A NOTE ON DENSITY CHANGE PATTERNS IN CHARRED WOOD[1]

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ABSTRACT

Apparent and real densities of seven species of wood and chars were measured. The chars had been prepared by heating in flowing nitrogen at rates of 1, 10 and 50 C/min. Generally, maximum rate of change was between 300 and 350 C. The decrease continued up to 600 C, the maximum charring temperature.

Keywords: Charcoal, apparent density, real density, hardwoods, softwoods.

INTRODUCTION

The amount of charcoal obtained from a known amount of wood (the yield) and the subsequent use of this charcoal are in large part determined by the physical and chemical properties of the parent material (Humphreys and Ironside 1974; Petroff and Doat 1978). At a given temperature, high density woods such as oak and hickory yield more char than do low density woods such as basswood or cottonwood. Density, a function of both mass and volume, constantly changes during the charring or coaling process. According to Wenzl (1970), pyrolysis of charring of wood results in an increase in the real density (ρ_0) of the material while the apparent density (ρ) of the char decreases.

Blankenhorn et al. (1978) determined apparent density and real density of carbonized black cherry (*Prunus serotina* Ehrh.) using mercury porosimetry methods. They defined apparent density as the oven-dry mass of the sample divided by the gross volume of the sample determined in mercury at atmospheric pressure. Real density was defined as the sample oven-dry mass divided by the sample volume at the maximum mercury penetration pressure, 60,000 psig. Over the range of temperatures studied, ambient to 900 C, apparent density decreased from 0.611 g/cm³ to 0.414 g/cm³. Real density also decreased, from 1.33 g/cm³ to 1.27 g/cm³. This contrasts with the real densities of pure carbons, which range from 1.88 g/cm³ for amorphous carbon to 2.25 g/cm³ for graphite carbon to 3.51 g/cm³ for diamond carbon (Mantell 1968).

Slocum et al. (1973) found that the apparent densities of oak and hickory charcoal were significantly less than those of the parent wood reaching minimum values at 600 C. At 800 C, apparent density had increased slightly.

Harkins and Ewing (1921) found that beechwood charcoal had a real density (ρ_0) of 0.521 g/cc in mercury, 1.644 g/cc in water, and 1.665 g/cc in ether. Cedarwood charcoal densities were reported as 0.815 g/cc in mercury, 1.499 g/cc in water, and 1.504 g/cc in ether. Howard and Hulett (1924) used helium absorption to evaluate the densities of several types of carbon including wood charcoal. They found that willow charcoal had $\rho_0 = 1.44$ g/cc. This note presents the patterns of real and apparent density change for seven species of wood.

METHODS AND MATERIALS

Matched samples (1 cm × 1 cm × 1 cm) of southern pine (*Pinus* spp.), western redcedar (*Thuja plicata* Donn), Douglas-fir (*Pseudotsuga menziesii* [Mirb.] Franco), redwood (*Sequoia sempervirens* [D. Don] Endl.), white oak (*Quercus* spp.), basswood (*Tilia americana* L.), and hard maple (*Acer* spp.) were heated to temperatures of 300, 350, 400, and 600 C at rates of 1, 10, and 50 C/min in a flowing N_2 atmosphere (Beall 1977). Control (uncharred) samples and samples heated to 250 C at the 1° rate were also studied. The southern pine samples were split into earlywood and latewood samples under a dissecting microscope before the density determinations were made. The apparent densities of the wood and chars were measured using pycnometric displacement of water (Stamm 1964). Two determinations were made for each treatment.

Real densities (ρ_0) of wood and selected chars were determined by flotation of 10 to 20 mg of material in a mixture of carbon tetrachloride ($\rho_0 = 1.59$ g/cc, 20°/4°) and benzene ($\rho_0 = 0.88$ g/cc, 20°/4°) at 30 ± 0.1°C (Beall 1972b; Stamm 1964). The wood and char samples used for the measurements were ground to pass a 40-mesh screen and be retained on an 80-mesh screen. Duplicate measurements were made for each sample. All data were analyzed using standard analysis of variance techniques.

