PRODUCTION AND CHARACTERIZATION OF ACTIVATED CARBONS FROM CEREAL GRAINS

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Keywords: Activated Carbons, Cereal Grains, Surface Fractal Dimension, Small-Angle X-ray Scattering

INTRODUCTION

The term, activated carbon, is a generic name for a family of carbonaceous materials with well-developed porosities and consequently, large adsorptive capacities. Activated carbons are increasingly being consumed worldwide for environmental applications such as separation of volatiles from bulk gases and purification of water and waste-water streams. The global annual production is estimated to be around 300 million kilograms, with a rate of increase of 7% each year [1].

Activated carbons can be prepared from a variety of raw materials. Approximately, 60% of the activated carbons generated in the United States is produced from coal; 20%, from coconut shells; and the remaining 20% from wood and other sources of biomass [2]. The pore structure and properties of activated carbons are influenced by the nature of the starting material and the initial physical and chemical conditioning as well as the process conditions involved in its manufacture [3].

The conventional method of manufacturing activated carbons involves two steps. In the first step, the raw material, usually of lignocellulosic origin, is carbonized in an inert atmosphere. The second step entails the physical activation of the resulting char of a low adsorptive capacity with either steam or carbon dioxide at a temperature usually exceeding 800° C [4]. The significance of these two steps have been described in detail elsewhere [5].

Although the general two-step procedure for generating activated carbons from lignocellulosic precursors has been well documented in the literature, knowledge of the specific variables involved is essential for a particular feedstock for developing the porosity and adsorptive capacity sought in a given application. In this sense, the current work investigates the evolution of the porosity of activated carbons generated from the pyrolysis and physical activation of novel feedstocks with a very low content of ash - kernels of cereal grains such as corn and hard red winter wheat (HRW). These grain kernels, either edible or off-grade are abundant and relatively inexpensive. The porous structures of both non-graphitizable charcoals obtained by the carbonization of the kernels and those of the resulting activated carbons have been characterized by the methods of physisorption. Specifically, the total micropore volumes and surface areas have been determined at various temperatures of carbonization and degrees of activation. Furthermore, an investigation of the probable fractal nature of the pore interfaces of a representative sample of HRW charcoal has been conducted through small-angle X-ray scattering.

THEORETICAL

Small Angle X-ray Scattering

X-rays are scattered primarily by the electrons of an irradiated material. The distribution of electrons throughout the material is not homogeneous, and the electronic density (number of electrons / unit volume) varies in different regions of the sample. Small-angle X-ray scattering (SAXS) by a material occurs as a consequence of this inhomogeneity in the electron density existing on length scales appreciably larger than the normal distances between atoms [6, 7]. As a result, the structures of various disordered materials can be investigated by SAXS over length scales varying from 5 to 4000 Å [8]. A schematic of a typical SAXS system is shown in **Figure 1**. Conventionally, small angles imply that the values of the scattering angle, 2θ, are no greater than 6 degrees.

The relationship between the intensity of the scattered X-rays, I(q), and the scattering wave-vector, q, for a porous material has been described in detail elsewhere [9, 10]. Of relevance to this work is the scattering from systems of isotropic, i.e., randomly oriented, independent scatterers, with an average particle or pore dimension, d, wherein I(q) can be approximated by the Guinier equation

$$I(q) = I(0) \exp[-(qR_g)^2 / 3] \qquad (1)$$

for values of qd not appreciably greater than 1.0 [6]. The mean radii of gyration of the scatterers, R_g, can be evaluated in this regime from the slope of a plot of the natural logarithm of I(q) versus q^2. An order-of-magnitude estimate of d is obtainable from R_g if the shape and charge distribution of the scatterers are known; usually, $2R_g < d < 3.5 R_g$ [11]. Specifically, if the system of scatterers can be assumed to be composed of identical, spherical pores of radius r_0, then the relation, $r_0 = 1.3 R_g$, can be applied to obtain r_0 [6].

