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Time domain-nuclear magnetic resonance study of chars from southern hardwoods ☆

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Abstract

Chars from the thermal degradation of silver maple (*Acer saccharinum*), red maple (*Acer rubrum*), sugar maple (*Acer saccharum*), and white oak (*Quercus* spp.), performed at temperatures from 250 to 350 °C, were examined using time domain-nuclear magnetic resonance spectroscopy. Prior to analysis, the chars were equilibrated under conditions insuring the presence of bound water only and both bound water and free water. Transverse relaxation times were found to be related to the moisture content of the chars, which varied with temperature. At elevated temperatures the number of signals assigned to free water decreased, indicative of an increase in pore size within the chars.

Keywords: Char; Moisture content; Relaxation; Southern hardwoods; Time domain-nuclear magnetic resonance

1. Introduction

The use of wood charcoal has been known to exist for thousands of years and is a major fuel source for a large proportion of the world's population. As a consequence there has been considerable research into this material. In addition to fuel, charcoal is used in the purification of water and liquid consumables, and as a reaction catalyst. As might be expected, the charcoals used in these varying applications have different properties, and therefore must be produced under diverse conditions.

The long history of charcoal use and extensive research efforts notwithstanding, there is still little control over the products or efficiency of the manufacturing process at the industrial level. To address this, the current paper seeks to apply low-field, time domain-nuclear magnetic resonance spectroscopy (NMR) as a probe to assess the properties of charcoals.

This method, related to magnetic resonance imaging, is applied as a quality control tool in various manufacturing settings including consumer products (foods and cosmetics), textiles, and well-logging in oil exploration. The instrumentation is compact, economical, requires minimal sample preparation and is rapid to perform.

In earlier work reported in the literature, time domain NMR spectroscopy has been used in the examination of wood, paper, and cellulose to elucidate the nature of water present in the material, and the impact of processing thereon. In a magnetic field, the hydrogen nuclei in a sample are aligned parallel or anti-parallel to the field. The application of a radio-frequency pulse will perturb the nuclei from their equilibrium condition, inducing a magnetic field. The time required for the decay of this magnetic field can be measured. This process is described by the spin-lattice (or longitudinal) relaxation time (T_1) and the spin–spin (or transverse) relaxation time (T_2). The former is a measure of rate at which energy is exchanged

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between the hydrogen nuclei and their surroundings, while the latter is concerned with the dissipation of energy to neighboring nuclei.

Among the first reported applications of relaxation rate measurements in wood dealt with quantifying and visualizing bound water and free water. Menon et al. [1], reported that free induction decays could be used as an absolute measure of moisture content, that T_1 values differed between western red cedar and Douglas fir, and that three T_2 values could be detected. The T_2 values were assigned to water in the cell wall, water in the rays and latewood tracheids, and water in earlywood tracheids. Menon et al. [2] used T_2 values and anatomical results to map moisture content distributions across several annual rings. Araujo et al. [3] developed and verified a model for the diffusion of water through heartwood and sapwood in spruce and redwood based on T_2 relaxation times, as related to anatomical features in wood. The nature of water in wood as studied by NMR has been evaluated for western red cedar [4,5] and white spruce [6], with the potential application of magnetic resonance imaging explored. NMR analysis of the heartwood and sapwood of maritime pine has shown that these tissues can be identified and that heartwood may exhibit material with longer relaxation times, attributed to the extractives that are present [7].

In general, these examinations of moisture content by NMR have relied on T_2 relaxation times, but Guzenda et al. [8] found that spin-lattice (T_1) values could also be correlated with moisture content. Spin-lattice relaxation times have also been used to assess the effect of pH on wood, indicating that the polymers are most mobile under neutral conditions, which is interpreted in terms of the ionization of functional groups that are present [9,10].

While the bulk of the foregoing work has concentrated on the relationship between wood and water as evaluated by NMR spectroscopy, other studies have used this technique to assess the nature of the wood as the result of various treatments. Although most of the observable relaxation times are still associated with the protons in water, the change in the behavior of the water is a reflection of the changes in the lignin and polysaccharides due to the conditions to which the wood has been subjected.

Paper has been extensively studied by an Italian group that has reported on the properties of historical papers [11,12], and the effects of sizing, pulping process, and enzymatic attack on contemporary material. Spin-lattice relaxation times have been determined for a number of different papers dating from the 15th and 16th centuries [11], and it was found that three components exist for both the cellulose and water. Plots of the longer relaxation times for cellulose and water revealed a linear relationship, interpreted as indicating the presence of a spin diffusion mechanism. Linear but poorer relationships are reported for the slow and intermediate relaxation times for the cellulose and water, taken to mean that paramagnetic species are present resulting in inefficient spin diffusion processes.

