MECHANICAL AND CHEMICAL MODIFICATION OF WOOD MATERIALS – COMPRESSED WOOD AND OXIDIZED CHARCOAL

Vasily I. Patyakin,[a] Uzum U. Sugaipov,[a] Alexei R. Birman,[a] Sergei M. Bazarov,[a]
Yuri N. Pilshikov,[b] Andrei A. Spitsyn,[b] and Howard D. Mettee[c*]

Mechanical compression and electrolyte infusion of wood, pyrolysis, and chemical activation of the resulting charcoals produced enhanced abilities to adsorb lead ion and benzene from model polluted water solutions. Iodine number (F) and methylene blue (E) indices also showed enhancement of surface activity. Ultrasonic techniques revealed a loss of pore structure during wood compression, as water infiltration likewise indicated for the resulting charcoals, but there was not necessarily a loss of adsorption ability for the above adsorbents on subsequent charcoals. Aspen based charcoals activated by pressurized H_2O_2 showed the most promise among those tested.

Keywords: Wood; Activated charcoal; Wood compression; Adsorption properties; Porosity; Water filtration

*Contact Information: a: Department of Mechanical Technology, St. Petersburg Forest Technical Academy, 5 Institutsky Per., St. Petersburg, 194021, Russia, Tel/Fax (812) 550-01-91; b: Department of Forest Chemistry, SPFTA, Tel (812)550-02-53, Fax (812)550-08-15;c: Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555; *Corresponding author: hdmettee@ysu.edu*

INTRODUCTION

The use of active carbon to remove toxic contaminants from polluted air and water has found wide technological application in recent decades (Bansal and Goyal 2005; Mulkin et al. 2000). However the conditions of high temperatures (900-1000 ^{o}C) for prolonged periods normally used to produce active carbon from charcoal prompted us to look for a more moderate approach. The substitution of rapidly growing softwoods, physically compressed to achieve the mechanical strength of slower growing hardwood charcoals, suggested itself as a plausible alternative. In general, the yields of charcoal from hardwoods exceeds that of softwoods for the same pyrolytic conditions (Pyalkin 1998).

A number of chemically treated woods show increased porosity (Moroz and Zavyalov 1976), increased yields of charcoal (Kyslitsyn et al. 1970), and enhanced adsorption characteristics (Bansal, Donnett and Stoeckli 1988). Therefore the effect of infusion of ammonium chloride into the wood prior to compression, and the effects of "shock" temperature and peroxide treatments on resulting charcoals, were chosen as important influences to investigate. Aspen and oak raw materials were chosen as prototype soft and hardwoods, because aspen reaches harvestable maturity in 5 years, whereas oak and other hardwoods require 20-25 years to reach this stage. The use of thermo-compressed virgin fir-wood and the benefits of physical and chemical activation of the resulting char have recently been reported in this journal (Khezami et al. 2007).

EXPERIMENTAL

Raw Materials and Compression

Aspen (*Populus tremula*) and white oak (*Quercus alba*) samples from the US and Russia were approximately 6 and 80 years old, respectively. Five 30x30x30 mm blocks of each were cut from the native, room-dried materials for pyrolysis. Larger pieces of each wood were cut to surround the test cubes within the pyrolysis retort. Cylindrical samples of 35 or 40 mm diameter, by 50 mm length, of aspen were compressed to 2 or 3 times their native (dried apparent) density by pressing them through an extruding die using a 40 metric ton press (TASH OPM3, Model OKS 1671M). Rectangular samples (235x50x50mm) of aspen or pine (*Pinus sylvestris*) were compressed in a reinforced rectangular die using a 100 ton press (Zavod Tyazheovo Kuzhecho -1974). In both presses the compression direction was perpendicular to the grain axes. Typical designs of these wood compression fittings are to be found in the classical Russian text (Vennik and Korystin 1964). There were no degrees of freedom for expansion of the wood during compression, as the wood samples were contained in all directions. During compression ultrasonic vibrations were coupled to the die housings by means of stainless steel, water cooled, electromagnetic vibrator (UZG3.4) operated at 400 V and 10 A. Following compression, the samples were locked into their die or press form, taken to a heating oven and cured for two hours at 150 ^{o}C. This latter step was taken to insure relaxation of the tension in the wood samples in their compressed states.

Mechanical Properties

The modulus of elasticity was measured by the speed of sound along the fibers of the wood by Leontev, L.L. in the SPFTA Wood Science Department using an Ultrasonic YK-14P device, No. 2495. The familiar formula $M = C^2\rho$ equates the modulus (M) to the sound velocity in the wood (C) and the density (ρ).