The scattered intensity has been shown to be proportional to q^{-4} or θ^{-4} [6, 12] when the boundaries of the pores can be considered as smooth, i.e., free from irregularities. When the surfaces of the pores are fractal [13 -15], the scattered intensity takes cognizance of the surface irregularities, and can be described by the following relationship for values of qd far greater than 1.0 [10, 16]

$$I(q) = \pi I_e \delta^2 N_0 \Gamma(5-d_{SF}) \sin[0.5\pi(d_{SF}-1)] / q^{(6-d_{SF})} \qquad (2)$$

or equivalently,

$$I(q) = I_0 q^{-\alpha}; \alpha = 6 - d_{SF} \qquad (3)$$

where I_0 is a constant, and d_{SF} is the surface fractal dimension. Since d_{SF} is bounded in the interval between 2.0 and 3.0, it is obvious from Eq. 3 that α can take on values between 3.0 and 4.0. When d_{SF} approaches 3.0, however, I(q) vanishes according to Eq. 2; this apparent dilemma has been discussed at length elsewhere [9,10,17].

EXPERIMENTAL

Treatment of Raw Material

Whole grain kernels of corn and hard red winter wheat (HRW) were procured from a local source. The hull, i.e., the outer portion or the pericarp, constitutes a very small fraction of the total weight of the kernel, especially for corn. The moisture content in the grains, as determined by air-drying, was around 10%. The kernels were carbonized batchwise in 2-3 gram lots in an inert atmosphere of nitrogen flowing within a bench-scale tubular furnace [18]. Each batch of kernels was placed in a vertical, cylindrical wire-guaze reactor suspended inside the tubular reactor. The retention time of the kernels in the reactor was sufficient to allow complete devolatilization at a specified temperature of carbonization or pyrolysis; hence, the resultant charcoals were deemed terminal. These charcoals were obtained from the pyrolysis of the kernels in a single-stage as well

as a two-stage process. The single-stage process carbonized the kernels in one single step at a specified temperature. The two-stage process carbonized the kernels at a low temperature in the range from 250 to 300° C followed by that at a specified temperature. The kernels were pyrolyzed over a temperature range of 250 to 850° C. The charcoals generated by both processes were rapidly cooled to room temperature by quenching in a stream of nitrogen gas of 99.99% purity.

Physical Activation

The experimental set-up for the physical activation of the ensuing charcoals with CO_2 gas of 99.5% purity, was similar to that for carbonization. The vertical configuration of the reactor ensured that the reactant gas was forced directly through the char bed, thus minimizing the influence of film mass transfer resistances during activation. The charcoals after activation for the desired period of time, deemed as activated carbons, were purged in a stream of nitrogen of 99.99% purity. The activation was performed at a temperature of 850° C, for durations ranging from 0.5 to 6 hours.

Characterization of Charcoals and Activated Carbons

Both charcoals and activated carbons obtained were characterized by nitrogen adsorption at 77.4 K. A fully automated Nova-1200 instrument manufactured by Quantachrome Corporation determined the volumes adsorbed at various relative pressures. The duration of adsorption for each data point was approximately one hour in all the measurements. The surface areas were calculated by the BET method while the total micropore volumes were estimated by applying the D-R equation [19].

Small Angle X-ray Scattering

The X-ray scattering data were obtained with the aid of the SAXS system at the National Center for Small-Angle Scattering Research, Oak Ridge, Tennessee. The wavelength associated with the X-ray measurements was 1.54Å. The data on the scattered intensities were corrected for the effects of background scattering, slit-length collimation, and photoelectric absorption by the sample [11, 22].

RESULTS AND DISCUSSION

Pyrolysis

The elemental compositions of the two grain kernels are compared in **Table 1**; they are similar in that their contents of ash, i.e., mineral matter, are low. **Table 2** lists the terminal yields of the charcoals obtained from the single-stage pyrolysis of the grain kernels at various temperatures. The yield for HRW is always higher than that for corn at each temperature of carbonization. This may be attributable to a higher weight ratio of the hull to the kernel in HRW than in corn.

