 2000 the surface area is provided by non-porous carbon particles of a size where gas

and liquid diffusion processes would not be restricted as might be the case for “slit pores” of a smaller pore diameter. As has been noted previously the wide distribution of pores between 10-100 nm diameter is a characteristic that is unique to this Cabot material. The narrow slit pores commonly believed to provide a majority of the surface in charcoal samples is not present in this sample to any appreciable extent, see Figure 2. As one can see from the information obtained by the HRPDA one can obtain information that allows one to build a detailed “blue-print” of the internal void structure in porous solids. It is appropriate to explain in some detail the periodic pattern of pores of about 11–14 nm diameter separation exhibited in Figure 1, which is, in fact, the “blue-print” of the structure of the BP 2000 material. These periodic pattern of pores are due to clusters of primary particles, often referred to as “bunches-of-grapes” believed by the manufacture to be caused by an irregular oval shape of about 800 nm for the long axis. The accuracy of the measure of 0.1 – 0.2 nm from the experimental technique leaves little doubt that the structure that gives rise to the pore distribution is due to a regular and periodic attachment between these “bunches-of-grapes” building up a robust and strong particle whose size is about 1 μm diameter spheres for the *as received* BP 2000 material. The key point is that a complex distribution of pores in a material such as BP 2000 can be deciphered by the characterization tools described in this paper. This can be further understood by noting that Figure 2 shows that a majority of the surface area is provided by small pores in the BP 2000 sample, as is common with most porous materials of interest in catalysis. But what is novel about this particular material is that such a large amount of the pore volume is provided by intermediate size mesopores and macropores. Figure 2 is a companion to Figure 1 which allows a mental picture to be formed of the structure of the material. Despite the abundance of detailed information we are quite interested in obtaining some Transition Electron Micrographs of this BP 2000 material to better translate the information provide from the pore distribution analysis into a robust model of this interesting material.

A useful application of the HRPDA technique to biochar samples would be the ability to estimate the amount of a biochar material in soil, and to track any transformations in the structure over time. This technique works especially well when the void spaces in the mixture of materials are sufficiently different that the measured pore volume *in a certain region* becomes a “finger-print” for the amount of the material in the mixture. We have taken advantage of this application possibility of HRPDA by characterizing weighed amounts of Black Pearls 2000 in a loess soil sample (obtained from cliffs in Natchez, Mississippi). One can see in Figure 3 that there is a straight line relationship of the experimental Brunauer Emmett Teller (BET) surface area of weighed amounts of 1, 3, and 5 wt. % BP 2000 in this loess soil. If one plots the experimental values of the measured pore volume analysis versus the weighed amounts in the soil one also sees a straight line relationship, see Figure 4. These results point the direction of applying this HRPDA-technique to establish the amount of a porous biochar material in any soil where the biochar amendment material will probably have a lower intrinsic surface area and pore volume than BP 2000. Nevertheless, we believe that this HRPDA-approach can be extended to get detailed information about the distribution of pores within the dilute biochar-material in the soil sample, and, also, establish changes that occur as a function of time that the amendment has been in the soil. *There may not be another technique*

that can give such accurate information of the structural transformations of biochar materials in soil samples over time and in different soils.