RESULTS AND DISCUSSION

Apparent density

Changes in apparent density (ρ) for the seven species of wood and char are shown in Table 1. Analyses of variance indicated significant differential treatment responses for each species. Duncan's (1975) mean separation test was used to define these differences. Southern pine earlywood ρ decreased 28% when heated from ambient to 600 C at a rate of 1 C/min (referred to hereafter as 600/01). The lack of clearer treatment responses for this set of data might be due to an incomplete separation of the earlywood ($\rho = 0.275$) from the late ($\rho = 0.715$).

Douglas-fir ρ decreased 56% when heated from ambient to 600 at the 1 C rate, western redcedar ρ decreased 30%, white oak ρ decreased 21%, hard maple ρ decreased 21% and basswood ρ decreased 38%. In most cases, the apparent densities measured at 400 and 600 C were not statistically different. Species-to-species comparisons were not performed on the data. The major breakpoint in the data usually occurred in the 300 to 350 vicinity. This probably reflects the changes in the internal wall structure resulting from the breakdown of cellulose. The density of the wood is the weighted sum of the densities of the components

Table 1. *Apparent density of wood and charcoal determined pycnometrically in water.*[a]

Treat-ment	Southern pine		Douglas-fir	Redwood	Western redcedar	White oak	Hard maple	Basswood
	EW	LW						
Control	0.275 AB	0.715 AB	0.510 A	—[b]	0.248 AB	0.601 AB	0.537 A	0.358 A
250/01	0.284 AB	0.701 ABC	0.278 CDE	0.293 A	0.233 AB	0.613 A	0.566 A	0.329 A
300/01	0.247 AB	0.684 ABC	0.275 DE	0.259 ABC	0.254 AB	0.589 AB	0.510 AB	—[b]
350/01	0.286 AB	0.520 CDEF	0.278 CDE	0.213 ABC	0.175 DE	0.599 AB	0.456 BC	0.247 BC
400/01	0.232 AB	0.456 F	0.202 F	0.164 C	0.153 DE	0.567 ABC	0.442 C	0.204 C
600/01	0.197 AB	0.647 ABCDE	0.226 EF	0.180 BC	0.174 DE	0.477 CD	0.423 C	0.220 C
300/10	0.306 AB	0.674 ABCDE	0.330 BC	0.299 A	0.245 AB	0.602 AB	0.554 A	0.291 AB
350/10	0.219 AB	0.699 ABC	0.361 B	0.262 ABC	0.216 BC	0.504 BCD	0.458 BC	0.246 BC
400/10	0.236 AB	0.596 ABCDEF	0.212 F	0.233 ABC	0.157 DE	0.425 D	0.421 C	0.221 C
600/10	0.231 AB	0.449 F	0.205 F	—[b]	0.188 CDE	0.486 CD	0.456 BC	—[b]
300/50	0.334 A	0.721 A	0.307 CD	0.264 AB	0.248 AB	0.549 ABC	0.528 A	0.318 A
350/50	0.282 AB	0.497 DEF	0.312 BCD	0.261 ABC	0.266 A	0.535 ABC	0.543 A	0.243 BC
400/50	0.166 B	0.528 BCDEF	0.195 F	0.173 BC	0.193 CD	0.408 D	0.427 C	0.200 C
600/50	0.168 B	0.491 EF	—[b]	—[b]	—[b]	—[b]	—[b]	0.191 C

[a] Those means in the same column followed by the same capital letter are not significantly different at the 0.05 probability level.
[b] Missing sample.

TABLE 2. *Real densities (g/cc) of a southern pine and white oak wood and charcoal.* [a]

Treatment	Southern pine		White oak
	EW	LW	
Control	1.452	1.463 A	1.461 A
250/01	1.439 A	1.449	1.450 A
300/01	1.415　B	1 412　B	1.368
350/01	1.387　　C	1.332	1.274　　BC
400/01	1.377	1.362　C	1.286　B
600/01	1.343　　D	1.316	1.250　　D
300/10	1.427	1.444	1.457 A
350/10	1.387　C	1.409　B	1.261　　CD
400/10	1.337　D	1.336	1.240　　D
600/10	1.367	1.307	1.141
300/50	1.441 A	1.461 A	1.457 A
350/50	1.410　B	1.430	1.322
500/50	1.353	1.358　C	1.240　　D
600/50	1.339　D	1.348	—[b]

[a] Those values in the same column followed by the same capital letter are not significantly different at the 0.05 probability level.
[b] Missing sample.