The yields of charcoals obtained from the single-stage process and the corresponding two-stage process are compared in **Table 3.** It is evident that the yield of each species obtained from the former is lower than that from the latter, particularly for HRW. Note that the temperature of pyrolysis for the first stage of the two-stage process has been optimized to maximize the surface areas of the resultant charcoals as determined by the BET method. This optimum temperature is approximately 270 ° C.

The surface areas of charcoals obtained from the two kernels by both processes are displayed in **Table 4** for various temperatures of carbonization. The table indicates that the surface areas increase sharply at temperatures ranging between 650° C and 700° C. This increase corresponds to the complete breakdown of the initial cellulosic skeleton of the grains and the formation of a three-dimensional network composed of subunits known as elementary crystallites [20]. A distinct reduction in the surface areas, however, is observable when the temperature of pyrolysis exceeds 750° C; this is attributable to the effects similar to those involved in graphitization [20]. Also note that the surface area of the HRW charcoal by the two-stage process is nearly twice as high as that by the corresponding single-stage process, while that of the corn charcoal is not affected as much. Further work is anticipated to facilitate the rationalization of this observation.

The experimentally obtained adsorption isotherms are shown in **Figure 2** for the charcoals generated by both processes at different temperatures of carbonization. The isotherms are clearly of Type I [21], typical of microporous materials. The enhancement of the microporous nature of the HRW charcoal from the single-stage process with an increase in the temperature of carbonization from 700 to 750° C is evident. Furthermore, the volumes adsorbed by the charcoals produced by the two-stage process are considerably higher than those by the corresponding single-stage process at all relative pressures. Note, however, that these volumes have been determined under conditions of pseudo-equilibrium. The drawbacks of nitrogen adsorption to characterize microporous solids are well known [3, 21]; nevertheless, the volumes adsorbed by the charcoals at a given relative pressure can be compared with one another, since the duration of adsorption in each case is identical and sufficiently long.

Physical Activation

The BET surface areas of activated carbons obtained from the physical activation of the two charcoals generated by both processes, are presented in **Table 5** for various degrees of burn-off. The maximum value attained for the surface area is 1750 m^2/ g, corresponding to a HRW activated carbon with a burn-off of approximately 60%, as shown in the table. This carbon has been obtained from the HRW charcoal generated by the two-stage process at 700° C. The total micropore volume, W_0, estimated from the D-R equation [19] for each activated carbon is also listed in **Table 5**. The general trend exhibited by the surface areas and W_0's of most commercial activated carbons with an increase in the degree of burn-off [3] is clearly discernable. However, the maximum surface area of activated carbons produced from corn charcoals generated by both processes does not exceed 700 m^2 /g. The limiting factor in enhancing the development of their surface areas is the low density and hardness of the feedstock. The loss of strength and hardness experienced by the corn charcoals is appreciable, especially when the degree of burn-off exceeds 30%. Consequently, there is a constraint for developing the microporous nature of these activated carbons.

The nitrogen adsorption isotherms of the aforementioned activated carbons of HRW are shown in **Figure 3**; similar isotherms have been obtained for those of corn and hence, have not been illustrated. Note that the volumes adsorbed near the vicinity of the "knee" of the isotherm are considerably higher than those for the corresponding charcoals shown in **Figure 2**. This effect is expected as the purpose of physical activation is to remove tarry deposits generated by the carbonization process from the entrances of narrow pores as well as to widen existing pores, thereby increasing the accessibility of the finer pores to molecules of adsorbate. Consequently, an appreciably larger internal surface area is "seen" by nitrogen in these activated carbons.