Pyrolysis

All pyrolysis tests were carried out in a stainless steel, sealed rectangular retort, contained in a ceramic lined muffle furnace (SNOL8, 2/100) whose temperature was controlled by a programmable timer (Varta TP 403) and measured by thermocouples in both the oven wall and the pyrolitic chamber. The exhaust gases were vented through a condenser which liquefied the condensable vapors, while the non-condensables passed through gas volume counter (GSB-400, GOST 6463-53) and then to a fume hood for burn off. The general design is that of Pyalkin (1998). The temperature-time profile used earlier by Novolokin (2002), consisting of an approximately linear increase from 20 – 600 ^{o}C over an 8 hour period, was chosen for our work to maximize the yield of charcoal.

NH_4Cl Infusion

Cylindrical aspen samples were set in steel centrifuge cells in a 15% solution of electrolyte, and samples were spun in an Einz Janetzki-KG centrifuge, Type S52. The upper ends of the cylinders were slightly above liquid surface to insure atmospheric pressure here, while the liquid experienced the centrifugal force developed by 500 rpm rate of rotation at a radius of 45 cm. The use of colored dyes in test solutions showed a homogeneous perfusion of color throughout the aspen wood cylinders.

Densities

GOST standard methods 10220-62 and 7657-84 were used to measure the apparent and true densities of the charcoals, as well as to calculate their porosities. Accordingly, absolutely dried (120 ^{o}C/ 2 hr) and measured cubes (10 , +/- 0.05 mm edges) were weighed (+/- 0.001 g) and immersed in boiling water for 1 hr, and then held under room temperature water for 24 hours. Water penetrated the exposed larger macro and meso pores, but not the smaller micro and sub micro (as well as isolated) pores. Then the cubes were removed, surface dried and re-weighed to determine the volumes of water absorbed by them. The true density did not include the volume of absorbed water (larger pore volume) in the cube, whereas the apparent density does.

Iodine Number and Methylene Blue

These familiar tests were based on GOST method 4453-48 and MPTU method 6-16-1003-67, as described by Kolshkin and Mikailov (1972). The methylene blue (MB) method was designed for active carbon and measures the number (n) of mL of a 0.15% solution decolorized by 0.10 g of active carbon. The MB index E(%) = 5n, thereby corresponding to 100 % when 20 mL (0.030 g MB) are decolorized. We diluted this 0.15 % of MB solution 32 fold to bring its optical density within the linear range (OD = 0.1 - 0.9) at 540 nm. A linear Beer's Law plot under these conditions was obtained, and on this scale, E was calculated as follows.

$$E = 1.56\,[1 - (OD_5/OD_0)]\ \ (\%) \qquad [1]$$

OD_5 and OD_0 refer to the optical densities of the 32-fold diluted 0.15% solution at 540 nm. OD_0 is that of the original solution, and OD_5 is measured after 5 minutes exposure of 0.100 g charcoal (normally 0.3-0.5 mm particle size) to 10 mL of solution, followed by filtration through a sintered glass funnel.

The iodine number F(%) involves the titration of standard solutions of 0.10 N iodine and sodium thiosulfite. These solutions are prepared from premixed or weighed "fixanals" (standard titers broken open before dilution). Under the present conditions,

$$F = 12.7\,[V' - V^*]\ \ (\%) \qquad [2]$$

where V' is the volume of standard $S_2O_3^{2-}$ used to titrate 10.0 mL of standard I_2 solution, and V* is the volume of $S_2O_3^{2-}$ used to titrate 10.0 mL aliquots of 100.0 mL I_2 solution exposed to 1.0 g charcoal particles (normally 0.3-0.5 mm size) for 30 min. An F value of 100% corresponds to the absorption of 0.10 g I_2 by the charcoal.

Particle Size Separator

To obtain particle sizes of known range, the charcoals were first ground by hand in a mortar and pestle, and then separated by a columnar series of vibrating sieves operated by a Vibrotechnic BT-208.00.000, or on occasion using a series of hand operated sieves (0.2 -2.0 mm particle size). The Vibrotechnic column gave particles 0.1 – 0.3 mm and 0.3 – 0.5 mm.

FTIR

Fourier Transform Infrared spectra were obtained via KBr pellets containing 2-5 mg of freshly ground charcoal subparticles and KBr pressed at 210 bar using a Monitoring FTIR FSM 1201 in the Organic Chemistry Department of SPFTA.

