Effect of bead milling on chemical and physical characteristics of activated carbons pulverized to superfine sizes

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Abstract

Superfine powdered activated carbon (S-PAC) is an adsorbent material with particle size between roughly 0.1 to 1 μm . This is about an order of magnitude smaller than conventional powdered activated carbon (PAC), typically 10 to 50 μm . S-PAC has been shown to outperform PAC for adsorption of various drinking water contaminants. However, variation in S-PAC production methods and limited material characterization in prior studies lead to questions of how S-PAC characteristics deviate from that of its parent PAC. In this study, a wet mill filled with 0.3–0.5 mm yttrium-stabilized zirconium oxide grinding beads was used to produce S-PAC from seven commercially available activated carbons of various source materials, including two coal types, coconut shell, and wood. Particle sizes were varied by changing the milling time, keeping mill power, batch volume, and recirculation rate constant. As expected, mean particle size decreased with longer milling. A lignite coal-based carbon had the smallest mean particle diameter at 169 nm, while the wood-based carbon had the largest at 440 nm. The wood and coconut-shell based carbons had the highest resistance to milling. Specific surface area and pore volume distributions were generally unchanged with increased milling time. Changes in the point of zero charge (pH_{PZC}) and oxygen content of the milled carbons were found to correlate with an increasing specific external surface area. However, the isoelectric point (pH_{IEP}), which measures only external surfaces, was unchanged with milling and also much lower in value than pH_{PZC} . It is likely that the outer surface is easily oxidized while internal surfaces remain largely unchanged, which results in a lower average pH as measured by pH_{PZC} .

Keywords: activated carbon, pulverization, oxidation, pH shift, surface area, pore distribution

1. Introduction

Activated carbon adsorption is a best available technology for the removal of small molecular weight organic contaminants from water (Clark and Lykins, 1990; Crittenden et al., 2005a; Osantowski and Wullschleger, 1986). Powdered activated carbon (PAC) is a common form of activated carbon, produced by grinding larger granular activated carbon particles (GAC) (Neely and Isacoff, 1982; Snoeyink and Chen, 1985). PAC is defined as particles passing through an 80-mesh sieve (177 μm) (ASTM Standard D5158-98, 2013) but typical particle sizes are between 10 and 50 μm . A recent development in activated carbon technology is to further reduce the size of PAC. Superfine powdered activated carbon (S-PAC) is activated carbon that has been reduced to sizes near or less than one micrometer.

S-PAC can improve adsorption kinetics for small molecules and circumvents competition with larger molecules, such as natural organic matter (NOM) (Ellerie et al., 2013; Heijman et al., 2009a; Matsui et al., 2013, 2009). The mechanism for faster adsorption lies in shortened diffusion-limited adsorption pathways, which allows faster transport to terminal adsorption sites for small molecules (Ando et al., 2010; Ellerie et al., 2013; Matsui et al., 2008; Pelekani and Snoeyink, 2000). Terminal sites for small molecules lie in micropores where sorption occurs due to increased sorption strength for pore diameters less than twice an adsorbate diameter (Li et al., 2002). Conversely, adsorption of large molecules is only governed by external surface area and not by the characteristics of inner pores. In the shortened pathways of S-PAC, the time of transport for small molecules is decreased, but the rate of large molecule adsorption to outer surfaces and pores remains the same. The increase in the rate of large molecule adsorption due to increased specific external surface area is much less than the increase in small molecule

adsorption due to the shortened diffusion pathway. As a result, particle size is the main driving force behind improved kinetics. However, changes in other physical and chemical properties can also impact adsorption performance. For example, it is possible for pulverization to shift the distribution of pore sizes by exposing smaller diameter pores, effectively becoming larger diameter pores (Dunn and Knappe, 2013; Ellerie et al., 2013; Matsui et al., 2014). An in-depth examination of carbon characteristics on adsorption performance revealed that carbon properties, namely hydrophilicity in the form of oxygen content, had strong impacts on the penetration of depth of adsorbates (Matsui et al., 2015).

Since S-PAC is not commercially available, there is no standard production method. Individual groups have produced their own materials or outsourced their production on a case-by-case basis, so material production parameters may vary widely. These parameters have been rarely reported as there is no available guidance regarding parameters to be controlled and recorded. S-PAC researchers describe production through wet milling using phrases such as wet grinding in a bead mill, pulverization in a ball mill, wet mill micro-grinding and micro-grinding in a wet bead mill (Ando et al., 2010; Ellerie et al., 2013; Heijman et al., 2009a; Matsui et al., 2007). Wet milling generally encompasses high velocity contact between grinding media and the product material—activated carbon in this case—while suspended in a carrier fluid. Grinding media can be made from a variety of materials and in a variety of sizes; none of the previous studies specifically describe the grinding media used. Additionally, the carrier fluid and additives such as surfactants are not described, though many are available for enhancing grinding performance. The specific outcome of grinding depends on these factors since it is the result of energy transfer from the rotation of the mill through the grinding media and the carrier fluid.