Small-Angle X-ray Scattering

The corrected scattering curve for a HRW charcoal generated by the single-stage process at 700° C is depicted in **Figure 4**. The charcoal sample has been chosen to illustrate its unique scattering behavior. Note

that the intensities are expressed in dimensionless units, i.e., relative to an arbitrary system of measurement in terms of counts per second. Thus, the plot involves the relative rather than the absolute intensity since the latter requires determining the cross-sectional areas of the scattering medium, a task not done in the present work.

A prominent power-law regime is discernable in **Figure 4** over an interval spanning nearly three orders of magnitude in values of q ranging from 3.7×10^{-4} Å^{-1} to 9.3×10^{-2} Å^{-1}. This large range in q or equivalently, nine orders of magnitude in I(q), is unprecedented and rarely encountered in SAXS analysis. To date, the only other material that has exhibited a similar scattering behavior over a comparable range in either q or I(q) is Beulah lignite coal [8, 16]. This type of scattering is yet to be fully understood; it is plausible that the average size of the macropores in this charcoal is so large that it satisfies the condition, qd being far greater than 1.0, even near the smallest values of q resolvable by experiment [8]. Accordingly, the minimum value of d for this sample is 2500 Å.

In the outer part of the curve, the intensity is observed to decay much more slowly relative to the power-law region. This slowly-decaying outer part is ascribed to the scattering from the micropores [22, 23]. Hence, the porous structure of the HRW charcoal can be characterized by two different length scales corresponding to the macropores and micropores. Therefore, the total intensity scattered can be considered to be the sum of the intensities from the two types of pores provided that they scatter independent of each other.

Surface Fractal Dimension from SAXS

The exponent, α, in Eq. 3 has been recovered from weighted, first-order least-square fit of the data [24], over the range of q shown in **Figure 4**. This procedure assigned a weight to every data point of the corrected intensity that is inversely proportional to the square of the calculated statistical uncertainty in the value of the corrected intensity [10]. The value of α thus obtained for the HRW charcoal is 3.55 ± 0.10, over the interval, 3.7×10^{-4} Å^{-1} $< q < 9.3 \times 10^{-2}$ Å^{-1}. The non-integral value of α implies that the interfaces of the pores of the charcoal, producing the scattering in this range of q, can be considered to exhibit fractal properties, or alternatively, the power-law distribution of these pores can be associated with a non-integral dimension [14, 23]. Consequently, the d_{SF} for this sample evaluated on the basis of Eq. 3 is 2.45 ± 0.10.

The length scales, ξ's, corresponding to the power-law regime can be estimated from the approximate Bragg relation, $\xi = \pi / q$ [25]; hence, the property of geometrical self-similarity is satisfied over yardsticks ranging from approximately 35 Å to 8500 Å. From this size range, it is evident that the interfaces of the macropores as well as those of the mesopores of the HRW charcoal are surface fractals [9]. This fact is yet to be verified by other techniques such as scanning electron microscopy and atomic force microscopy. Nonetheless, marked increases are expected in the values of d_{SF}'s for the grains upon carbonization [10]; the degradation and subsequent rearrangement of the carbon skeleton combined with the violent release of the volatile matter are likely to generate rough interfacial surfaces. Considering the unusually large span of the length scales associated with the self-similar behavior of the pores, however, the results of the present investigation should be interpreted with discretion until it is fully corroborated by evidence from independent techniques. We are in the process of analyzing the SAXS behavior of other charcoals and activated carbons obtained from the grains under different process conditions. It is desirable to compare and contrast the scattering behavior of these charcoals and activated carbons and interpret the results based on similarities / differences expected in their pore structure.