Model Solution of Pb^{2+} and C_6H_6 in Water

A model solution of contaminated water consisting of 1.0 ppm in both lead and benzene was chosen to test the kinetics and comparative capacities of the various charcoals after selected times of exposure. A general dose of 1.0 g charcoal particles (0.1 -0.3 mm size) was used per 100 mL of test solutions, which were then exposed for various time intervals, filtered and analyzed. The St. Petersburg State Center for Research and Control of Water performed these analyses using an IRIS Intrepid II XDL inductively coupled plasma spectrometer for lead (Jarrell Ash), and a purge and trap gas chromatograph Agilent 6850 for benzene. Their standard methods were AES-ESP for lead, 3.19.08-96 for benzene, and RF 1.31.2000.00132 for both. Because benzene caused a small matrix interference in the analysis of lead ion, the filtered solutions were treated with several drops of concentrated nitric acid before the analysis.

Thermal and Chemical Shock Experiments

A series of thermal and chemical shocking experiments were conducted at temperatures below the normal range for production of active carbon to see if ordinary charcoal could be improved upon with respect to its adsorbent properties by our tests. The T-shock experiments were performed by simply heating crucibles of ground and sieved charcoal at 750 ^oC for 15 min. The C-shock conditions included reacting 2.0 g samples of sieved particles with 5 mL of neutral 10 % H_2O_2 (diluted Bekton Reagent, 40%, GOST 177-88) in tightly sealed stainless steel capsules, which were then immersed in a hot metal bath (Pb, Sn, Bi, Cd) held at 275 ^oC after immersion of the capsules. This exposed the charcoal to both elevated temperatures and pressures for brief periods of time. The peroxide concentration was determined independently by acidic permanganate titration (Alexeev 1972).

RESULTS AND DISCUSSION

Yields, Densities and Porosities

Table 1 compares the above parameters for various aspen and oak based charcoals, including the earlier results of Novolokin (SPFTA, 2002).

Table 1. Yields, Densities, and Porosities of Charcoals from Aspen and Oak.

Sample	Yield (%)	Apparent Density (g/cm^3)	True Density (g/cm^3)	Pore Volume (%)	Pore Amount (cm^3/g)
Nat. Aspen	20	0.22	1.00	75	3.10
2x Comp. Aspen	28	0.44	0.98	55	1.30
3x Comp. Aspen	33	0.60	0.83	28	0.47
Nat. USA Aspen	27	0.20	0.63	70	3.50
Nat. Oak	30	0.42	0.92	64	1.95
Nat. USA Oak	29	0.48	0.89	46	1.00
Aspen + NH_4Cl	44	0.28	1.20	80	3.40
2x Comp. Aspen + NH_4Cl	47	0.89	1.80	45	0.58
Nat. Aspen (Lit.)*	-	0.28	0.82	78	2.8
1.2x Comp. Aspen*	-	0.33	1.09	72	2.2
1.5x Comp. Aspen*	-	0.42	1.25	70	1.7

* Novolokin, A.A.(2002), Candidate Dissert. 5454, SPLTA.

It is clear that the yield of aspen charcoal (based on the mass of dry wood) was increased by compression to an extent greater than oak if compressed to one-third of its original volume. If the aspen was saturated with a 15 % NH_4Cl (also a flame retardant) solution, its yield is increased by a factor of two, or even more if compressed before pyrolysis.

Not unexpectedly, there was an increase in “apparent” (usual) density of the charcoal induced by compression or infusion of the original wood. In general, this is caused by a reduction or filling of pore space. Novolokin noticed similar behavior. What is perhaps less obvious is the reason why small degrees of compression (range 1 – 1.5) of the wood lead to an increase in “real” (excluding pore volume) density, but for greater degrees of compression (range 2 -3) a decrease occurs. Figure 1 shows this inversion. The pore loss was relatively small (78 to 70 %) at lower compressions, so that the added mass of carbon matrix caused a real density increase. However, at higher compressions there was a catastrophic loss of pore volume (75 to 28%) so that even the added mass of carbon matrix was outweighed by the increase in its volume. These findings are consistent with the pioneering work of Abe et.al. (2001) on the compression and subsequent carbonization of Japanese cedar (*C. japonica*) sapwood. Their results showed a threefold increase in apparent density and a two-thirds decrease in pore volume for pores larger than 30 nm (mid-mezo to macro). They also found that pores smaller than 30 nm were not lost by compression of the precursor wood using nitrogen absorption techniques. (Water likely penetrates to the smallest mezo pore size of 1.5 nm, corresponding to a thread of 4-6 molecules in diameter, so the two methods are not exactly comparable.)