It should be emphasized that the HRPDA-technique also gives quite accurate information for samples even with low surface area and low pore volume. Accurate information was obtained even for the case of a commercial charcoal material with a surface area of 2 m²/g, see Table 3. When this low surface area charcoal was subjected to eight freeze-thaw-freeze (FTF) cycles with water in the void spaces of the sample the volumetric-dosing-nitrogen data was sensitive enough to detect changes in the pore volume and a near doubling of the surface area, Table 3. It is exactly this great precision in doing the analysis of porous solids that has been so useful to understand such issues in catalysis as deactivation caused by structural changes of the oxide support materials. We also did the Hg porosimetry of the commercial charcoal sample due to the fact that this sample exhibited about a 2 cc/g water adsorption capacity as measured by the water uptake within an intact briquette. The explanation for this relatively high water adsorption capacity is due to very large micron, or micrometer, diameter particles having void space between the mainly non-porous particles. The fact that these particles are mainly non-porous comes from the low BET surface area obtained by the HRPDA analysis. When the material is subjected to FTF-conditions then the particles start to fracture as revealed by the overlay in Figure 5. This change of particle size is also picked up by the information shown in Figure 6. The pore size shifted from 3-4 microns to 1.5 microns after 8 FTF-cycles. It is useful to consider at this point in the discussion that a 40 pound quantity of this same charcoal saturated with water was cycled to FTF-conditions for over a month in a large cement mixing tray through the month of March in New Jersey. After just a few weeks time of repeated FTF-cycles the material was reduced to fine rubble. It seems clear that this charcoal material over time will not retain the void capacity present in the briquette. In fact, due to the low surface area which would have relatively low ion-exchange-capacity, and the steady decrease in the water adsorption capacity over time with FTF-cycles a typical barbecue charcoal would be predicted to be a very poor soil amendment material. A case could even be made that fracturing of the structure over time could lead to loss of permeability of the soil. The estimated pore volume for the FTF-treated charcoal was 0.2 cc/g based on water uptake by the incipient, or dry, impregnation method. Despite this possibility of a negative impact on soil productivity, 2" and 5" beds of this briquette charcoal, after being converted to fine rubble by FTF-conditions, were covered with sod. For over five months the overlay of sod has not been negatively impacted by the 100% charcoal beds below the sod layer. These tests suggest that at least for conditions with high rain fall levels it may be possible for such modest surface area charcoals to serve as a synthetic soil for some period of time.

The broader issues of the impact of FTF-conditions on real biochar materials will have to be resolved in future work. We have learned that FTF-cycling of BP 2000 breaks the quite hard 1mm spheres into much smaller particles, and that the particle size continues to decrease with the number of FTF-cycles. Our opinion is that this does not bode well for the more fragile walls of the slit pores found in many charcoal materials that are probably more easily transformed by FTF-conditions. The characterization of BP 2000

after eight FTF-cycles provides convincing evidence of the effectiveness of the FTF-cycles in shattering the large particles producing quite small particles of about 2-3 micron, or micrometer, diameter, see Figure 7 and Figure 8. What is especially intriguing is that despite this dramatic reduction in the particle size the BET surface area is almost unchanged compared to the *as received* sample, 1475 compared to 1498 m²/g, respectively. Note also that the sample after the FTF-cycles retains the characteristic and unique wide distribution of pores between 10-100 nm diameter. Note in Figure 7 the changes in the pore distribution comparing the *as received* and the freeze-thaw cycled sample which clearly shows a decrease in pores at around 90 nm or 900 Å diameter. Figure 8 shows the pore volume of the *as received* and the freeze-thaw cycled sample indicates that pore volume is being generated by fracturing of larger structures that produces measured pore volume between these fragmented particles. Consistent with this is the increase in the differential pore volume at 50 Å diameter, for example, where there is none in the original material. The 50 Å diameter pores are probably associated from particles of various sizes that are formed in the process of break down of the “bunch-of-grape” structure believed present in the original material. There seems to be no major differences in the pore distribution below 50 Å diameter that would indicate fracturing of the primary particles within the BP 2000 material. We would tentatively ascribe the stability of the pores below 50 Å diameter as being due to the primary particles being present in the structure as chains of the primary particles that have some built in flexibility. One can not rule out completely that the primary particles have been fractured by the freeze-thaw cycle but are showing similar pore distribution because they are present as individual particles that are loosely aggregated. Such primary particles may be hard to analyze if the bonding has been disrupted, or not, in the freeze-thaw cycling test due to their tendency to re-associate during the subsequent sample drying and handling procedure. Regardless, Figure 9 shows the optical microscope measurement of the BP 2000 material after eight FTF-cycles showing a particle of about 3 micron diameter. We are going to continue to investigate the transformations induced in carbon blacks, biochars, and other porous materials as a function of FTF-cycles to better access the potential need for novel approaches to make biochar-like materials from non-conventional materials. In addition, we are planning to do Transition Electron Microscopy of the freeze-thaw cycled material to better understand the results from the detailed N₂ porosimetry results.