(Beall 1972b). Crystalline cellulose has a density of about 1.53 (Stamm 1964), while hardwood hemicelluloses have a density of about 1.457 and softwood hemicelluloses, 1.534 to 1.798 (Beall 1972b). Hardwood lignins have a density of about 1.366, while that of softwood lignin is somewhat less, 1.347 (Stamm 1969).

The apparent density values for these samples are much lower than the values given by Beall (1977) even though the specimens are identical. This is probably due to the method of determination. However, the degree of density loss among the samples is comparable as are the patterns of density loss determined by Beall (1977).

Changes in heating rate data indicate a time lag possibly due to the mass of the sample allowing the buildup of an internal temperature gradient. At the highest heating rate, 50 C/min, the 300 C sample was heated for only 6 min, then the furnace was opened and the sample allowed to cool in flowing nitrogen to ambient temperature. The samples would retain some of their heat for a short time but the interior of the sample may not have equilibrated. While 300 C seems to be a fairly high temperature, this is just above the threshold for cellulose decomposition (Beall 1972a; Hileman et al. 1976).

TABLE 3. *Real densities (g/cc) of wood and charcoal heated at 1 C/min.* [a]

Treatment	Douglas-fir	Redwood	Western redcedar	Hard maple	Basswood
Control	1.472	—[b]	1.450 A	1.457 A	1.445 A
250/01	1.458	1.430	1.440 AB	1.452 A	1.438 AB
300	1.433	1.404	1.423　B	1.422	—[b]
350	1.419	1.342 A	1.352　　C	1.328	1.422　B
400	1.332	1.350 A	1.349　C	1.321	1.353　　C
600	1.310	1.298	1.257	1.214	1.338　C

[a] Those values in the same column followed by the same capital letter are not significantly different at the 0.05 probability level.
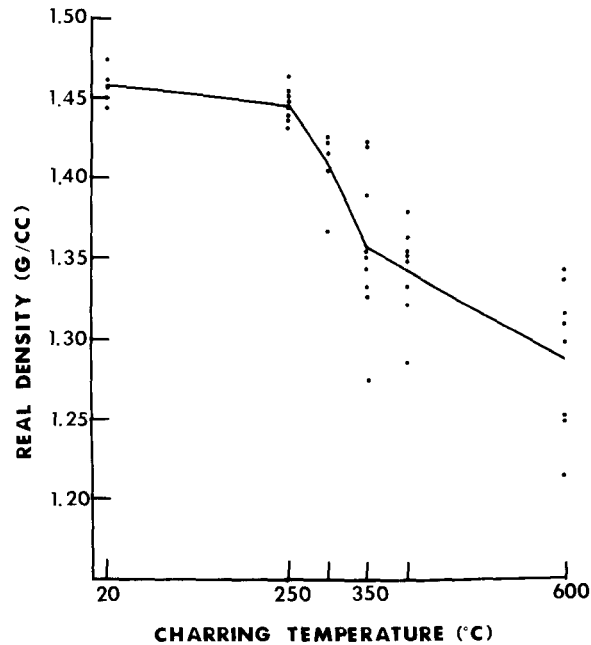[b] Missing sample.

Fig. 1.   Change in real density of wood and char substance for all species heated at the 1 C/min rate as a function of charring temperature. The solid line is used to illustrate the overall trend.