Historical papers from the 17th century have also been examined by the use of a newly developed method using an NMR-MOUSE (mobile universal surface explorer), a mobile sensor that can be used for nondestructive, single-sided testing of organic materials [12]. T_2 relaxation times were found to range from a short time of about 0.027 ms to a longer time in the range of 0.4–1.8 ms, the latter of which is taken as an indicator of the condition of the paper. Contemporary papers treated with sizing exhibited shortened spin-lattice relaxations, attributed to paramagnetic species in the sizing [13], while enzymatic treatment resulted in a readily observable reduction in T_2 [14].

Fungal and enzymatic attack as examined by NMR have also been reported for solid wood [14–16]. In the former work, magnetic resonance imaging was found to be capable of detecting early stages of fungal decay with more sensitivity than measurement of either mass or strength loss. Similarly, enzymatic attack was readily observed by differences in the T_2 values assigned to a component with an intermediate relaxation time of 0.1–0.5 ms.

Wood that has been subjected to thermal treatments has been examined using NMR to determine the affect of temperature on T_1 and $T_{1\rho}$ [17,18]. Using a heat treatment that has been proposed to impart decay resistance and dimensional stability to wood, it was reported that relatively mild conditions (115 °C) resulted in a shortened T_1. At elevated temperatures (180 and 230 °C) the relaxation times increased as did the distributions, taken as an increase in pore size [17]. In another study, wood charred to temperatures of up to 350 °C was examined with NMR to determine $T_{1\rho}$ values via three different techniques (direct $T_{1\rho}$ determination, variable spin lock and variable contact time). In this technique-oriented study [18], the variable contact time experiment was found to overestimate the relaxation time, while this is rectified by use of the variable spin lock experiment. The direct observation detected a short relaxing component not seen in the former methods.

In the current work, hardwoods from the southern United States that are typically used in filtration and purification applications have been charred over a wide temperature range, conditioned to varying moisture contents, and evaluated using low-field NMR. The objective of this work is to determine how changes in the processing temperature and species affect the properties of the charcoals, as reflected by the behavior of the water present.

2. Methods and materials

In the current work, silver maple (*Acer saccharinum*), red maple (*Acer rubrum*), sugar maple (*Acer saccharum*) and white oak (*Quercus* spp.) were heated in an inert environment to temperatures of 250, 275, 300, 325, and 350 °C for 2 h, along with an untreated control. As would be expected, the color of these chars darkened from light brown to black with increasing temperature. Samples approximately 1 cm × 2 cm × 5 cm were cut and were placed in an excess of deionized water, vacuum was drawn until the samples were saturated, and analogous samples were equilibrated at relative humidities of 88%. These conditions were used to provide samples with only bound water from the latter, and both bound water and free water from the former process.

NMR analyses were done using a Bruker mq20-Minispec, with a 0.47 T permanent magnet (20 MHz proton resonance frequency), operating at 40 °C. The transverse (T_2) relaxation times were determined using the Carr–Purcell–Meiboom–Gill (CPMG) sequence. For the samples that were equilibrated in a dessicator, 128 echoes were collected, with a pulse separation of 0.1 ms; the acquisition of 32 scans and a 5 s recycle delay. For the saturated samples the pulse separation was increased to