Concluding Remarks

A “blue-print” of the internal pore structure of carbon blacks can be obtained using high-resolution N₂ porosimetry, even for the case of dilute levels of the carbon black in soil. A complex distribution of pores for Cabot’s Black Pearl 2000 show periodic regularity from the analysis which reflects the fact that there is a regular structural unit which can be described as a “bunch-of-grapes” built from the primary, or elementary, building block within the carbon black. It was demonstrated in this work that the BET surface area and the pore volume obtained from N₂ porosimetry can give detailed information about the amount of the carbon black present in the soil.

By Combining Hg porosimetry and N₂ porosimetry information on structural changes over a wide range of particle sizes, and the related void spaces between these particles, can be obtained. It is

believed that such techniques may prove useful in developing the structure-function relationships of biochar soil amendment materials, and their changes over time in the soil. One example examined in this paper is the structural changes that are induced by cyclic freeze-thaw tests for a low surface area commercial charcoal compared to the original material.

N₂ porosimetry combined with particle size analysis provides a window into changes of a high surface area and high pore volume Cabot carbon black before and following cyclic freeze-thaw tests. In the case of BP 2000 it is apparent that the majority of the surface area and pore volume is retained following freeze-thaw cycles which reduce the particle size to about 3 micron size. It is important to establish that biochar materials used in soils subjected to freeze-thaw cycles are not undergoing structural changes induced by the internal tensile stress of expanding ice crystals.

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Tables

Table 1 Properties of Cabot Black Pearl 2000 Carbon Black

Sample	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	t-plot Micropore Area (m ² /g)
Black Pearls 2000	1500	3.0	1123

Table 2 Porous Properties of Mixtures of BP 2000 and Mississippi Loess

Sample	BET Surface Area (m ² /g)	Total Pore Volume (cc/g)	t-plot Micropore Area (m ² /g)
Mississippi Loess	20	0.02	7
1 wt.% Black Pearls 2000/Loess	40	0.07	28
3 wt.% Black Pearls 2000/Loess	70	0.13	50

Table 3 Properties of Charcoal Before and After Freeze-Thaw-Freeze Treatment

Sample	BET Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)
Charcoal	2.9	0.006
Charcoal with 8 Freeze-Thaw-Freeze Cycles	5.5	0.009

Figures

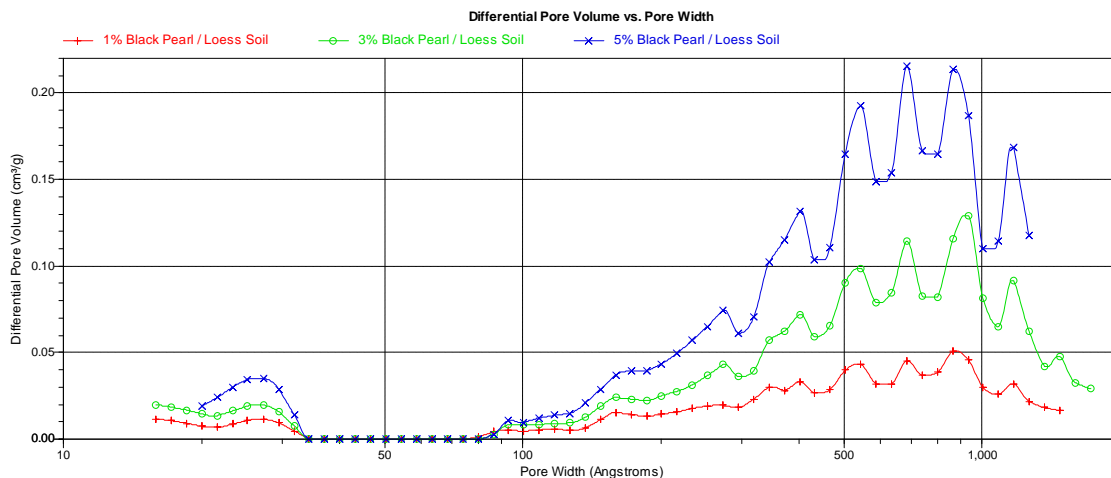


Figure 1 Differential Pore Volume vs. Pore Width for 1, 3, and 5 wt. % Black Pearl 2000 and Mississippi loess using Micromeritics ASAP 2420 instrument.