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73 Among carbons, differences in abrasion resistance, also termed hardness, affect the rate of
74 particle breakdown. Abrasion is a surrogate measure of hardness since harder carbons have a
75 reduced tendency to degrade upon impact than softer carbons (Toles et al., 2000; Yalcin and
76 Arol, 2002). Activated carbons are relatively soft; commercial coal and wood based carbons
77 were found to have a Mohs hardness between 2 and 3 on the 1–10 Mohs hardness scale (Patni et
78 al., 2008). Carbon hardness depends on the carbon precursor. Coconut shell and other nut shells
79 are very hard precursors (Heschel and Klose, 1995; Mohd Din et al., 2009). Of coal carbons,
80 bituminous coal-based carbons are harder than lignite-based carbons (Greenbank and Spotts,
81 1993). Wood-based carbons have a much wider range of hardness, from softer than lignite coal-
82 based carbons to as hard as coconut-shell based carbons, depending on the type of wood
83 (Hernández et al., 2014).

84

85 Wet milling is designed to physically alter the carbon but may also cause chemical changes,
86 which is important for activated carbon applications since chemical characteristics play large
87 roles in adsorption processes (Karanfil and Kilduff, 1999; Karanfil et al., 1999; Li et al., 2002;
88 Quinlivan et al., 2005). Surface functional groups affect the type of molecules that are
89 preferentially adsorbed (Apul et al., 2015; Karanfil and Kilduff, 1999; Pendleton et al., 1997).
90 Carbon modification has been explored for enhanced or targeted contaminant removal (Akmil
91 Başar et al., 2003; Dastgheib et al., 2004; Liu et al., 2009). For example, oxidation of carbon
92 results in increased adsorption of metal cations but decreased adsorption of low molecular
93 weight organic compounds (Biniak et al., 1999; Jia and Thomas, 2000; Karanfil and Kilduff,
94 1999; Tessmer et al., 1997). Activated carbon typically has oxygen content around 3–4% by

mass; those modified to increase oxygen-containing functional groups can have contents around 10% (Apul et al., 2013; Li et al., 2002).

Due to the small sample size of S-PACs in previous studies combined with limited characterization data, trends in material changes as a result of PAC size reduction cannot be determined. Most recently, Matsui et al. (2015) measured a large number of parameters regarding milled carbons; however, the study measured properties of only one particle size and did not examine changes as a result of milling. Hence, the main objective of this study was to systematically examine a number of carbon types under varying degrees of milling in order to elucidate specific effects of wet milling on the chemical and physical characteristics of activated carbons.

2. Materials and Methods

2.1 Activated Carbon

Activated carbon materials were obtained from several commercial sources and chosen to cover a range of characteristics. Seven commercial carbons were used with variation in specific surface area, pore volume, and pH_{PZC} : Watercarb-800 (bituminous coal, Standard Purification), Filtrasorb 400 (bituminous coal, Calgon), PAC 20 B (bituminous coal, Norit), Hydrodarco 3000 (lignite coal, Norit), Hydrodarco B (lignite coal, Norit), Aqua Nuchar (wood, Mead Westvaco), and Aquacarb 1230C (coconut shell, Siemens). The carbons are labeled as BC1, BC2, BC3, LC1, LC2, WD, and CS, respectively (Table 1). BC1, BC3, LC2, and WD were received as PAC, and they were sufficiently small to pass the 200 μm mesh screen within the bead mill. LC1, BC2, and

CS were received as GAC, and they were processed using a coffee grinder and sieved through a #100 screen (150 μm openings) to isolate the smaller particles for milling.

Table 1: Measured characteristics of parent PAC materials: specific surface area, total pore volume, and point of zero charge (pH_{PZC}). Seven PACs were milled including coal, wood, and coconut shell based materials.

Origin Material	Label	Product Name	PAC Size (μm)	Specific Surface Area (m^2/g)	Specific Pore Volume (cm^3/g)	pH_{PZC}
Bituminous Coal	BC1	Watercarb-800	12.3	644	0.35	10.37
Bituminous Coal	BC2	Filtrisorb 400	11.3	1038	0.67	8.65
Bituminous Coal	BC3	PAC 20 B	13.6	880	0.48	9.79
Wood	WD	Aqua Nuchar	11.3	1676	0.89	6.20
Coconut Shell	CS	Aquacarb 1230C	11.3	1027	0.72	10.79
Lignite Coal	LC1	Hydrosorb 3000	12.8	660	0.61	5.39
Lignite Coal	LC2	Hydrosorb B	13.5	505	0.39	11.40

2.2 Bead Mill

PAC was pulverized to S-PAC using a bead mill (MiniCer, Netzsch Premier Technologies, Exton, PA, USA) containing 0.3–0.5 mm yttrium-stabilized zirconium oxide ceramic beads. The mill was operated at 85% loading capacity; 120 mL of beads were measured with a graduated cylinder and added to the 140 mL mill. Thus, the design mill void was 20 mL, but the total mill void was 50 mL after accounting for void space when measuring the beads. The 120 mL loading volume corresponds to approximately 2 million beads. PAC was added to the mill as a slurry comprised of 24 grams of dry carbon in 300 mL of distilled and deionized water (DDI) with 18

MΩ resistivity, yielding a percent solids concentration of approximately 6–7%. The slurry was kept chilled at 10 °C during milling.

It is common in milling applications to use a dispersant to aid the milling process. Without dispersants the breakup of particles results in an increase in solution viscosity; dispersants help maintain fluidity and decrease pumping energy. One dispersant type (Reax, Mead Westvaco) was tested to evaluate its effects on carbon milling; however, all of the samples used for further characterization were milled with no dispersant addition.