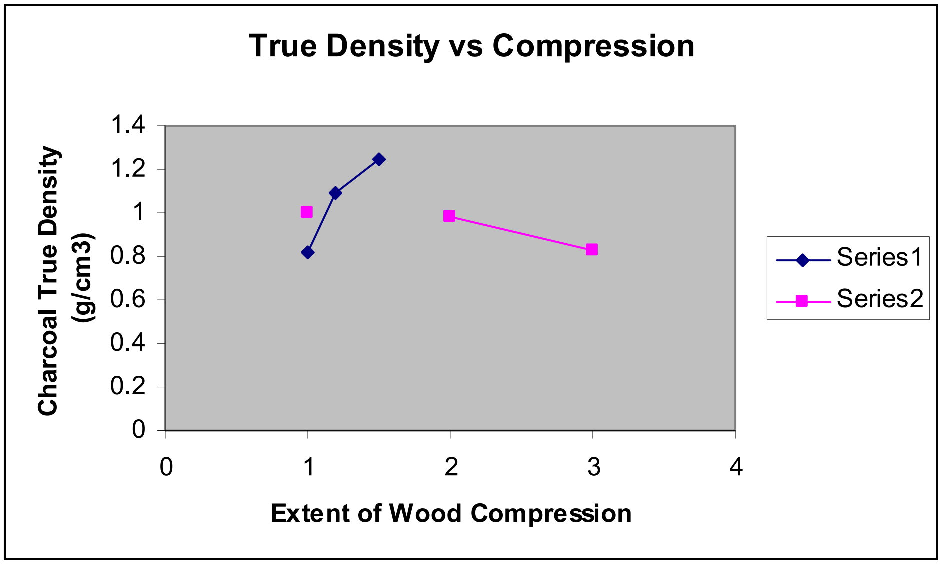

Fig. 1. Aspen charcoal true density as a function of extent of wood compression. Series 1 Novolokin (2002), Series 2 Present work.

The increase in pore volume seen for NH_4Cl infused wood precursor parallels that observed for birch using various electrolytes (Moroz and Zavyalov 1976), but this increase was completely offset by the effects of compression of the wood. Both Russian and American aspen samples had similar porosities, but the Russian oak exceeded that of the USA in this capacity.

Elasticity Modulus and Wood Porosity

The effect of compression on these properties was examined using pine sorted by their room dried apparent densities into three groups. The group of median density was chosen as a control group to compare the effects of compression on the other two groups – 1 and 2. Table 2 presents the findings. Note that the control group did not change its apparent density within experimental error on the day the compressed samples were tested.

Table 2. Compression of Native Pine (*P. sylvestris*)

Group – Uncomp.	**Avg. Den. (kg/m^3)**	**Moisture (%)**	**Elast. Modulus, M (GPa)**	**Specif. Elast. Modul. (10^{-6} m^2/s^2)**	**Abs. Dry Den. (kg/m^3)**	**Porosity (%)**	**Den. Inc. Comp. (Fct)**	**Elast. Modulus Incr. (Fct)**	**Spec. Elast. Modulus Dec. (%)**
Control	525 +/- 3	9.57 +/- 0.14	17.43 +/- 0.08	33.2 +/- 0.2	530 +/- 4	67.1 +/- 0.3			
Group 1	512 +/- 3	9.51 +/- 0.09	15.6 +/- 0.3	30.2 +/- 0.7	486 +/- 4	68.2 +/- 0.3			
Group 2	576 +/- 3	9.58 +/- 0.06	19.1 +/- 0.4	33.0 +/- 0.4	552 +/- 4	63.9 +/- 0.3			
Group – Compressed 1 and 2									
Control	523 +/- 1	9.3 +/- 0.1	17.17 +/_ 0.09	32.80 +/- 0.15				0.98	1.25
Group 1	1 110 +/- 35	5.2 +/- 1.5	30.7 +/- 1.2	27.7 +/- 0.3		28.8 +/- 1.4	2.16 +/- 0.09	1.97 +/- 0.08	8.47
Group 2	1 167 +/- 12	6.5 +/- 1,8	36.7 +/- 1.3	31.5 +/- 1.0		25.0 +/- 1.8	2.02 +/- 0.04	1.93 +/- 0.07	4.69

It is clear that the modulus of elasticity increased in parallel with apparent density upon compression, both by about a factor (Fct) of two. This is because the modulus reflects the loss of porosity, in that the speed of sound increases under compression.