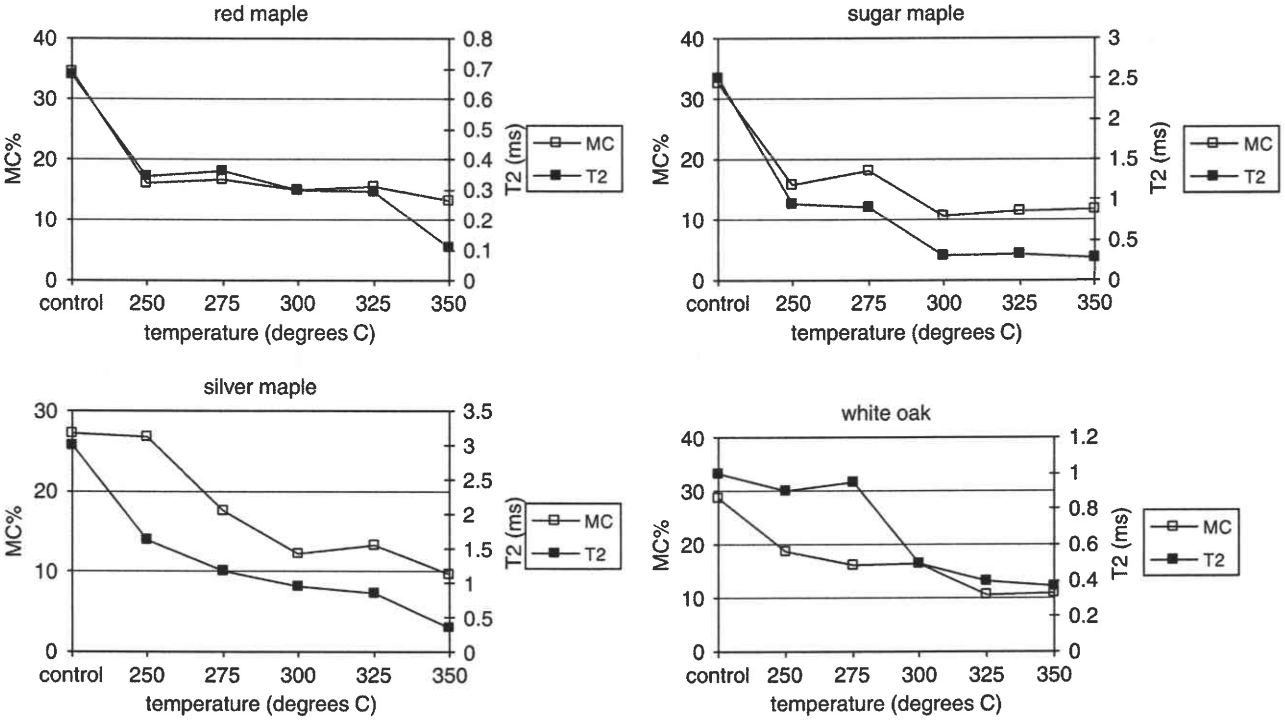

Fig. 1. Plots of moisture content (dry basis) and T_2 as a function of temperature, for samples equilibrated over deionized water in a dessicator.

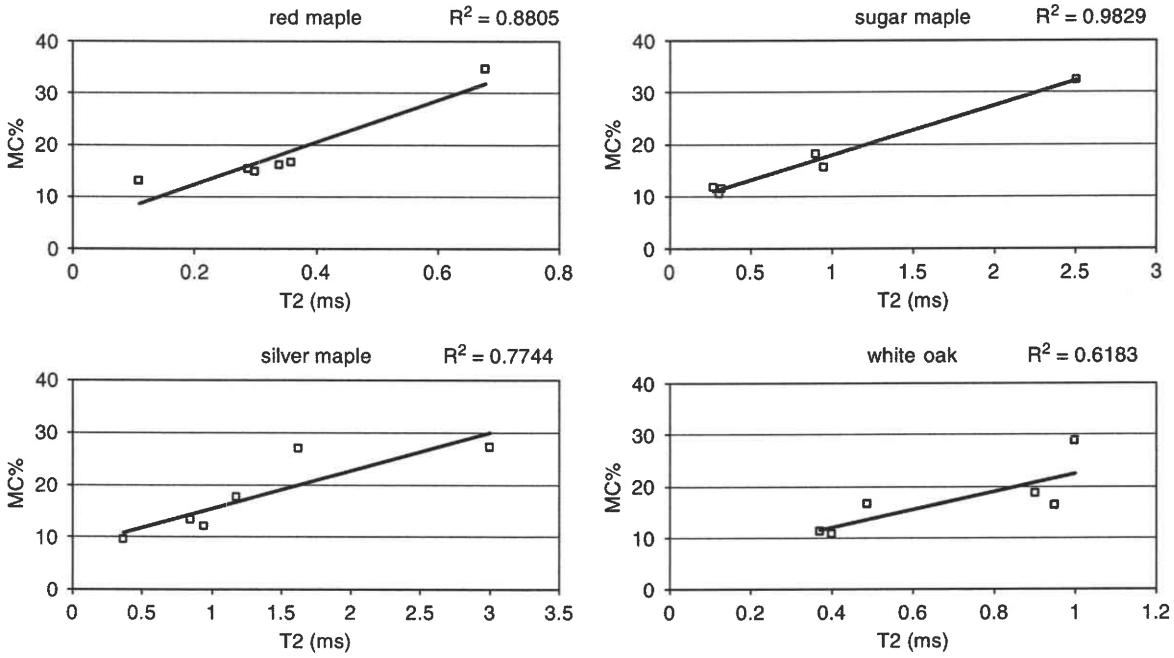

Fig. 2. Plots and linear regression results of moisture content (dry basis) vs. relaxation time for samples equilibrated over deionized water in a dessicator.

0.3 ms and 5000 echoes were collected, with all other values unchanged. The magnetization decay curves were analyzed using monoexponential and biexponential fitting routines to determine discrete values for T_2. In addition, Contin, which fits the curve using a Laplacian transformation as described by Provencher [19], was used to determine relaxation time distributions.

After the NMR analyses were completed, dry-basis moisture contents were determined by oven drying each char sample at 105 °C over night.