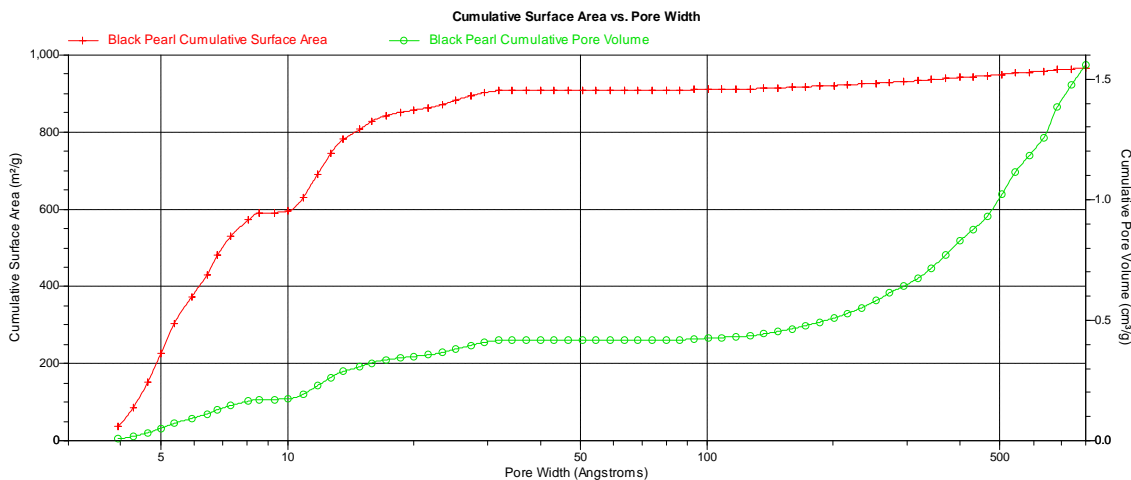


Figure 2 Cumulative Surface Area vs. Pore Width (left axis) and Cumulative Pore Volume vs. Pore Width (right axis) for Black Pearl 2000 using Micromeritics ASAP 2420 instrument.

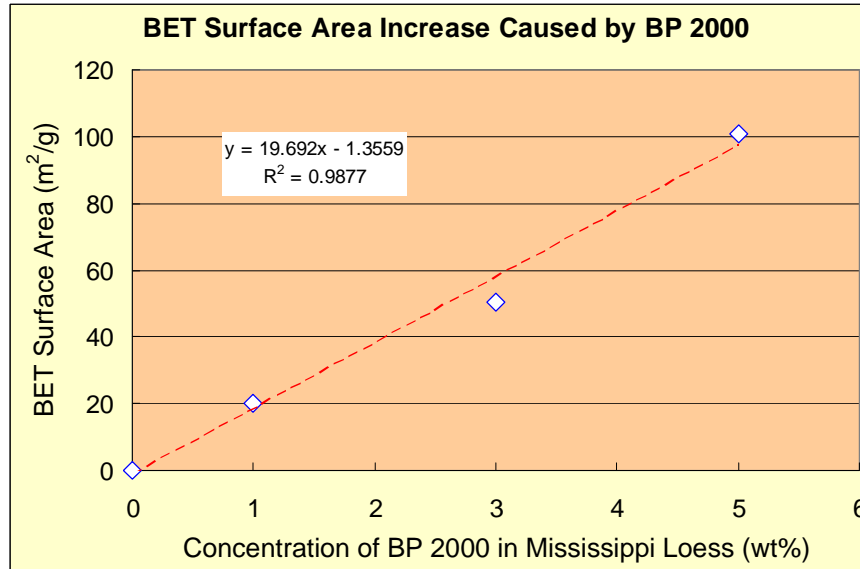


Figure 3 BET surface area of mixtures of Black Pearls 2000 and Mississippi loess as a function of amount of Black Pearls 2000 present in the mixture measured using a Micromeritics ASAP 2420 instrument.