When the “specific” elasticity modulus (M divided by density) was examined, it did not change nearly as much, and it even decreased slightly. The pore percentage diminished by even more than a factor of two upon compression. Figure 2 shows an approximately linear relationship between the elasticity modulus and the apparent density. The line may be extended to near 50 for the critical density of 1.5 g/cm^3, corresponding to the absence of pore structure and the onset of a new high molecular weight polymer material (O).

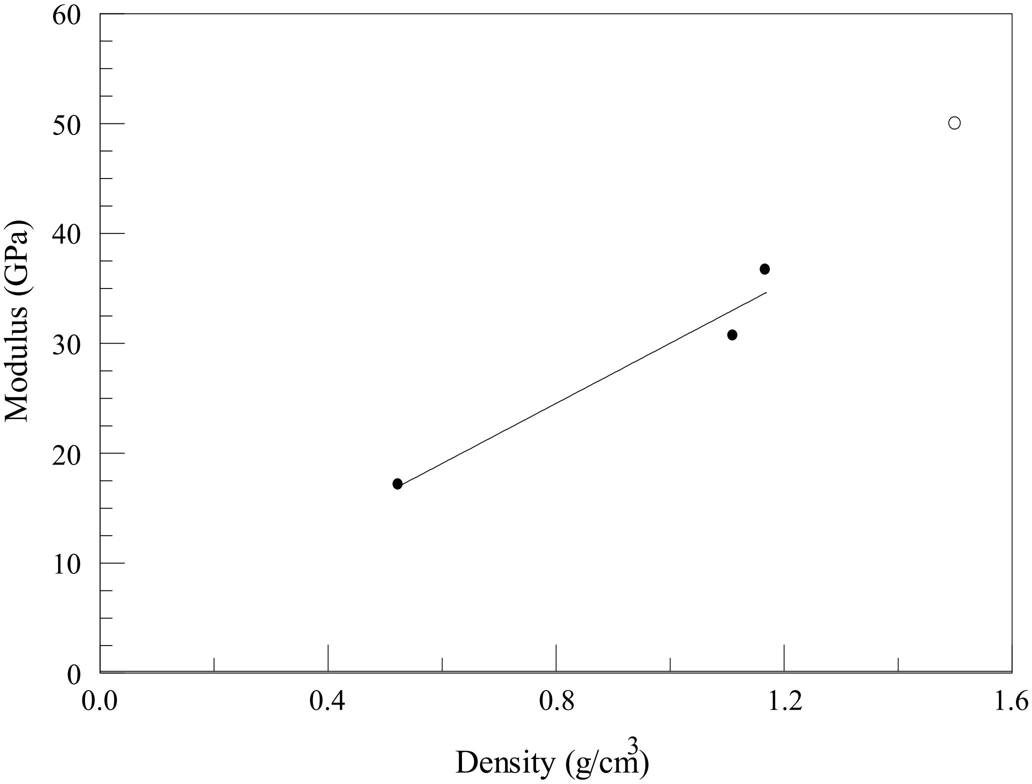

Fig. 2. Elasticity Modulus vs Apparent Wood Density (● = data)

Adsorbent Activity

Table 3 presents the iodine numbers and methylene blue test results with some variance of particle size. It was not always possible to obtain particles within the range of 0.3 - 0.5 mm normally used. However the alternate size range of 0.2 – 2.0 mm is not far different, as little of the mass distribution of particles was between 0.5 – 2.0 mm. These results are used to interpolate trends.

It should also be noted that the size of the I_2 molecule (0.4 nm) and MB (2.0 nm) compare with the Dubinin (1960) pore size range of micro- (0.6 – 1.5 nm), meso- (1.5 - 100 nm), and macro-pores (100 -200 nm). Of the two, only I_2 was capable of penetrating all three pore categories. MB was limited to the larger meso and macropores. In addition to the steric differences, the reactivity for I_2 is normally considered to be addition across olefinic double bonds, and we might expect it to couple to unpaired electrons as well.