All S-PAC samples were produced using the same flow rate, mill loading, and mill rotational speed; thus, the rate of energy transfer to the carbon particles was kept constant through all tests. Total energy applied was varied by changing the total milling time, which varied from one pass through the mill to six hours. In the one-pass scenario carbon was fed into the mill and then collected as product in the output. This was repeated once more for the two-pass scenario. Each pass took approximately 45 seconds. In all other millings, the carbon slurry was recirculated through the system by connecting the output line back to the feed tank.

2.3 Characterization Methods

Milled and unmilled carbons were analyzed for physical and chemical parameters. Elemental analysis, measuring weight percent compositions of carbon, oxygen, hydrogen, and nitrogen, was performed using a Flash Elemental Analyzer 1112 series (Thermo Electron Corporation). Sizes for particles less than 6 μm in diameter were measured using dynamic light scattering (DLS) with a Zetasizer NanoZS (Malvern, Worcestershire, UK). Readings were taken in distilled water after bath sonication and Z-avg hydrodynamic diameters are reported. Particles larger than 6 μm

were measured by optical microscopy imaging using a Zeiss Axioskop 2 Plus optical microscope with a Zeiss AxioCam MRc5 camera attachment running AxioVision AC version 4.2 software. Particles were sonicated in DDI before imaging and Zeiss Immersionsol 518C immersion oil was used to view the particles at 40x magnification. The images were processed using ImageJ software to determine the average Feret diameter of the particles and the particle size distribution. Particles were also visually observed with scanning electron microscopy (SEM, Hitachi SU6600) after sputter coating with platinum for 3-minutes.

Nitrogen gas adsorption was performed at 77 K with an ASAP 2020 analyzer (Micromeritics Instrument Corp. U.S.) and pore size distributions were determined using density functional theory (DFT) and calculated surface area from the Brunauer-Emmett-Teller (BET) equation. The DFT model allows for categorization of pore volumes into micropore (< 2 nm), mesopore (2–50 nm), and macropore (> 50 nm) fractions.

pH_{PZC} in the bulk material was measured by a pH drift method where the point of zero charge is defined as the pH where no drift occurs after 48 hours (Dastgheib et al., 2004; Lopez-Ramon et al., 1999). For each pH point and carbon, 100 mg of dry carbon were added to 20 mL of pH adjusted 0.1 M NaCl in a CO₂-free atmosphere in a glove box. After a minimum of 48 hours on a shaker table, pH was measured in each vial and compared to a no carbon blank. The isoelectric point (pH_{IEP}) of the carbon was determined by measuring the zeta potential of S-PACs using the Zetasizer NanoZS (Malvern, Worcestershire, UK) and observing the pH that produced a zeta potential reading of zero. Samples were prepared by probe sonication in DDI and manually titrated for pH adjustment.

3. Results and Discussion

3.1 *Milling*

Each pass through the mill corresponded with approximately 5 seconds of contact time through the 50 mL mill void. Thus, a milling time of 30 minutes corresponded to approximately 40 passes through the mill and a total milling time of 200 seconds, based on average residence time. However, due to short circuiting and dead zones within the mill feed tank, the true number of passes was likely higher for some particles and lower for others. Additionally, viscosity increased at different rates for each carbon, so the number of passes made by one carbon may differ slightly from the number made by a different carbon due to a changing flow rate. DDI was added as needed during milling to decrease viscosity and allow for complete mixing.

To examine the effect of dispersant on milling, WD was milled with varying dispersant concentrations. Dispersant mitigated viscosity increase, reducing the need to add DDI, and did not affect the particle size reduction. Notably, the coconut shell-based carbon, CS, did not noticeably increase in viscosity though no dispersant was added. As mentioned previously, none of the samples milled with dispersants were used for further characterization in this study.

3.2 *Carbon Particle Size*

PAC particle sizes were very similar among carbons, with median sizes ranging from 11 to 14 μm (Table 1). Milling times as brief as one pass through the mill resulted in particle sizes near or below one micrometer and subsequent milling further reduced median particle sizes but with diminishing returns (Figure 1). Due to the different analytical measurements for determining

particle size above and below 6 micrometers—DLS for smaller particles and visible-light microscope image analysis for larger ones—comparison of S-PAC size with parent PAC is indirect. The hydrodynamic diameter measurements from DLS are found using models that assume spherical shape. The spherical assumption is supported by SEM images, especially for particles milled for longer times, but particles milled for shorter times have more angularity. SEM also qualitatively supports Z-avg particle size measurements with observable declines in particle size as milling time increases. Images of PAC and all S-PACs from BC1 taken by SEM at 10,000 times magnification reveal the range of particle sizes from large PAC and 1 pass particles to small particles after 6 hrs that have a tendency to aggregate (Figure 2). The smallest particles—after 1 hr, 2 hrs, and 6 hrs—were also imaged at 20,000 times magnification where individual particles are more clearly identifiable (Figure S1).