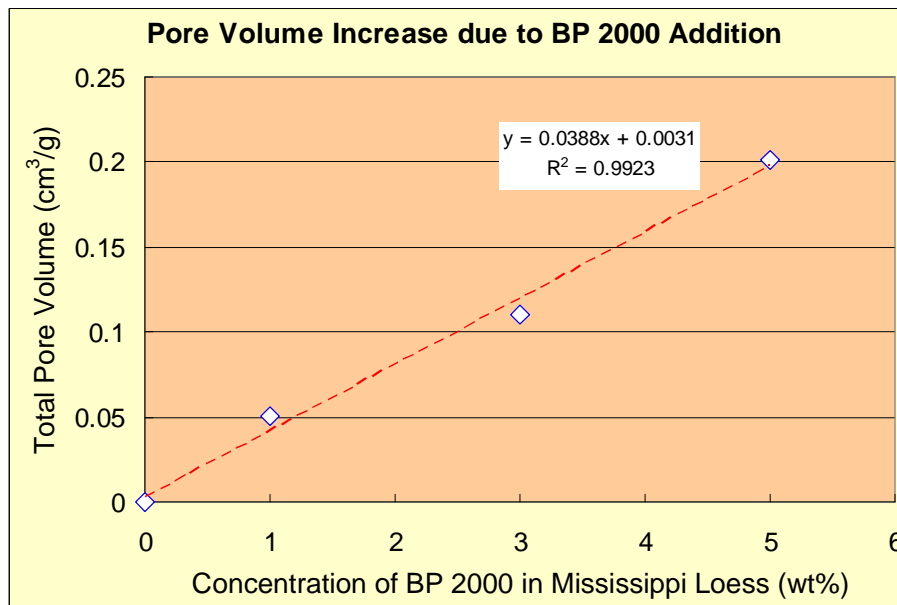


Figure 4 Pore volume of mixtures of Black Pearls 2000 and Mississippi loess as a function of amount of Black Pearls 2000 present in the mixture measured using a Micromeritics ASAP 2420 instrument.

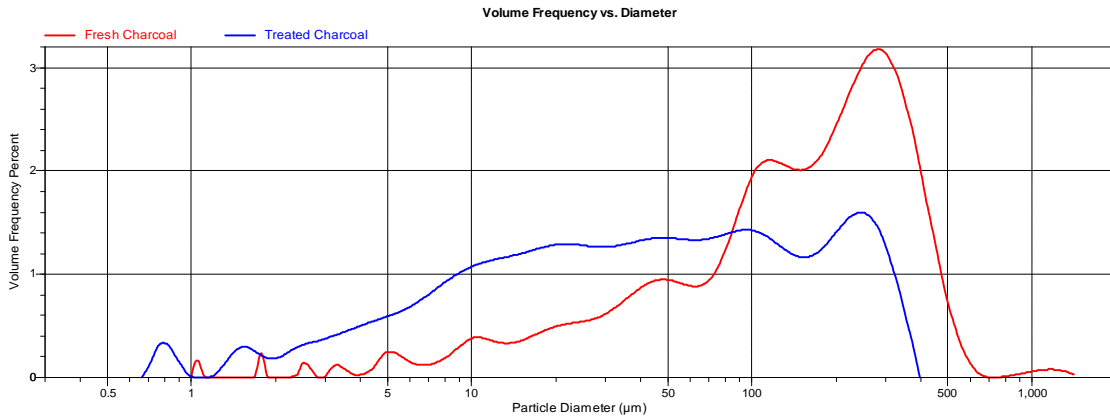


Figure 5 Particle size distribution of a Kingsford charcoal before (Fresh Charcoal) and after freeze-thaw-freeze treatment (Treated Charcoal) using a Micromeritics Saturn Digisizer instrument.