As a cationic dye, MB would be attracted electrostatically to anionic surface groups such as deprotonated carboxyl or phenolic groups, as would be expected at neutral pH. In addition, as a fused tricyclic ring system, MB would also be attracted by dispersion forces to the graphitic aromatic rings lying in the microplanes of the pore walls and on external surfaces. Turning to the tabulated values for F and E, there seems to be no marked difference between F or E for various natural aspens, though it could be said that the effect of compression is to increase them. Interestingly, oak has a higher iodine number than aspen (greater proportion of micropores), but little if any tendency to adsorb methylene blue (fewer oxidized groups, fewer meso and macropores).

Table 3. Iodine Number (F) and Methylene Blue (E) Indices for Various Charcoals

Wood/Sample	F (%)	F(%)	F(%)	E(%)
Part. Size (mm)→	<0.1	0.1`-`0.3	>0.5	0.3 - 0.5
Nat. Aspen	22.6	(16)	11.4	0.54
2x Comp. Aspen			10.2	0.55
3x Comp. Aspen		26.6	(13 – 18)	0.66
US Aspen			8.9	0.50
Nat. Oak	46.9	(33)	17.7	0.0
US Oak			14.0	0.43
Aspen + NH_4Cl			1.3*	0.84
Aspen/NH_4Cl/2x Comp.			2.5*	0.86
T-Shock. Aspen			39.4	0.71
T-Shock. Oak			34.0	0.83
T-Shock Aspen/3x Comp			33.0	0.73
C-Shock Aspen/ 5 min.			39.4*	0.90*
C-Shock Aspen/ 10 min.			35.5*	0.96*
C-Shock Aspen/ 20 min.			33.0*	0.94*
C-Shock Aspen/ 30 min.			38.1*	0.70*
Aspen Bark			15.2*	0.82*

Values in ( ) are interpolated. * Values are for 0.2 – 2.0 mm particle size

Looking more carefully at the 0.1 – 0.3 mm values for aspen and oak, the 3x compressed aspen does appear to have a greater F value (26.6) than the interpolated value of (16), based on the proportionate increase in F as the particle size decreases (and surface area per gram increases). It is not quite the value of oak yet (33), but it is approaching it. Because the general trend to increase these indices with compression of the wood is at odds with the earlier conclusion that overall porosity, both as a % and an absolute quantity, is decreasing with compression, then one is forced to conclude there are more active groups exposed by compression. This can be understood if it is remembered that mechanisms of adsorption include the feature that most of the reactive groups lay close to the edges of the graphitic microfragments and not in their planar aromatic interiors. Thus it would appear that compression of the wood causes further fragmentation of these graphitic "islands" in the resulting pyrolysed charcoal, creating more edges and potential reactivity.

The simultaneous loss of iodine number but gain in methylene blue for the aspen infused with NH_4Cl is particularly intriguing. The physical effect of this electrolyte was to significantly expand the porosity for the uncompressed aspen, which was offset by 2-fold compression (Table 1). It should not be overlooked that there were high concentrations of the electrolyte left within the smaller pores and on the surface of the larger ones. These would serve to polarize the surface double layer to such an extent that the nonpolar I_2 molecule might encounter some difficulty penetrating the surface barrier to react with surface double bonds. Because MB is a cation under these conditions, it would share the polar character of this layer and find much less difficulty in penetrating it.

The temperature-shocked aspen and oak charcoals showed both enhanced iodine number and methylene blue, but most markedly for iodine number, by a factor of about 3.5. Clearly there were more micropores opened, and possibly more fragmented micrographitic particles (and edges) created, by this treatment, or perhaps both. Although the increase in E appeared more modest (factor of 1.5), it too was not trivial. There appeared to be no advantage to compressing the aspen if it was subjected to the T-shock technique.

The H_2O_2 chemically shocked aspen charcoals also showed both enhanced iodine number (factor of 4) and methylene blue index (factor of 2). This might in part be due to the artifact of a smaller particle size, though ranging from 0.2 – 2.0 mm is not so very different from 0.3 – 0.5 mm. Little mass distribution lies at the extreme ends of the larger range. Even so, these numbers are all internally comparable. They suggest an opening of pores effect of the same magnitude as the much higher temperature thermal shock, and the creation of more active centers than this method, according to both I_2 and MB. It should not be overlooked that this method also produces pressures of several hundred atmospheres within the capsule for these brief periods as well as the oxidizing condition ($T = 275\ ^{o}C$).

Lead and Benzene Kinetics of Adsorption

Finally, Table 4 presents the lead ion and benzene adsorption from a test solution of 1.0 ppm in both components to simulate a toxic drinking water. We chose a dose rate of 1.0 g/100 mL of solution for convenience, but actual experiments often used 0.50 g/50 mL.