Mean Radii of Gyration

The mean radii of gyration, R_g, of the micropores of the HRW charcoal has been obtained by applying the Guinier equation, Eq. 1, to the outer portion of the curve shown in **Figure 4**. Note that this equation is valid only when the product, qR_g, is not appreciably greater than 1.0. Furthermore, the scattering system must be composed of randomly oriented, independent scatterers [11]. The R_g thus obtained for the HRW charcoal is approximately 6.7 Å. The intricacies involved in the procedure for computing R_g from the Guinier plot have been expounded elsewhere [10]. This value of R_g or equivalently, the average pore size d, compares favorably with the characteristic average dimension of the micropores, B, computed from the D-R equation [19]. Hence, the analysis has revealed that the results from SAXS are consistent with those obtained from adsorption data.

SUMMARY

Whole grain kernels of HRW and corn are potentially viable feedstocks for producing activated carbons with high surface areas. These activated carbons have been obtained by the physical activation of charcoals generated by a single-stage as well as a two-stage pyrolytic process at 850° C in an atmosphere of CO_2. For both kernels, the terminal yield of charcoals and the surface areas of the corresponding activated carbons obtained by the two-stage process at various temperatures of carbonization are appreciably higher than those by the single-stage process. Moreover, the surface areas and the total micropore volumes of the HRW activated carbons, produced from charcoals generated by the two-stage process at an optimum temperature of 700° C, are comparable to those of commercial carbons. The investigation has also shown that whole grains of HRW are preferable to those of corn, on account of the superior textural characteristics of the resulting charcoals and their greater resistance to abrasion during the activation process. The SAXS analysis has revealed the fractal nature of the interfaces of pores over unexpectedly large length scales in a HRW charcoal chosen for illustration as a representative surface fractal system. In addition, the SAXS analysis has confirmed the existence of two independently scattering entities of vastly different dimensions in this sample. These results obtained from the pyrolysis of a naturally occurring product may prove to be beneficial for investigating the influences of fractal surfaces on the rates of heterogeneous gas-solid reactions.

ACKNOWLEDGEMENT

The authors are grateful to Dr. Paul Schmidt for his assistance in obtaining the X-ray scattering data. This is contribution #90-323-J, Department of Chemical Engineering, Kansas Agricultural Experiment Station, Kansas State University, Manhattan, KS 66506.

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Table 1. Elemental Analysis of Grains

Element	Corn (%)	HRW (%)
Carbon	46.4	45.3
Hydrogen	7.2	6.6
Oxygen	43.1	45.1
Nitrogen	0.1	0.1
Ash	1.5	1.6

Table 2. Effect of Temperature on Charcoal Yields from the Single-Stage Process

Temperature (°C)	Corn (%)	HRW (%)
270	44.2	47.6
350	32.9	34.3
450	18.2	20.8
650	13.7	17.7
700	12.2	15.6
750	10.4	13.5

Table 3. Comparison of Charcoal Yields from the Single-Stage and Two-Stage Processes

Temperature (°C)	Corn (%)		HRW (%)	
	Single-Stage	Two-Stage$^{\delta}$	Single-Stage	Two-Stage$^{\delta}$
650	13.7	18.5	18.3	24.9
700	12.2	17.2	15.6	22.7
750	10.4	14.8	13.5	20.3

δ : Temperature of the first stage was 270° C

Table 4. BET Surface Areas of Charcoals

Temp. (°C)	Corn (m^2/g)	HRW (m^2/g)
575$^{\alpha}$	15	13
650$^{\alpha}$	37	57
700$^{\alpha}$	72	110
750$^{\alpha}$	70	84
800$^{\alpha}$	16	14
850$^{\alpha}$	5	8
700$^{\beta}$	109	200
850$^{\beta}$	24	25

α : Single - stage process
β : Two-stage process

Table 5. Textural Characteristics of Activated Carbons$^{\delta}$

Burn-off (%)	Temp. of Pyrolysis	Corn		HRW	
		BET(m^2/g)	W_0 (cm^3/g)	BET(m^2/g)	W_0 (cm^3/g)
10	700° C$^{\beta}$	325	0.10	190	0.03
20	700° C$^{\beta}$	390	0.12	434	0.11
30	700° C$^{\beta}$	525	0.19	600	0.23
50	700° C$^{\beta}$	695$^{\tau}$	0.24	1350	0.51
60	700° C$^{\beta}$	—	—	1750	0.68
20	700° C$^{\alpha}$	303	0.08	333	0.07
30	700° C$^{\alpha}$	407	0.14	435	0.10
20	300° C$^{\alpha}$	375	0.11	405	0.10
30	300° C$^{\alpha}$	500	0.18	564	0.19

