A NOTE ON THE THERMALLY INDUCED CHANGES OF INTERVESSEL PITS IN BLACK CHERRY (*Prunus serotina* EHRH.)

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ABSTRACT

Dimensions of intervessel pits decrease as charring temperatures increase to 600 C; above 600 C pit apertures remain relatively constant. Reported increases in density of chars above 600 C are attributed to coalescing of the cell wall or changes in intercellular interstices shrinkage.

Keywords: Chars, rate carbonization, intervessel pitting, coalescing, pit measurements, SEM.

INTRODUCTION

The thermal degradation of wood as a route to an alternate energy source, chemical feedstock, or as a composite member has been investigated by various authors (Shafizadeh 1968; Knight et al. 1976; Soltes and Elder 1978; Blankenhorn et al. 1978). The liquid fraction derived from the thermal treatment of wood has been found to be a complex mixture of organic chemicals (Goos 1952). The solid carbonaceous char has been examined by McGinnes et al. (1976). Both product groups offer large potential as raw materials. Understanding this raw material base will provide data to assure wise use.

Studies of the anatomy of chars have shown that as the cell wall coalesces, the anatomical properties remain intact while relative dimensions change (Knudson and Williamson 1971). Slocum et al. (1978), Moore et al. (1974), and Blankenhorn et al. (1972) determined the rate of volumetric and other changes in char with process temperature changes. Wenzl (1970) showed that real density increased with increasing charring temperatures while apparent density decreased up to process temperature of 600 C, then increased slightly with continued temperature increases. Inflections in trends of the dynamic modulus (Blankenhorn et al. 1972) and external dimensions (Moore et al. 1974) of the char occur near 600 C. Such studies indicate that the rate of change of the anatomical properties may change at 600 C. The purpose of this study is to report on the observed changes in intervessel pore dimensions in the char of black cherry (*Prunus serotina* Ehrh.) throughout a range of temperatures from 250 C–1,000 C in order to correlate reported changes in properties of char with changes in intervessel pit dimensions.

As stated by Beall et al. (1974), shrinkage during carbonization must be understood if anatomical dimensions are to be measured. Yellow poplar carbonized at a maximum 600 C exhibited tangential vs. radial (T/R) dimension ratios that differed from moisture loss ratios, with a resultant char T/R of 1.23 vs. 1.78 for moisture changes. Dimensional changes of white oak carbonized at 700 C were reported to be consistent with the 1.73 value for T/R shrinkage associated with moisture loss (McGinnes et al. 1971). Tangential to longitudinal (T/L) ratios were 2.35 and 1.93 for the yellow poplar 600 C and 400 C chars, respectively, vs. 2.26 for the white oak at 400 C. Moore et al. (1974) showed shrinkage in samples carbonized in temperatures from 200 C to 400 C (473K to 673K) with a T/R of 1.3. Birch carbonized at 300 C (573K) exhibited a longitudinal shrinkage of nineteen percent. The longitudinal shrinkage continued to the 700 C (973K) maximum tested. Each of these studies showed a considerable difference between longitudinal shrinkage associated with moisture loss and that which occurs during carbonization. Much of the longitudinal shrinkage in the carbonized samples occurred after the tangential and radial dimensions had stabilized. Thus, at the lower temperature changes, pore dimensions should reflect changes in radial and tangential planes while later changes may occur in the longitudinal plane at the higher temperatures. This study also looked at the changes in the dimensions of the pores in relationship to the charring temperature.

McGinnes et al. (1974) found that upon commercial charcoaling, eastern red cedar and shortleaf pine showed significant amounts of shrinkage in the tangential diameter, the radial double cell-wall thickness, and the tangential double cell-wall thickness. White oak that had been charcoaled exhibited significant shrinkage in tangential vessel diameters, ray cell length, ray cell double cell-wall thickness and fiber double cell-wall thickness (McGinnes et al. 1976). Charcoaling seemed to have reduced the size of the bordered pits in shortleaf pine.

The work presented in this paper has been accomplished with scanning electron microscopy. This technique has been found to be an excellent way to examine charcoal samples. Light microscopy of charcoal has been attempted using polyethylene glycol as an embedding medium, but has given only marginally successful results (McGinnes et al. 1974). Because of the high carbon content of the samples, metallic coating, a requirement for most scanning electron microscopy, may be deleted; but coating has been shown to enhance resolution (McGinnes et al. 1974) and was used in this study.

METHODS AND MATERIALS

Samples of black cherry (*Prunus serotina* Ehrh.) were obtained that had been heated to temperatures of 250, 320, 350, 400, 500, 600, 700, 800, 900 and 1,000 C. (Blankenhorn et al. 1978). Samples were heated at 3 C/min in an atmosphere of flowing nitrogen to the target temperature. Once maximum temperature was attained, it was maintained for 2 h; then the sample was allowed to cool at 2 C/min to ambient temperature.