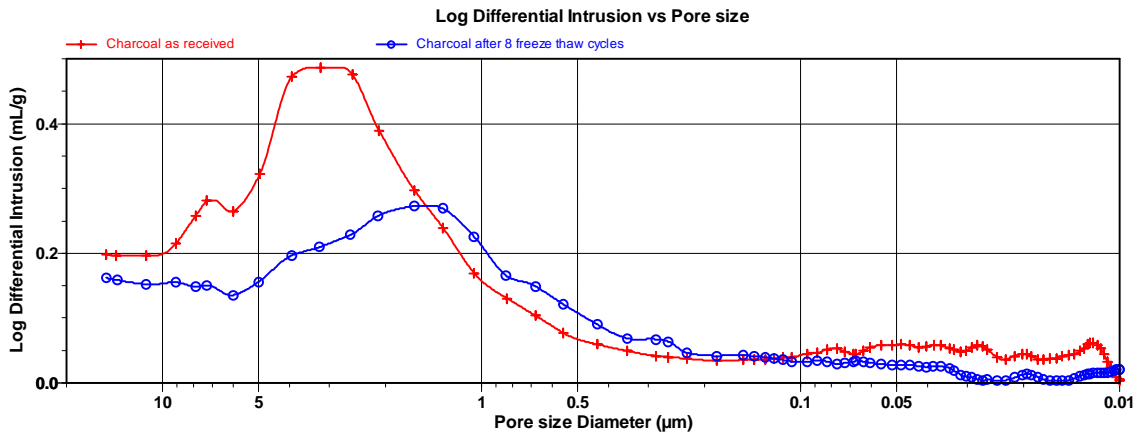


Figure 6 Pore size distribution of Kingsford charcoal before (Charcoal as received) and after freeze-thaw-freeze treatment (Treated Charcoal) using a Micromeritics Saturn Digisizer instrument.

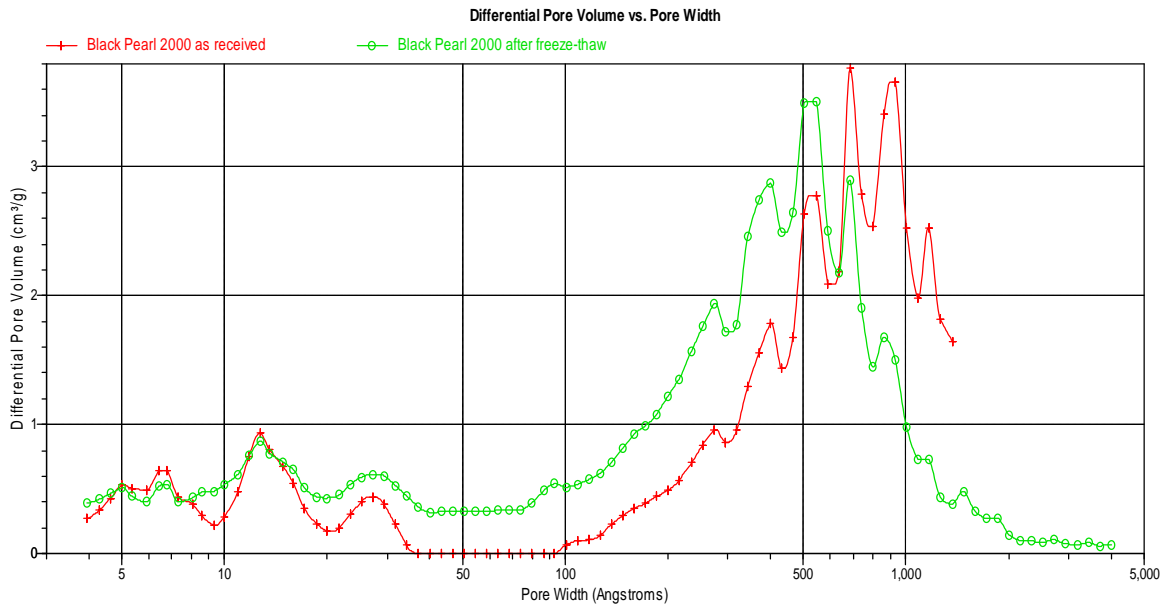


Figure 7 Pore size distribution of Black Pearl 2000 and after freeze-thaw treatment using a using a Micromeritics ASAP 2420 instrument.