The longest milling times resulted in the smallest particle sizes for each carbon. Most carbons reduced to median particle sizes of 200–400 nm; the largest size was 440 nm for WD after 6 hours of milling and the smallest was LC2 at 170 nm after 4 hours of milling (Figure 1). In addition to producing the smallest S-PAC, LC2 also had the largest reduction in size in the shortest time; particles had a median size of 342 nm after 5 minutes and 270 nm after 20 minutes. The second lignite-based carbon, LC1, also exhibited relatively fast size reduction resulting in a median size of 390 nm after 15 minutes; however, it did not continue decreasing in size with further milling, with a size of 324 nm after 6 hours. WD, BC2, and CS had little particle breakdown under short milling times, with median sizes above 700 nm and up to 1000 nm in the case of WD after one pass through the mill.

Overall, CS and WD were the slowest to decrease in size during milling, as seen by a low slope in its concentration over milling time (Figure 3). Concentration was calculated from number-based particle size distributions measured in triplicate and conservation of mass; particle volumes calculated from the distribution bins were divided into the total initial mass to arrive at a total particle number. LC2 had the fastest breakdown (i.e. the fastest increase in particle concentration), followed by BC3, while BC1, BC2, and LC1 had similar rates. Rates of breakdown are interpreted as ease of milling—faster breakdown rates correspond to softer carbons that are more easily milled.

The particle size results indicate that the same milling energy has different effects for different carbons. The three bituminous coals exhibited similar milling responses. The lignite coals acted similarly at first, but one continued to decrease in particle size while the other leveled off. Both WD and CS remained as large particles after initial milling, though CS responded to continued milling while WD did not. Thus, the rates of particle breakdown as well as the minimum achievable particle size were highly specific to each carbon and generalizations based on material are difficult to draw.

3.3 Carbon Chemical Properties

The majority of PACs had a basic pH_{PZC} , though WD was neutral and LC1 had an acidic pH_{PZC} . As milling time increased, the pH_{PZC} of all carbons decreased and the oxygen content of all carbons increased (Table 2). (Carbon, hydrogen, and nitrogen were also measured, though no clear trends with milling time were noticed [Table S1]). LC1 and LC2 had the least observed pH_{PZC} change, shifting down about half a pH point, while the other carbons dropped

approximately two pH points over the longest milling times. BC1, BC2, and BC3 had similar PAC oxygen content around 2%, and increased to 4.87%, 6.45%, and 7.86%, respectively. WD had the highest initial oxygen content, 7.14%, as well as the highest final oxygen content, 10.50%. CS experienced the smallest increase in oxygen content from 3.38% to 5.38%. pH_{PZC} values were inversely correlated with oxygen content (Figure S2). CS, BC2, and BC3 correlated with an R^2 above 0.95 while WD and BC1 had R^2 values of 0.90 and 0.83, respectively. A decrease in pH_{PZC} and an increase in oxygen content as a result of milling have been reported previously (Dunn and Knappe, 2013). The data shown here for several milling times provide convincing evidence that these changes are directly caused by milling.

pH_{IEP} values could be expected to decrease as did the pH_{PZC} values. Interestingly, pH_{IEP} did not change appreciably with milling time; some variability was observed as milling progressed, but overall trends were nearly flat. As such, pH_{IEP} did not correlate with oxygen increases. Additionally, the values were notably lower than pH_{PZC} values, ranging from approximately 2.4 to 4.2 for the S-PAC of four carbons. The pH_{IEP} of PAC could not be measured using the electrophoretic mobility technique since the PAC particles settled too quickly; it is unknown whether the pH_{IEP} changed during the initial pass of PAC through the mill.

Table 2: Surface charge properties measured by point of zero charge, isoelectric point, and percent oxygen content. The difference between pH_{PZC} and pH_{IEP} is shown as ΔpH . Carbons are distinguished by material and milling time. Dashed lines indicate that measurements were not taken.

Carbon	pH_{PZC}	pH_{IEP}	ΔpH	Oxygen Content (w/w%)	Carbon	pH_{PZC}	pH_{IEP}	ΔpH	Oxygen Content (w/w%)
BC1					WD				
PAC	10.37	--	--	2.41	PAC	6.20	--	--	7.14
1 pass	9.31	3.27	6.04	2.79	1 pass	6.25	2.48	3.77	7.25

15 min	9.09	2.92	6.17	3.51	5 min	6.03	2.78	3.25	7.80
30 min	8.92	2.71	6.21	4.19	10 min	5.72	2.87	2.85	7.85
1 hr	8.07	2.57	5.50	5.23	20 min	5.82	3.06	2.76	8.30
2 hrs	8.10	4.17	3.93	5.87	1 hr	5.11	2.67	2.44	9.15
6 hrs	7.75	2.64	5.11	7.86	6 hrs	4.95	2.84	2.11	10.50
BC2					CS				
PAC	8.65	--	--	2.29	PAC	10.79	--	--	3.38
1 pass	8.62	3.32	5.30	2.34	1 pass	10.73	2.39	8.34	3.71
15 min	8.65	3.85	4.80	2.82	2 pass	10.44	2.86	7.58	3.84
30 min	8.25	3.91	4.34	3.28	5 min	10.57	3.15	7.42	3.91
1 hr	6.78	3.86	2.92	3.95	10 min	10.47	3.09	7.38	3.99
2 hrs	6.7	3.71	2.99	5.29	20 min	10.33	2.75	7.58	4.06
4 hrs	6.42	3.87	2.55	5.34	4 hrs	8.00	3.39	4.61	5.38
6.33 hrs	5.74	4.36	1.38	6.45	LC1				
BC3					PAC	5.39	--	--	3.42
PAC	9.79	--	--	1.6	15 min	5.52	--	--	--
1 pass	9.37	--	--	2.23	30 min	5.55	--	--	--
5 min	9.00	--	--	2.44	6 hrs	4.85	--	--	6.76
10 min	8.72	--	--	2.94	LC2				
20 min	8.50	--	--	3.44	PAC	11.58	--	--	5.52
2 hrs	7.38	--	--	4.85	1 pass	9.55	--	--	--
4 hrs	7.05	--	--	4.87	5 min	9.39	--	--	--
					10 min	9.28	--	--	--
					20 min	9.22	--	--	--
					4 hrs	9.01	--	--	9.49