Carbon and hydrogen percentages for each sample were determined by a commercial laboratory (Galbraith Laboratories, Inc., Knoxville, TN) and the oxygen percentage was calculated by difference.

3. Results and discussion

The relaxation time and moisture content results for the samples conditioned in a dessicator over deionized water are as shown in Fig. 1. As would be expected, single predominant peaks representing the bound water were identified by NMR. In the current work (Fig. 1), the bound-water relaxation times for the controls ranged from 2.5–3 ms for silver maple and sugar maple to 1–0.75 ms for red maple

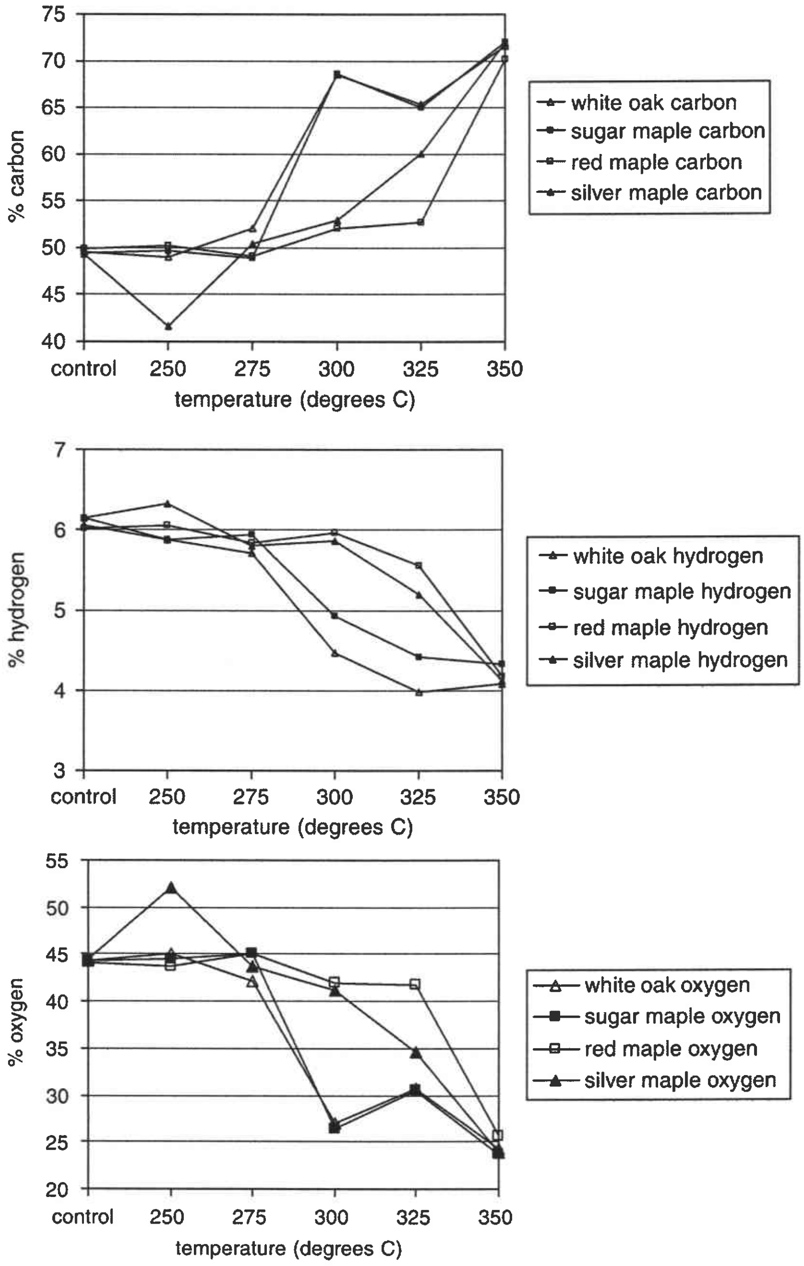

Fig. 3. Carbon, hydrogen and oxygen percentages as a function of temperature.

and white oak. Upon char formation, the relaxation time decreased for all four species and dramatically so for the maples even at 250 °C, becoming relatively constant especially beyond 300 °C. In contrast, the T_2s for the white oak samples are fairly constant up to 275 °C, and decrease sharply at 300 °C, beyond which little change is observed. Similarly, the moisture content decreased with treatment temperature, and in the cases of red maple and sugar maple, closely parallels the relaxation time. Correlations of moisture content with T_2 (Fig. 2) reveal very high R^2 values for red maple and sugar maple, with lower but still reasonable relationships for silver maple and white oak. Since, among the more common uses of time domain NMR is the determination of moisture content in quality control applications, these correlations are not unexpected. For the purposes of the current work, the observations might be interpreted in terms of extended relaxation times occurring due to interactions between water molecules, which would be much more frequent at higher moisture contents. In contrast, the relative isolation of the water molecules at lower moisture contents would reduce such interactions, resulting in a decrease in the relaxation times. Finally, while