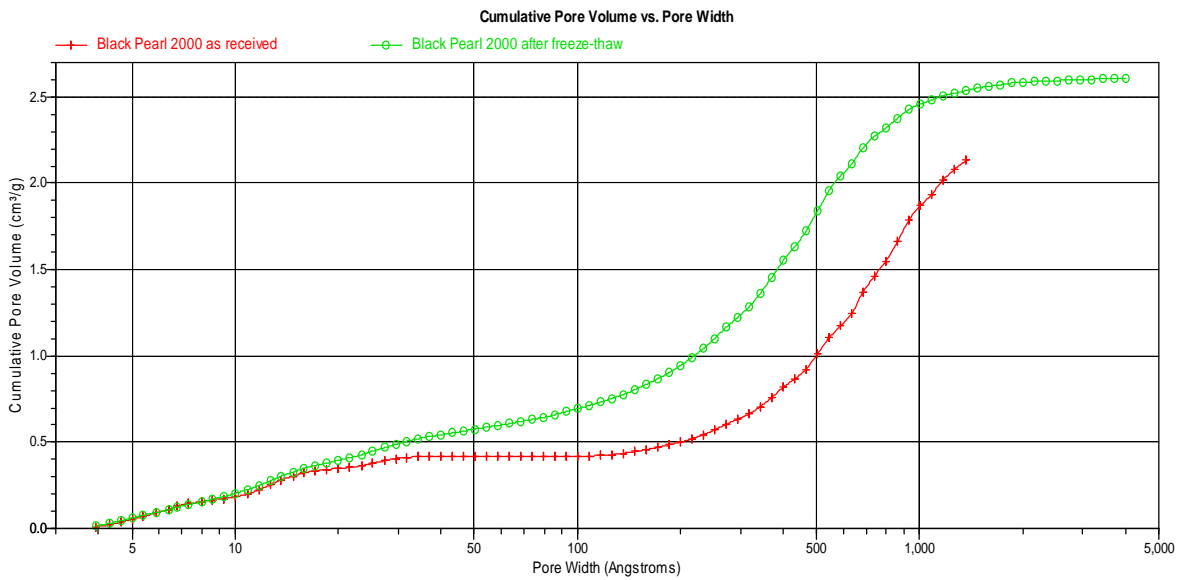


Figure 8 Pore volume measurement of Black Pearl 2000 and after freeze-thaw treatment using a using a Micromeritics ASAP 2420 instrument.

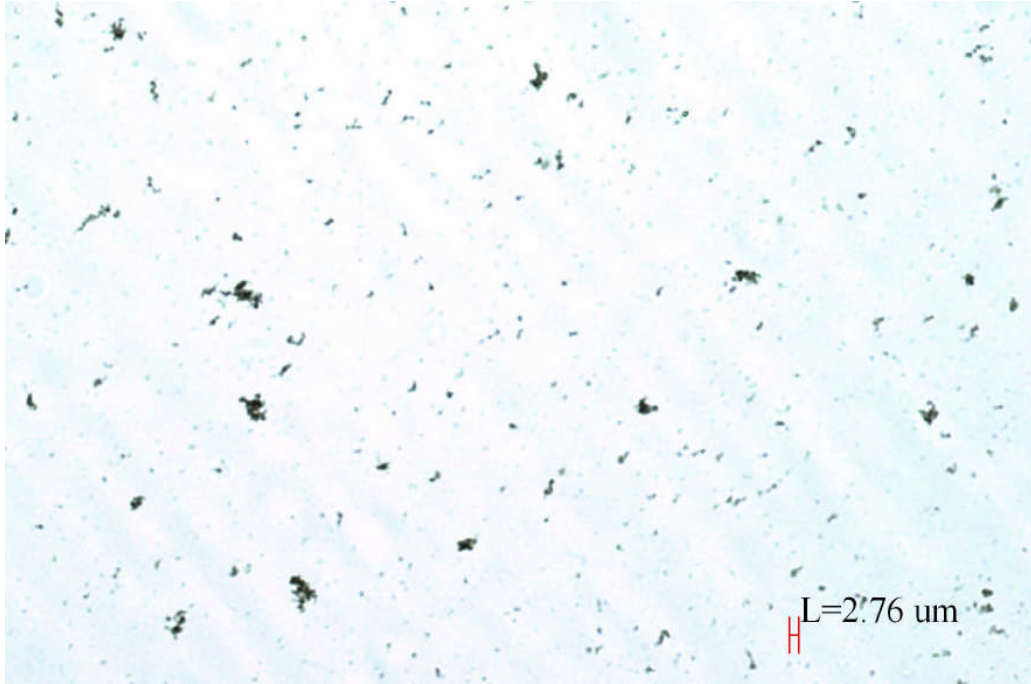


Figure 9 Micrograph of the freeze-thaw treated Cabot Black Pearl 2000 showing the ~ 3 micron size of the carbon black material due to the freeze-thaw cycle.