The difference in pH_{PZC} and pH_{IEP} is a result of the qualities measured by each technique. The pH drift method for pH_{PZC} utilized in this study used a 48 hour equilibration time, thus allowing for complete diffusion of solutes into and out of carbon pores. The pH_{PZC} is thus a measure of acidity throughout the carbon material. pH_{IEP} measurements are based on electrophoretic movement which is affected only by charges on the outer surface of the carbon; charged functional groups within the pores should have little or no effect on pH_{IEP} . There are two possible mechanisms for a decreasing pH_{PZC} and unchanging pH_{IEP} : either chemical changes are only occurring at internal sites, which are measured by pH_{PZC} but not pH_{IEP} , or chemical changes are happening rapidly at external sites, wherein all S-PAC have the same external condition and the average pH value decreases as particle size decreases and total external surface area increases. The second scenario is consistent with previous work in activated carbon where it has

been reported that incomplete oxidation results in preferential oxidation on the external surface, and can be indicated by measuring both pH_{IEP} and pH_{PZC} (Menendez et al., 1995). The low and unchanging pH_{IEP} values imply that there are similar external surface charge densities of an acidic nature on all S-PAC, regardless of milling time. Correlation between pH shifts and specific external surface area, calculated from particle size measurements, reveal that the second mechanism is more likely; the difference between pH_{PZC} and pH_{IEP} is used as the correlating pH factor here and is termed ΔpH (Figure 4). WD, CS, and BC2 had R^2 values above 0.90 while BC1 had a poor correlation due to an outlier point. Oxygen increases also correlated strongly with specific external surface area, which is consistent with the idea that oxidation is happening primarily on the external surfaces (Figure 5). The concept of an easily oxidized surface, once exposed to the abrasive milling environment, is sketched in Figure 6 and shows (a) the initial surface oxygen groups (b) the breakup of particles to create new external surface area, and (c) the subsequent oxidation of those new surfaces.

Manifestation of oxygen on the outer surfaces occurs in multiple ways, such as through the formation of organic surface functional groups, or through inorganic oxidation. The variety of oxygen-containing surface functional groups that can occur at graphite edges in activated carbon have been documented (Biniak et al., 2007; Boehm, 1994). Based on the approximate mass of oxygen attached to S-PAC as a result of milling—2–5% by weight, or 0.13–0.31 mmol of oxygen per gram of carbon—the external surface concentration of oxygen-containing functional groups is on the order of 0.02 mmol/m². In order to evaluate the possibility that some of the oxidation was inorganic, we compared ash content to oxidation. Ash content did not change appreciably as PAC was milled to S-PAC (Figure S3). Percent oxygen increase between PAC

and S-PAC correlated well with total ash content, and even better when only considering potentially reactive elements: Ca, Mg, Zn, Cu, Mn, Fe, and Al (Figure S4). The high correlation is likely the result of thorough surface oxidation on elements evenly distributed throughout the carbon matrix, however, its contribution is limited: for a concentration of divalent elements of approximately 10 mmol per gram of carbon, it is likely that only 1% of those elements would be accessible on external surfaces for oxidation, or 0.01 mmol/m².

3.4 Carbon Physical Properties

Total pore volume and distributions of volume to micropores, mesopores, and macropores shifted slightly as a result of milling (Table 3). BC1, BC2, BC3 and CS increased in the mesoporous fraction. BC2 increased in its macroporous fraction as well. WD had a decreased mesoporous fraction and an increased macroporous fraction. Primary and sub- microporous fractions—pores with diameters less than 1 nm (10 angstroms) and from 1 nm to 2 nm, respectively— were also examined due to their importance in adsorption of small molecules; however, there was little difference observed with respect to increased milling time (Stoeckli et al., 1993). Changes to pore volumes were not a distinct function of milling time, though it is reasonable that shifts in pore volume distributions following milling will trend towards increases in meso- and macroporous fractions as internal pores are opened. Most notable is the development of a mesoporous fraction in the longest milled S-PAC of CS where previously there was none. Typically—and CS PAC was no exception—coconut-shell based activated carbons are microporous upon activation (Crittenden et al., 2005b). Thus, despite a lack of direct correlation between milling and pore distribution changes to the carbons, changes were observed that may still have an impact on adsorption performance.

Surface areas were also generally unchanged, with the exception of WD, which decreased from over 1500 m²/g to 1000 m²/g. It is likely that WD had thinner pore walls than other carbons, as indicated by a high specific surface area, and thus had channels that were easily crushed during milling. In practice it may be possible to avoid crushing pore channels by optimizing milling conditions, including reduction of milling time, operation at lower mill power, or processing at a lower percent solids content.