Except for the small complication of detecting Pb^{2+} ion in the small amounts of benzene present (matrix interference), the kinetics of adsorption of these parameters reflects the potential of these forms of active carbon to accomplish this purpose. Furthermore, the results are parallel to those for iodine number and methylene blue.

The aspen-based charcoals showed a quick readiness to absorb lead ion, it being nearly 90 % adsorbed in the first 5 minutes, except for the case where it was both infused with NH_4Cl and 2-fold compressed prior to pyrolysis. Actually, compressing native aspen 3-fold made it even more effective as a charcoal in both speed (5 min) and final capacity. On the other hand, these same aspen-based charcoals were neither rapid nor complete in their ability to absorb benzene. The compressed-aspen and infused-aspen-based charcoals barely absorbed half the benzene in the first 5 minutes, though native aspen managed to scavenge 90 % an hour after exposure.

The Russian oak based charcoal behaved in just the opposite manner – being extremely quick to absorb benzene, essentially 95 % in the first 5 minutes, yet requiring an hour to absorb only 75 % of the lead. This parallels the reluctance of the oak-based charcoal to pick up methylene blue (E = 0.00), but at the same time it had a higher iodine number. Thus the oak charcoal has reacting groups which pick up benzene as they do iodine, and are generally superior to aspen based charcoals despite their reduced porosity.

The aspen charcoals with a higher porosity have attractive centers for lead ion just as they do for methylene blue, so presumably these centers occur in large enough pores for the MB ions to find them.

Table 4. Lead Ion (Pb^{2+}) and Benzene (C_6H_6) Levels (ppm) in Aqueous Solutions Exposed to Charcoal For Various Time intervals – Dose 0.50 g Charcoal/50 mL *

Original Charcoal Wood	**Contact Time (min) →**	**0**	**5**	**10**	**30**	**60**	**120**
	Parameter ↓	**ppm**	**ppm**	**ppm**	**ppm**	**ppm**	**Ppm**
Nat. Aspen	**Pb^{2+}** **C_6H_6**	0.55 1.2	0.035	0.030 0.26	0.017 0.16	0.016 0.12	0.036 0.09
3x Comp Aspen	**Pb^{2+}** **C_6H_6**	0.52 1.2	0.011 0.53				0.011 0.27
Nat. Oak	**Pb^{2+}** **C_6H_6**	0.71 1.1	0.386 0.04	0.24 0.025		0.168 0.009	0.141 0.005
Aspen + NH_4Cl	**Pb^{2+}** **C_6H_6**	0.93 1.1	0.094 0.58	0.092 0.57		0.075 0.45	0.055 0.36
Aspen + NH_4Cl, 2x Comp	**Pb^{2+}** **C_6H_6**	0.94 1.2	0.19 0.66	0.086 0.68		0.21 0.56	0.55 0.45
Nat. Aspen - H_2O_2 + Δ (5&10 min)	**Pb^{2+}** **C_6H_6**	1.0 1.4	0.020 0.08	0.03 0.02	0.03 0.02	0.03 0.01	

* Measured by St. Petersburg Center for Research and Control of Water using ICP (Jarrell Ash IRIS Intrepid II XDL for Pb^{2+} and GC (Agilent 6850/Purge and Trap) for C_6H_6.

The results for the NH_4Cl infused wood – pyrolysed to charcoal – showed interesting similarities with the iodine number/methylene blue results. As aspen-based charcoals they absorbed lead ions readily, although they were somewhat slower than the ordinary aspen. Benzene was even more poorly absorbed in these infused cases, and both of these findings can be accounted for by the presence of NH_4Cl in the bulk solution and on the charcoal surfaces repelling the non-polar benzene (as I_2), but attracting Pb^{2+} ion (as MB) and holding it the double layer, but not permanently binding it to active carbon carboxylate or phenolate groups. NH_4^+ ion would compete with lead ion for these sites. It is clear in retrospect that these infused charcoals should be flushed clean of the infusing agent before performing tests on the charcoal they helped modify. This extra processing step does not favor their adoption in producing improved charcoal water filters.

By far the most effective charcoals of the group examined in this work were those oxidized by high pressure, moderately high temperature (275 ^oC), and 10% H_2O_2. The resulting charcoal absorbed 98 % of the lead and nearly 95% of the benzene in 5 min, and continued to maintain or improve this performance in the remaining time. The technique provides both physical and chemical activation under relatively modest circumstances, and the resulting charcoal does not contain toxic adducts or require neutralization.