α : Single-stage process
β : Two-stage process
δ : Activation at 850°C with CO_2
τ : Condition of carbon was fragile

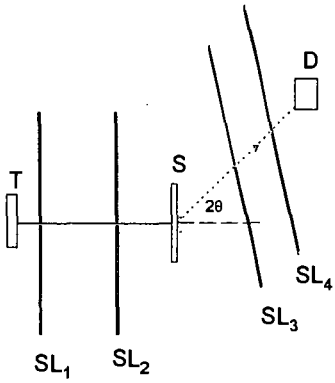

Figure 1. Schematic representation of a SAXS system: T is the X-ray tube; SL_1, SL_2, SL_3, and SL_4, the collimating slits; S the sample holder; and D the detector.

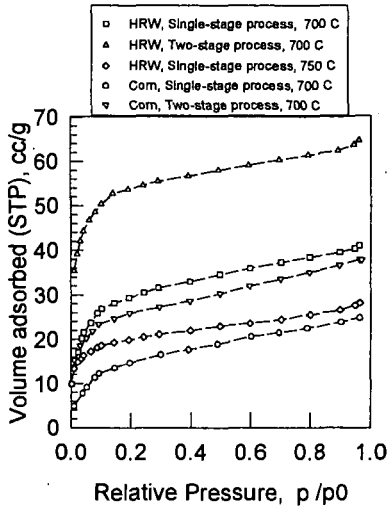

Figure 2. Adsorption isotherms for the charcoals obtained by both single-stage and two-stage processes at various temperatures.

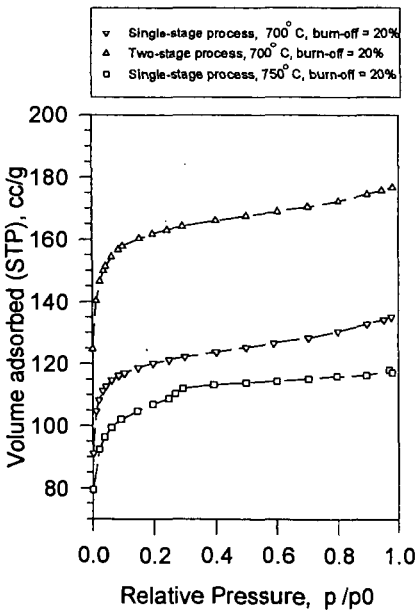

Figure 3. Adsorption isotherms of HRW activated carbons obtained from charcoals generated ted by both single-stage and two-stage processes at various temperatures.

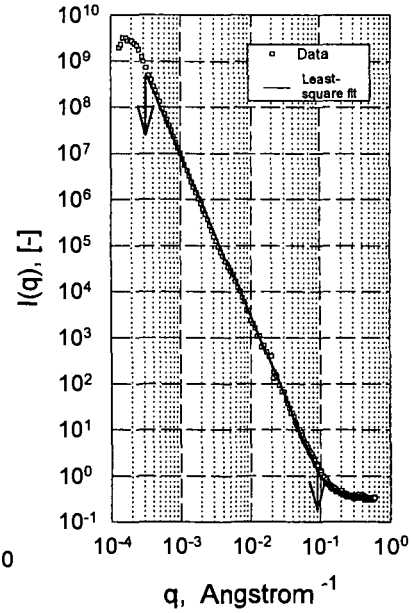

Figure 4. Relative scattered intensity versus the scattering wave vector for a charcoal of hard red winter wheat pyrolyzed at 700 C.