Table 3: Surface area and pore volume measurements for seven activated carbons.

Carbon	Specific Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Macropore Volume (cm ³ /g)	Mesopore Volume (cm ³ /g)	Sub-micropore Volume (cm ³ /g)	Primary Micropore Volume (cm ³ /g)
BC1						
PAC	644	0.35	0.04	0.09	0.08	0.14
1 pass	777	0.44	0.05	0.13	0.08	0.18
15 min	786	0.32	0.07	0.07	0.13	0.05
30 min	857	0.49	0.07	0.13	0.09	0.20
1 hr	872	0.35	0.10	0.09	0.12	0.04
2 hrs	642	0.53	0.23	0.15	0.13	0.03
6 hrs	762	0.69	0.11	0.33	0.10	0.15
BC2						
PAC	991	0.50	0.04	0.10	0.15	0.21
1 pass	917	0.46	0.03	0.11	0.16	0.16
15 min	1019	0.54	0.07	0.12	0.17	0.19
30 min	1179	0.67	0.10	0.19	0.20	0.18
1 hr	1047	0.58	0.09	0.15	0.16	0.18
2 hrs	1010	0.56	0.12	0.13	0.15	0.15
4 hrs	997	0.56	0.14	0.14	0.10	0.15
6.33 hrs	872	0.69	0.17	0.28	0.12	0.13
BC3						
PAC	890	0.48	0.03	0.14	0.11	0.20
1 pass	931	0.56	0.08	0.16	0.15	0.18
5 min	802	0.43	0.05	0.12	0.12	0.15
10 min	881	0.47	0.05	0.14	0.13	0.15
20 min	895	0.51	0.07	0.16	0.13	0.16
2 hrs	890	1.04	0.42	0.37	0.14	0.11
4 hrs	798	0.73	0.19	0.28	0.10	0.15
WD						
PAC	1676	0.89	0.03	0.49	0.37	0.00
1 pass	1642	1.05	0.05	0.68	0.32	0.00
5 min	1575	0.99	0.06	0.63	0.31	0.00
10 min	1542	0.96	0.07	0.60	0.30	0.00

	20 min	1521	0.91	0.06	0.55	0.29	0.02
	1 hr	1269	0.89	0.13	0.45	0.23	0.09
	6 hrs	1008	0.84	0.28	0.29	0.25	0.02
CS							
	PAC	906	0.47	0.12	0.00	0.09	0.26
	1 pass	1134	0.49	0.04	0.01	0.15	0.28
	2 pass	895	0.39	0.03	0.02	0.12	0.23
	5 min	932	0.42	0.04	0.02	0.13	0.23
	10 min	938	0.42	0.05	0.01	0.14	0.23
	20 min	1047	0.46	0.08	0.00	0.16	0.22
	4 hrs	1050	0.50	0.09	0.09	0.17	0.15
LC1							
	PAC	660	0.61	0.08	0.36	0.05	0.12
	15 min	--	--	--	--	--	--
	30 min	--	--	--	--	--	--
	6 hrs	713	0.69	0.12	0.40	0.06	0.12
LC2							
	PAC	505	0.39	0.05	0.19	0.04	0.11
	1 pass	--	--	--	--	--	--
	5 min	--	--	--	--	--	--
	10 min	--	--	--	--	--	--
	20 min	--	--	--	--	--	--
	4 hrs	555	0.56	0.14	0.33	0.08	0.01

Macropore (> 50 nm); mesopore (2–50 nm); submicropore (1–2 nm); primary micropore (> 1 nm)

3.5 Comparison with S-PAC in Literature

A handful of publications over the past decade have explored milled carbon for use as an adsorbent; however, since most of these studies focus on adsorption performance, few have reported detailed physical and chemical carbon characteristics differences (Ando et al., 2010; Dunn and Knappe, 2013; Ellerie et al., 2013; Heijman et al., 2009b; Matsui et al., 2005, 2015, 2014, 2013, 2009, 2008, 2007). Available characterization data was extracted from those publications and is presented in Table 4. Here we consider all reported carbons with sizes under one micrometer. All studies reported particle size, which have been measured by various techniques, including dynamic light scattering (DLS), laser light scattering (LLS), laser diffraction, LED measurement, and optical and scanning electron microscopy. After particle size, surface area, as measured by nitrogen adsorption, was the next most common parameter

reported. Since particle size and surface area are two characteristics often used to describe performance of PAC, reporting of these parameters is logical. Some papers have reported carbon characteristics not examined in this study, including uniformity coefficient and geometric standard deviation as related to particle size (Matsui et al., 2013), as well as acidic and basic functional groups as determined by Boehm titration (Matsui et al., 2015). The next most commonly reported parameters regard micropore fractions and mesopore fractions, though reporting is inconsistent; some studies report the volume of the pore fraction while others report the surface area of the pore fraction. The total pore volume is rarely reported. Lastly, pH_{PZC} has only been reported by Ellerie et al. (2013) and Dunn and Knappe (2013). Notably, only Dunn and Knappe (2013) have reported oxygen content (not included in Table 4). It is clear that data gaps exist for an analysis of S-PAC beyond particle size and select physical characteristics.