Because the peroxide-activated charcoals showed the most promise of any of the groups we examined, it was felt important to examine the effect H_2O_2 was having on the surface. FTIR is capable of revealing the presence of the carbonyl C=O of carboxylate groups and the C-O stretching of phenolates, so KBr pellets were prepared and the spectra for charcoals exposed 5, 10, 20 and, 30 minutes to the hot, pressurized, oxidizing conditions were run.

Only in the case of the 5 min spectra were there unmistakable shoulders at 1730 cm^{-1} appearing on a lower frequency band at 1620 cm^{-1}, and this occurred in all three 5-minute samples. Figure 3a shows these features.

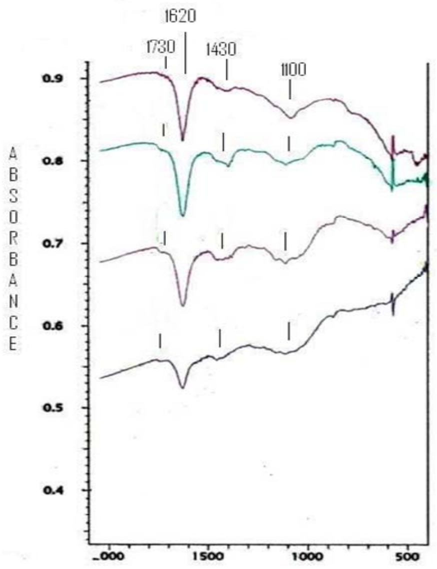

Fig. 3a. FTIR of KBr pellets of 5 min oxidized aspen charcoal – samples A,B and C and KBr (top).

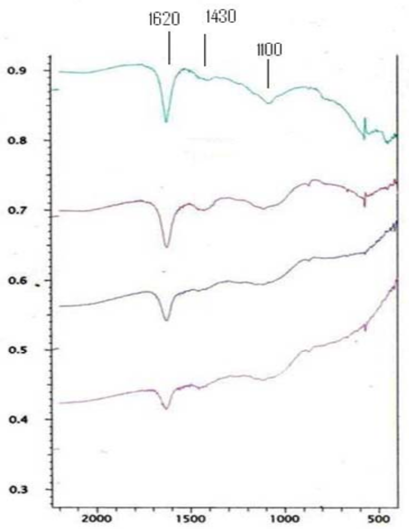

Fig. 3b. FTIR of KBr pellets of 10, 20 and 30 min oxidized aspen charcoal and nat. aspen (top).

The lower frequency main band in normal aspen had no such shoulders. The spectra for 10, 20, or 30 min. (Fig. 3b) also showed no evidence of the shoulders found for the 5 min spectra. It can be concluded that the major benefit arising from this treatment is realized in the first five minutes, and that this advantage may be at least partially lost by continued oxidative treatment. In general these surface oxide groups are typical of those reported numerous times before under such conditions. The paper by Beck et al. (2002) is a recent example which examines multiple processes using various analytical techniques.

The iodine number dropped (except for the 30 min value) for these heated and oxidized samples, and the MB index also showed a downward trend, although neither of these tests is entirely consistent. One explanation for this behavior is that the peroxide treatment indeed produced more surface active sites in the charcoal, mostly at the edges of the graphitic plates, but it may also partially destroy the plate structure itself needed to maintain them. Finally it should be pointed out that oxidized sites on the walls of pore interiors would likely not be detected by the infrared radiation. Thus, this method will underestimate the presence of such sites in the entire sample.

CONCLUSIONS

1. Compression of soft wood results in a loss of porosity but not necessarily in a loss of adsorbent activity of the pyrolysed, compressed product.

2. Strengthening of a soft wood's elasticity modulus occurs in proportion to the extent of compression.

3. Infusion of the softwood with NH_4Cl results in an increased porosity of the charcoal, whether the wood is compressed or not.

4. Wood compression causes a small degree of collapse of the pore structure of the resulting charcoal at low degrees of compression (to 1.5 times), and causes a major collapse of this structure at greater degrees of compression (to 2 and 3 times).

5. Aspen-based charcoals are successful in absorbing lead ion, but not as successful for benzene in competitive studies. Oak based charcoals efficiently absorb benzene but less so for lead.

6. Pressurized oxidation of aspen charcoal fragments at 275 ^{o}C with hydrogen peroxide results in enhanced adsorption qualities both for lead and benzene.

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