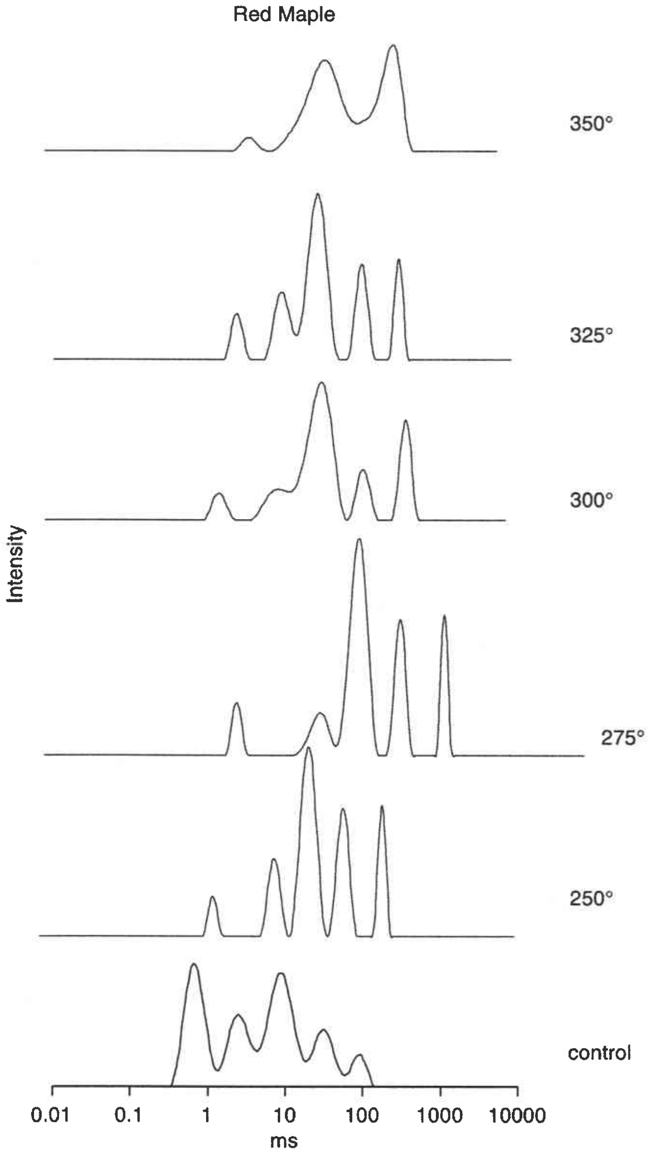

Fig. 4. Relaxation time distributions for saturated red maple.