Another data gap lies in the reporting of milling parameters. No paper has discussed the details of milling beyond a description of the grinding media and, in one case, the milling duration. It is clear from the number of variables present in wet milling, and the variety of carbons produced in this study, that processing details are important to reproducible data. For this reason, grinding is often viewed as an art, rather than a science. The most critical information to be reported relate to the transfer of energy: mill speed, milling duration, grinding media characteristics (size, composition, and loading rate), grinding carrier fluid plus dispersants used, and carbon loading rate (percent solids content). However, it is likely that all process variables play some role or another towards the final outcome, thus it is recommended that as many details be reported as possible, including such parameters as mill configuration, rate of flow, and temperature of milling.

374

375 The studies in Table 4 have found S-PAC to perform well, despite having few characterization
376 parameters. It is understood that the improved rate of small molecular adsorption is governed by
377 the path length, which is determined by particle size, a parameter that is reported in each study.
378 However, the changes to chemical and physical characteristics observed in this study, and which
379 likely have also occurred in carbons produced for previous studies, are known to have effects on
380 adsorption. The increasingly negative surface charges observed could result in shifts in the
381 adsorption affinity for hydrophobic compounds. Increases in the mesoporous and macroporous
382 fractions would increase the adsorption capacity for lower molecular weight NOM. Lastly,
383 optimization of S-PAC production is an important consideration. Between highly variable
384 grinding procedures and the heterogeneity of activated carbon, an S-PAC with particular
385 characteristics is produced. Additionally, extended milling yielded diminishing returns, thus
386 there is a tradeoff between energy input and production of a useful S-PAC. Material choice is
387 another major design consideration; for example, the lignite coals in this study reached small
388 sizes very quickly, but the bituminous coals were more predictable in breakdown. An
389 understanding of the grinding parameters and parent PAC that produce certain S-PAC types will
390 result in the ability to fine tune the process for creating an S-PAC with certain desired
391 characteristics.

Table 4: Characteristics for S-PAC reported in literature.

Carbon Name	Origin Material	Particle Size (d-50, nm)	Size Measurement Technique	pH _{PZC}	Surface Area (m ² /g)	Total Pore Volume (cm ³ /g)	Micropore Volume (cm ³ /g)	Micropore Surface Area (m ² /g)	Mesopore Volume (cm ³ /g)	Mesopore Surface Area (m ² /g)	Publication
Calgon 6D	Coal	18300, 1790, 950, 490	Microtrac LLS	6.52±0.12	--	--	0.30±0.03	--	0.12±0.02	--	Matsui et al., 2015
Calgon 6MD	Wood	670	Seishin LMS	--	--	--	--	--	--	--	Ando et al., 2010
		660	Seishin LMS	--	--	--	--	--	--	--	Ando et al., 2010
Calgon 6WD	Wood	16400,									
		1700, 830, 470	Microtrac LLS	8.61±0.02	--	--	0.36±0.04	--	0.14±0.02	--	Matsui et al. 2015
Calgon F100-D	Coconut Shell	47900,									
		1320, 1930, 940, 570	Microtrac LLS	6.87±0.28	--	--	0.39±0.03	--	0.08±0.02	--	Matsui et al. 2015
Calgon WPH	Coal	670	Seishin LMS	--	--	--	--	--	--	--	Ando et al., 2010
		37000	Optical Microscopy	6.1	900	0.46	0.70	--	0.01	--	Ellerie et al., 2013
Norit SHW Norit SX Ultra	Coal	240	Zetasizer DLS	5.7	773	1.01	0.27	--	0.29	--	Ellerie et al., 2013
	Wood	10600, 490	Microtrac LLS	8.56±0.06	--	--	0.25±0.03	--	0.26±0.02	--	Matsui et al., 2015
	Peat	800	Coulter LS	--	--	--	--	--	--	--	Heijman et al., 2009
Picahydro MP23	Wood	25200, 3100, 850, 520	Microtrac LLS	9.2±0.37	--	--	0.38±0.02	--	0.20±0.02	--	Matsui et al., 2014, Matsui et al., 2015
		680	Seishin LMS	--	--	--	--	--	--	--	Ando et al., 2010
Picahydro SP23	Coconut Shell	720	Microtrac LLS	--	--	--	--	--	--	--	Matsui et al., 2014
		500	Microtrac LLS	--	1220	--	--	1020	--	79	Matsui et al., 2014
		31000, 2560, 720, 500	Microtrac LLS	8.11±0.66	1230±60	--	0.44±0.01	--	0.10±0.02	--	Matsui et al., 2014, Matsui et al., 2015
Shirasagi-C	Wood	650	Seishin LMS	--	--	--	--	--	--	--	Ando et al., 2010
		850	Microtrac LLS	--	--	--	--	--	--	--	Matsui et al., 2014
		520	Microtrac LLS	--	1150	--	--	920	--	138	Matsui et al., 2014
		18000	Seishin LMS	--	--	--	--	--	--	--	Matsui et al., 2005
		600	Seishin LMS	--	--	--	--	--	--	--	Matsui et al., 2005
		770	Seishin LMS	--	--	--	--	--	--	--	Matsui et al., 2008