Samples were split to expose the tangential face and mounted on aluminum stubs. A drop of water, which contained a suspension of latex beads with a

TABLE 1. *Mean area, minor and major axis of intervessel pitting in black cherry* Prunus serotina *Ehrh measured on SEM photographs.*

Temperature (°C)	Planimeter measured area	Axis: Major mm	Axis: Minor mm	Calculated ellipse area
250	1.95^{AC}	1.85^{A}	0.61^{A}	3.52
320	3.16^{B}	1.78^{A}	1.05^{B}	5.88
350	2.31^{CD}	1.70^{A}	0.75^{CD}	6.08
400	2.66^{BD}	1.80^{A}	0.87^{E}	4.91
500	2.87^{B}	1.68^{A}	0.96^{B}	5.06
600	1.75^{A}	1.37^{B}	0.76^{CD}	3.26
700	1.59^{A}	1.31^{B}	0.80^{DE}	3.30
800	1.69^{AC}	1.37^{B}	0.67^{AC}	2.88
900	2.07^{AC}	1.35^{B}	0.79^{DE}	3.37
1,000	1.85^{AC}	1.34^{B}	0.66^{AC}	2.80

Conformity to an ellipse: Area measured = 0.5099 + 0.4254 area calculated, F = 387.10, r^2 = 0.6616 Values within a column with the same letter differ from all others at $P \leq 0.05$.

diameter of 0.481 micrometers, was placed on each sample. The beads were added so that experimental measurements on the photographs could be compared with a known dimension. Preliminary work indicated that working distance and accelerating voltage could not be held constant enough to give uniform magnifications that were critical for this work. After the water evaporated, the samples were coated with 200–300 Å of gold:palladium. Observations were carried out with a JEOL JSM-U3 scanning electron microscope at 0 tilt, 15 kV accelerating voltage, 13-mm working distance and 200 micrometer aperture diameter.

Micrographs of tangential intervessel pit apertures were taken at each temperature and at various locations on the surface of each sample. From each set of negative micrographs, twenty pit apertures were randomly selected, and their areas were measured with a planimeter. The major and minor axes were also measured with a micrometer. These and the planimeter readings were compared with average planimeter readings for the known diameter latex beads, so that absolute areas and dimensions could be calculated. The areal data were compared to that of an ellipse with major and minor dimensions equal to those measured on the photographs. The resulting data were examined with analysis of variance and regression techniques.

RESULTS AND DISCUSSION

The data from the measurement of pit apertures are presented in Table 1. Pit aperture area was found to differ by the analysis of variance and Duncan's miltiple range tests (Steel and Torrie 1960). The samples heated to 320, 350, 400 and 500 C were significantly lower than all others at the 5% level.

Results from the sample heated to 250 C are included for completeness, but little credence should be placed in them. Splitting of this sample occurred almost exclusively through the middle lamella, while all others failed almost exclusively through the cell wall itself. In order to include these data it must be assumed that the pit aperture is the same size at either end of the pit canal and the center of the cell-wall system.

The observations of previous authors, that the cellular integrity of the speci-

FIG. 1. Tangential intervessel pits of black cherry (*Prunus Serotina* EHRH) carbonized to 900 C showing latex beads used for calibration.

mens remained intact, (Blankenhorn et al. 1972) are confirmed. The cellular features of interest are readily recognizable even in the specimens heated to the highest temperatures. Splitting of the wood was found to occur through the middle lamella at the low temperature 250 C and through the cell wall at the higher temperatures (320 C and up). These observations confirm the results of Knudson and Williamson (1971).

The inflection point does occur at 600 C for areas and the major and minor axes (Fig. 1). The Duncan's test (Steel and Torrie 1960) indicates the major and minor axes of intervessel pits of black cherry that had been carbonized remain the same in charring temperatures above 600 C to 1,000 C. Blankenhorn et al. (1978) showed a linear relationship between apparent density and temperature to 600 C. Slocum et al. (1978) reported charcoal densities at a minimum when white oak and hickory were charred to 600 C. Apparently the coalescence of the cell wall at the lumen face ceases near 600 C, and changes in density and shrinkage of the cell in the longitudinal plane occur in the cell wall and between cells. Slocum et al. (1978) reported longitudinal shrinkage continued in samples held at 600 C for 2 h; however, longitudinal shrinkage did not continue in samples charred at 800 C regardless of dwell time. Sample density was minimal at 600 C as was sample mass. Density increased above 600 C charring temperatures. Changes in volume then must have continued in order for density to increase. From the results of this study, this volume change above charring temperatures of 600 C would occur within the cell wall and coalescense is not a surface phenomenon in the lumen.

The study shows a means to determining dimensions on SEM photos, that changes in intervessel pits occur up to 600 C in rate carbonized samples, and that density changes in char above 600 C occur as cell walls coalesce or shrinkage occurs between cell walls. The elliptical pattern of the intervessel pits is consistent with the change in the axes of the intervessel pitting in black cherry.

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