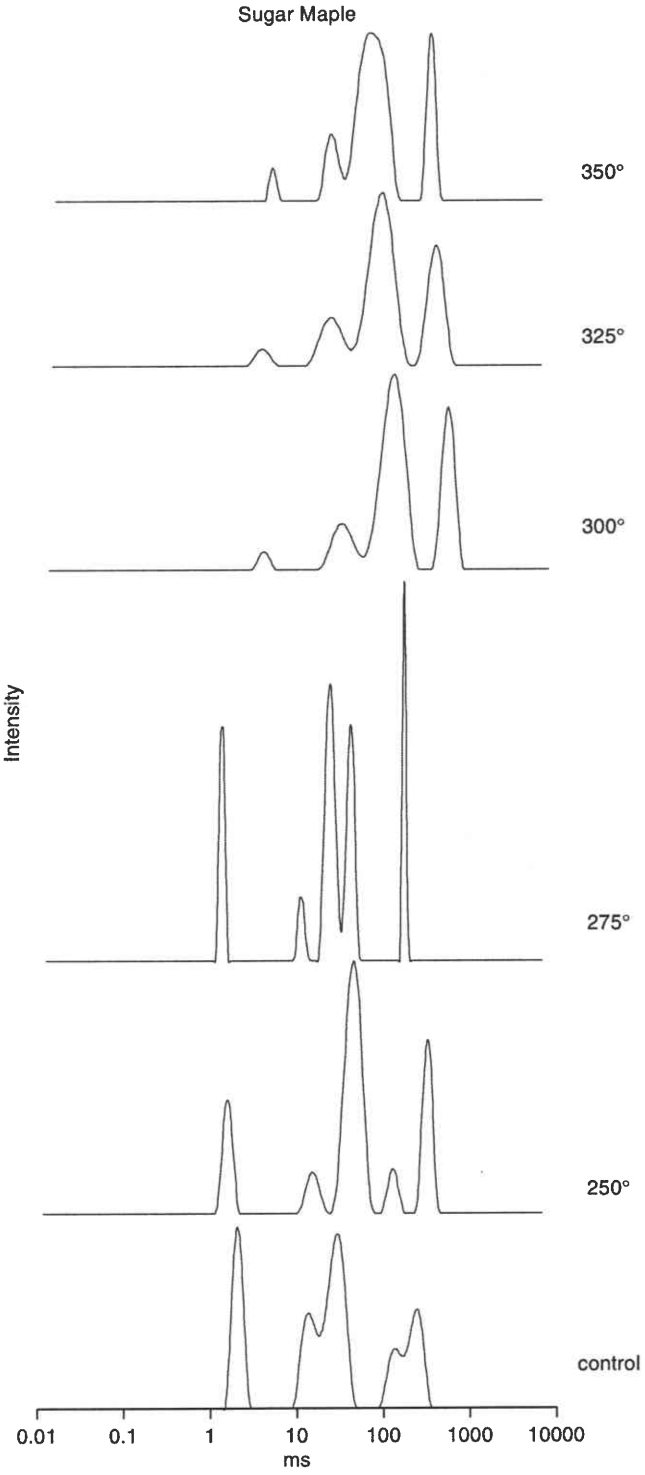

Fig. 5. Relaxation time distributions for saturated sugar maple.

it could be argued that residual volatiles in low-temperature chars could confound the moisture content determinations, no evidence of such material was observable by NMR.

Carbon, hydrogen, oxygen percentages for each sample are reported in Fig. 3, showing generally constant values up to 275 °C, beyond which the carbon percentage increases, while the hydrogen and oxygen percentages decrease. These trends are consistent with the moisture content and relaxation times from Fig. 1. Given that the oxygen and hydrogen percentages are decreasing with temperature, fewer sites will be available for water to interact with the cell wall, resulting in both lower moisture contents and shorter relaxation times.

The relaxation time distributions from Contin for the saturated samples are shown in Figs. 4–7. As would be expected, several peaks are present, representing both bound water and free water. In general, the control samples exhibit a well-defined peak at about 1 ms, assigned to the bound water, with 4–5 peaks at longer relaxation times due