Real density

While the apparent density data were sometimes ambiguous, the real density data were well defined. The real densities of the wood substance and of the char were determined for all of the southern pine earlywood and latewood samples as well as for the white oak samples (Table 2). For the other species, only the samples heated at the 1 C/min rate were analyzed (Table 3). The patterns of ρ_0 change were essentially the same for the southern pine samples as for the white oak. Not enough sample material was available to define differences among species due to chemical composition. Pyrolysis does result in a marked decrease in the density of the matrix substance in all cases as indicated in Fig. 1 when the densities for all species heated at the 1 C/min rate are plotted against charring temperature. Overall values (summed over all species) indicate that up to 250 C there was little change in density. Between 300 and 350, the overall mean decreased from 1.45 to 1.41 g/cc. The maximum rate of density change was between 300 and 350 C when the density decreased from 1.41 to 1.36 g/cc. These temperature domains are again synonymous with the thermal degradation of cellulose. Beall (1972a) indicates that lignin and hemicelluloses begin to decompose below 200 C, while cellulose decomposition begins at about 280 C. Miller and Gorrie (1971) found that cotton cellulose decomposition was most rapid at 350 C. Similar results have been noted by Hileman et al. (1976) and Shafizadeh and DeGroot (1976).

Above 350 C, density continued to decrease but at a much slower rate. Blan-

kenhorn et al. (1978) had noted similar decreases in apparent and real density for black cherry charred in a similar fashion. Petroff and Doat (1978) indicated that changes in density were also a function of the chemical composition of the parent wood material. While there are obvious differences in chemical composition in the several species used in this study, not enough samples were examined to draw definitive conclusions.

REFERENCES

BEALL, F. C. 1977. Properties of wood during carbonization under fire conditions. Pages 107–114 *in* I. Goldstein, ed. Wood technology: Chemical aspects (ACS Symposium Series No. 43). Washington, DC.

———. 1972a. Introduction to thermal analysis in the combustion of wood. Wood Sci. 5(2):102–108.

———. 1972b. Density of hemicelluloses and their relationship to wood substance density. Wood Fiber 4:114–116.

BLANKENHORN, P. R., D. P. BARNES, D. E. KLINE, AND W. K. MURPHEY. 1978. Porosity and pore size distribution of black cherry carbonized in an inert atmosphere. Wood Sci. 11(1):23–29.

DUNCAN, D. B. 1975. T-tests and intervals for comparisons suggested by the data. Biometrics 31:339–359.

HARKINS, W. D., AND D. T. EWING. 1921. A high pressure due to adsorption, and the density and volume relations of charcoal. J. Am. Chem. Soc. 21:1787.

HILEMAN, F. D., L. H. WOJCIK, J. H. FUTRELL, AND I. N. EINHORN. 1976. Comparison of the thermal degradation products of α-cellulose and Douglas-fir under inert and oxidative conditions. Pages 49–71 *in* F. Shafizadeh, K. V. Sarkanen, and D. A. Tillman, eds. Thermal uses and properties of carbohydrates and lignins, Academic Press, New York.

HOWARD, H. C., AND G. A. HULETT. 1924. A study on the density of carbon. J. Phys. Chem. 28:1082.

HUMPHREYS, F. R., AND G. E. IRONSIDE. 1974. Charcoal from New South Wales species of timber. Forestry Comm. New South Wales. Tech. Pap. 23. 41 pp.

MANTELL, C. L. 1968. Carbon and graphite handbook. Interscience. New York.

MILLER, B., AND T. M. GORRIE. 1971. Chars produced from cellulose under various conditions of thermal decomposition. J. Polym. Sci.:Part C 36-3-19.

PETROFF, G., AND J. DOAT. 1978. Pyrolyse des bois tropicaux. Influence de la composition chimique des bois sur les produits de distillation. Bois et Forets des Tropiques. 177:51–64.

SHAFIZADEH, F., AND W. F. DEGROOT. 1976. Combustion characteristics of cellulosic fuels. Pages 1–7 *in* F. Shafizadeh, V. K. Sarkanen, and D. A. Tillman, eds. Thermal uses and properties of carbohydrates and lignins. Academic Press, New York.

SLOCUM, D. H., E. A. McGINNES, JR. AND F. C. BEALL. 1973. Charcoal yield, shrinkage and density changes during carbonization of oak and hickory woods. Wood Sci. 11(1):42–47.

STAMM, A. J. 1969. Correlations of structural variations of lignins with their specific gravities. Tappi 52(8):1498–1502.

———. 1964. Wood and cellulose science. Ronald Press. New York.

WENZL, H. F. J. 1970. The chemical technology of wood. Academic Press. New York.