Taikou-W	Wood	650	Seishin LMS	--	--	--	--	--	--	Matsui et al., 2007
		880	Seishin LMS	--	--	--	--	--	--	Matsui et al., 2009
		800	Seishin LMS	--	--	--	--	--	--	Matsui et al., 2004
		11800 ^a	Horiba LLS	--	1170	--	--	--	--	Matsui et al., 2013
		^a 725	Horiba LLS	--	1110	0.62	--	--	--	Ando et al., 2010;
		13500 ^b	Horiba LLS	--	1070	--	--	--	--	Matsui et al., 2013
		^b 857	Horiba LLS	--	1130	--	--	--	--	Matsui et al., 2013;
		19000 ^c	Microtrac LLS	--	1070	--	990	--	124	Matsui et al., 2013
		^c 620	Microtrac LLS	--	1130	--	920	--	116	Matsui et al., 2014
		15400, 1550, 530	Microtrac LLS	7.96±0.56	--	--	0.39±0.01	--	0.11±0.01	Matsui et al. 2015
		15400, 1610, 550	Microtrac LLS	7.83±0.13	--	--	0.39±0.01	--	0.14±0.01	Matsui et al. 2015
		18900, 4930, 620	Microtrac LLS	7.81±0.31	--	--	0.40±0.03	--	0.15±0.01	Matsui et al. 2015
Unknown	Coconut Shell	10000	SEM Analysis	9.6	1070	--	0.395	--	0.072	Dunn & Knappe, 2013
		480	SEM Analysis	8.4	1090	--	0.378	--	0.343	Dunn & Knappe, 2013
		430	SEM Analysis	7.8	1120	--	0.396	--	0.438	Dunn & Knappe, 2013
Unknown	Lignite Coal	11000	SEM Analysis	10.7	507	--	0.140	--	0.386	Dunn & Knappe, 2013
		290	SEM Analysis	8.2	595	--	0.164	--	0.629	Dunn & Knappe, 2013
		180	SEM Analysis	8.5	607	--	0.175	--	0.514	Dunn & Knappe, 2013
Unknown	Wood	10000	SEM Analysis	10.7	912	--	0.313	--	0.225	Dunn & Knappe, 2013
		820	SEM Analysis	--	950	--	0.323	--	0.339	Dunn & Knappe, 2013
		210	SEM Analysis	7.9	917	--	0.294	--	0.565	Dunn & Knappe, 2013
Unknown	Wood	18000	SEM Analysis	4.9	1460	--	0.390	--	0.807	Dunn & Knappe, 2013
		1200	SEM Analysis	5.9	1400	--	0.393	--	0.742	Dunn & Knappe, 2013
		240	SEM Analysis	5.8	1270	--	0.370	--	0.675	Dunn & Knappe, 2013
Unknown	Bituminous Coal	14000	SEM Analysis	6.2	901	--	0.317	--	0.140	Dunn & Knappe, 2013
		600	SEM Analysis	6.7	879	--	0.300	--	0.251	Dunn & Knappe, 2013
		540	SEM Analysis	6.3	888	--	0.292	--	0.438	Dunn & Knappe, 2013

LMS = LED Measurement System; LLS = Laser Light Scattering; Coulter LS uses Laser Diffraction method; SEM = Scanning Electron Microscopy

4. Conclusions

The primary conclusions from this study are as follows:

- Pulverization of activated carbon by bead milling predictably reduces the mean particle size. The ability to reduce in size was generally related to the carbon precursor material; we observed faster size decline in the coal-derived carbons; however, we recognize that other wood and coconut shell carbons may behave differently than the samples used here. Successful pulverization in all carbon types supports the potential of S-PAC technology for application.
- Chemical property measurements led to discovery of an oxidative process occurring during bead milling. Oxidation appears to be most prevalent on external surfaces and the extent of surface oxidation did not increase with milling time. Since surface charge is known to affect adsorption processes, oxidation due to bead milling may affect S-PAC performance in relation to its parent PAC.
- Pore volume and surface area changes were not a predictable function of milling time; clear trends across all carbon types were not apparent. However, some changes in individual samples – particularly shifts towards meso- and macroporous fraction – are likely significant enough to affect adsorption performance in systems with competitive adsorption.
- Material reporting is lacking among S-PAC studies. Improved reporting of material processing and characteristics would improve the ability to predict which carbon materials will be easiest to mill and what surface chemistry changes to expect. This will enable more accurate design of future S-PAC processes.

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Figure Captions

Figure 1: Particle size of milled carbons with milling times varied from one pass through the mill to 6.3 hours. Data are split into two panes to avoid excessive overlap.

Figure 2: Scanning electron microscopy images (10K magnification) of all forms of BC1, including (A) PAC and all S-PACs. Particles visibly decrease in size as milling increases from (B) 1 pass to (C) 15 min, (D) 30 min, (E) 1 hr, (F) 2 hrs, and (G) 6 hrs.

Figure 3: Concentration of particles increases as particle size decreases. Concentrations were calculated from measured average particle sizes and conservation of mass.

Figure 4: The difference between pH measured using the pH_{PZC} method and the electrokinetic measurement of the isoelectric point is correlated with the S-PAC external surface area, which increases as particle size decreases.

Figure 5: Oxygen increased with newly revealed surface area as a result of milling. External surface area was calculated from Z-avg particle size measurements.

Figure 6: Illustration of PAC pulverization into S-PAC with proposed rapid surface oxidation.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Wet milling process

a

b

c

Oxygen-rich surface