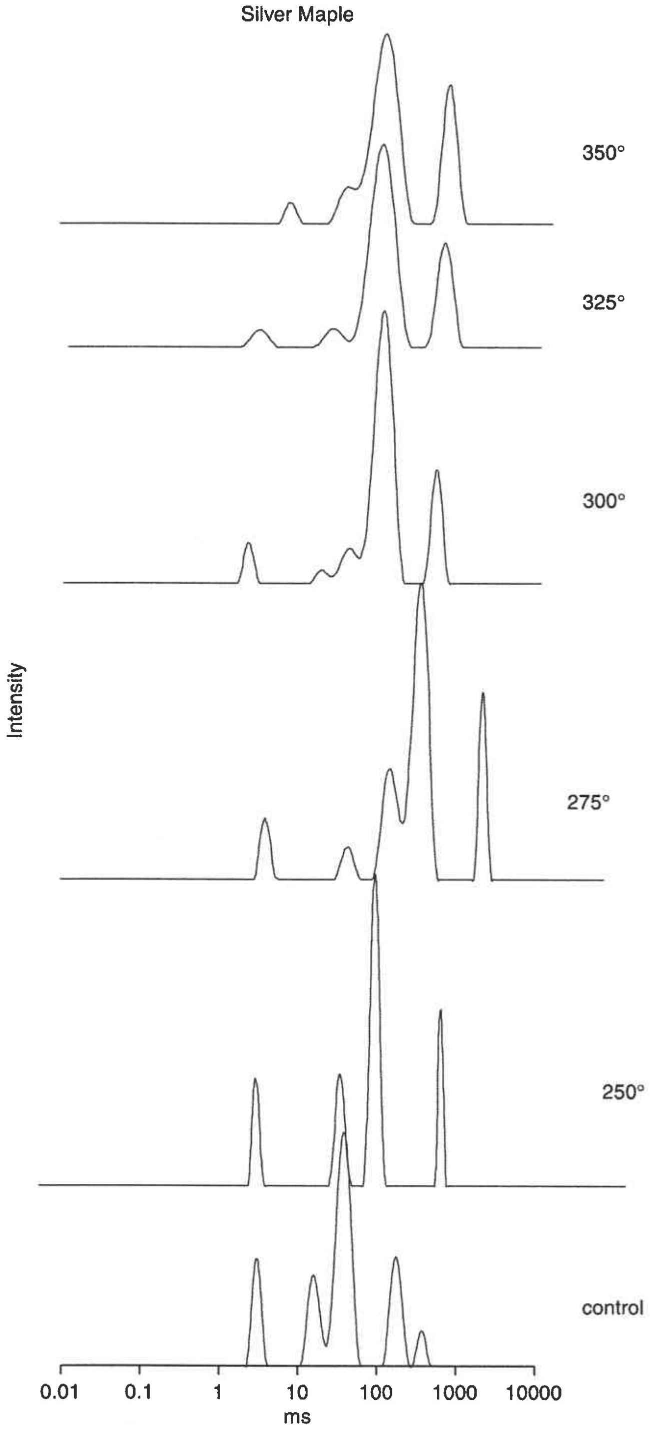

Fig. 6. Relaxation time distributions for saturated silver maple.

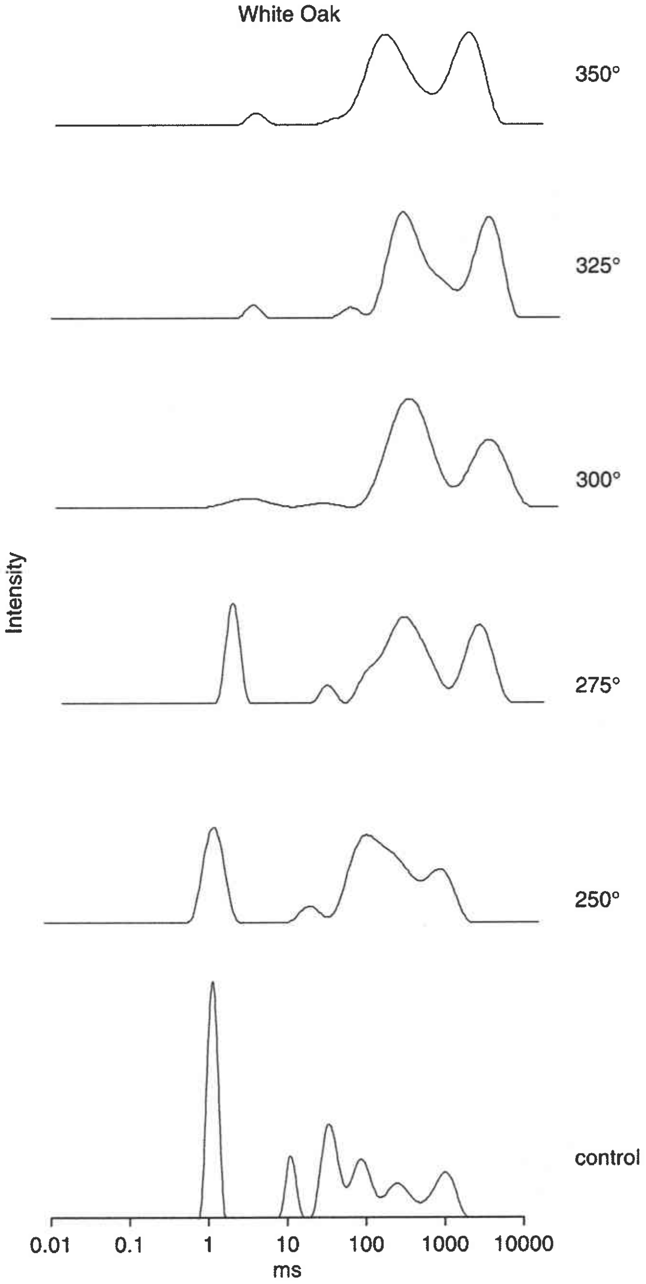

Fig. 7. Relaxation time distributions for saturated white oak.

to the bound water. The multiplicity of peaks with longer relaxation times may be due to varying environments in which the bound water occurs. The T_2 for the shortest relaxing peak is found to increase, while the relative amplitude decreases with temperature. It can also be seen that the number of free water peaks decreases with temperature, coalescing from 4–5 peaks to 2–3 peaks with relaxation times of about 100 and 1000 ms. This behavior is most apparent in the white oak sample, beginning at even 250 °C, while the maples require more severe conditions for this to occur. These observations may be due to the unification of smaller pores into larger openings, resulting in a more uniform environment in which the free water is contained.

The results from the discrete T_2 values are as shown in Fig. 8a–c. There is a general increase in relaxation times in all of these graphs, with white oak consistently longer than the maples. Furthermore, the T_2 values for the maples are relatively constant with temperature, while white oak exhibits a large change from 250 to 275 °C, after which the relaxation times are fairly constant. The moisture content of the saturated samples for each species as a function of temperature is shown in Fig. 8d. In contrast to the samples that were equilibrated in a dessicator over deionized water, the moisture content of these samples increases with temperature. Although the T_2 values and moisture content are both generally increasing with temperature, the correspondence between these values is not as great as was seen in the samples with only bound water; R^2 values were generally less than 0.50. The qualitative, positive relationship between moisture content for these samples and the discrete relaxation time is consistent with the more quantitative results found for the samples at lower moisture contents. It can also be seen from Fig. 8a–c that while the T_2 relaxation times (both mono- and biexponential) are similar for the maples, the white oak is quite different, probably due to the greater anatomical heterogeneity of the ring porous white oak, as compared to the diffuse porous maples.

In summary, when only bound water is present, the moisture content, spin–spin relaxation time, oxygen and hydrogen content all decrease with temperature, for all four species. These results are probably driven by the observed chemical changes. As the oxygen and hydrogen content decreases there are fewer sites on the charcoal surfaces with which water can interact, thus lowering the moisture content. This is reflected in the T_2 values, which are shortened as the amount of water decreases. The fluctuations observed in the data presented in Fig. 8 are no doubt due to the complex and differential alterations in both structure and chemistry resulting from the thermal treatments.

Upon saturation, the moisture content and T_2 values generally increase with temperature, consistent with the results seen at the lower moisture content. As temperature increased the number of peaks assigned to free water decreased, indicating that the environments in which the water is held are becoming more uniform. These

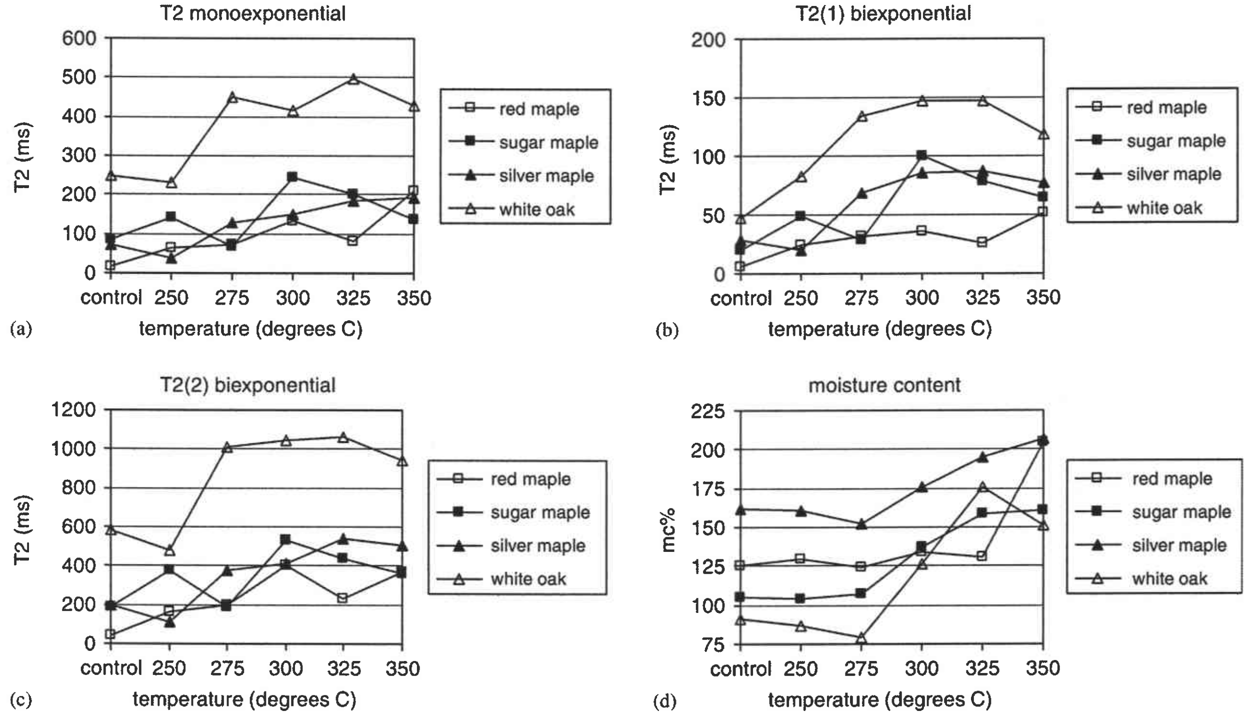

Fig. 8. (a) Discrete monoexponential relaxation times for saturated samples, (b) discrete biexponential relaxation times for saturated samples (short T_2), (c) discrete biexponential relaxation times for saturated samples (long T_2), (d) moisture content (dry basis) for saturated samples.

observations taken together may be interpreted as an increase in porosity with temperature. In conclusion, it can be seen that changes in chemistry and physical structure of the charred material affect the behavior of water, which is detectable with low-field, time domain-nuclear magnetic resonance spectroscopy.

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