

HEAT-INDUCED CHEMICAL AND COLOR CHANGES OF EXTRACTIVE-FREE BLACK LOCUST (*ROBINIA PSEUDOACACIA*) WOOD

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To investigate chemical and color changes of the polymeric constituents of black locust (*Robinia pseudoacacia*) wood during heat treatment, extractive-free wood flour was conditioned to 30% initial moisture content (MC) and heated for 24 h at 120 °C in either an oxygen or nitrogen atmosphere. The color change was measured using the CIELAB color system. Chemical changes of the wood components were determined by means of solid state cross-polarization/magic angle spinning ¹³C-nuclear magnetic resonance (CPMAS-¹³C-NMR), Fourier transform infrared (FTIR), diffuse reflectance UV-Vis (DRUV) spectroscopy, and elemental (CHN) analysis. The results showed that lightness (*L*^{*}) decreased, while chromaticity indexes (*a*^{*} and *b*^{*}) and chroma (*C*^{*}) increased after heat treatment. There was greater color difference (ΔE^*) in the samples heated in the presence of oxygen compared to nitrogen. CHN analysis showed an increase in hydrogen and oxygen and a decrease in carbon content. NMR spectra confirmed the cleavage of the β -O-4 structure in the lignin, resulting in a decrease in etherified lignin units and an increase in phenolic structures. DRUV and FTIR spectra confirmed the formation of extensive conjugated structures, such as unsaturated ketones and quinones due to the cleavage of the lignin units. Formation of quinones can be attributed to heat treatment in the presence of oxygen.

Keywords: Heat treatment; Wood; Chemical changes; Color; ¹³C-NMR; FTIR-ATR; DRUV

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INTRODUCTION

Heat treatment of wood has drawn a great deal of attention, being an ecological wood protection treatment that does not use any harmful chemicals (Wikberg 2004). Exposure of wood to high temperature changes both its chemical properties and its appearance (Nuopponen *et al.* 2004). This color change is often viewed positively, especially in hardwoods. It creates a potential for other wood species to reach new markets where more exotic hardwoods are normally used (Syrjänen 2001; Militz 2002; Patzelt *et al.* 2003; Bekhta and Niemz 2003; Christmas *et al.* 2005). Enhancing the appearance of less attractive wood without chemical additives is of great interest to researchers and consumers. A better understanding of the chemical property-appearance relationship of wood can provide competitive market advantage for forest products.

The chemical reactions that occur during heat treatment are often related to the formation of colored oxidation and degradation products involving the cell wall constituents and extractives located in cell vacuoles (Sehistedt-Persson 2003; Sundqvist 2004; Bekhta 2003). These changes are complex and are still far from being completely understood. Thermal modification of wood is commercially by far one of the most advanced processes, compared with other wood modification technologies that are already in the market (Gallum and Hill 2006). It is of fundamental importance to investigate the changes in wood constituents at the molecular level to develop new heat treatment techniques for producing high-quality wood products. Heat treatment is known to promote a range of chemical changes of the different wood constituents (Tjeerdsma *et al.* 1998). For example, it can lead to decomposition of hemicelluloses to furfurals and other colored compounds (Sivonen *et al.* 2002). The amorphous regions of cellulose can be degraded, which results in an increase in the degree of crystallinity (Bekhta and Niemz 2003; Koch 2000; Kodaera and Higuchi 1979) and hydrophobicity (Bhuiyan 2000; Wikberg 2004; Boonstra 2006). Lignin can undergo cleavage of β -O-4 linkages, resulting in higher concentrations of phenolic groups and a decrease of methoxyl content, leading to auto-condensation of lignin to a more condensed structure (Wikberg and Maunu 2004). At high temperatures, lignin can also produce complexes with phenolic catechin (Kosíková and Cosentino 1999) and cellulose.

Generally, the effects of heat treatment on wood depend on heating conditions including temperature, moisture content, and presence or absence of oxygen. The thermal decomposition reactions of the wood polymers can be accelerated by the presence of oxygen (Mitsui 2001; Bekhta 2003), but oxygen will lead to oxidative reactions that can be prevented by heating in an inert environment such as oil, nitrogen, or steam. In addition, according to Stamm (1956), thermal degradation is greater in a system where moisture is present. It is known that during thermal treatment of wood under moist conditions, carbonic acids, mainly acetic acid, are initially formed as a result of the cleavage of the acetyl groups of hemicelluloses (Kollmann and Fengel 1965; Dietrichs *et al.* 1978; Bourgois and Guyonnet 1988).

Clearly, a range of chemical reactions occur simultaneously when wood is heated, which creates more difficulty in determining the changes that take place in different wood polymers. Analysis of these changes is further complicated by interactions between the different wood constituents. Thus analysis performed on an isolated wood component such as lignin can yield a very different result compared with native wood. It is known that lignin is subject to degradation under heat treatment, which results in the formation of conjugated structures that can also contribute to color formation (Windeisen 2008; Yamauchi 2005). Hiltunen *et al.* (2006) reported the characterization of Brauns' lignin after vacuum drying process, which demonstrated that Brauns' lignin sustained a chemical change during vacuum drying of the wood, and that such a chemical change can affect wood color.

Black locust is a fast growing wood species with superior mechanical properties and is used in furniture manufacture, but its discoloration characteristics during the wood drying process limit its application. There is little knowledge about how the heat-induced chemical changes of this wood are related to its aesthetic characteristics. The present paper describes the effect of heat treatment on chemical and color change of some

polymeric constituents of black locust. There is a lack of sufficient information on chemical properties for this kind of wood species. It was concluded that this color change was caused primarily by changes in the chemical structures of polar extractives (Fan 2010). The current work investigated chemical changes of the extractive-free black locust wood flour after heat treatment under different conditions, with the objective of elucidating the effect of the major wood components, without the presence of extractives, on the color change of black locust wood during the drying process at high temperatures. Industrial experience and research have shown that discoloration of wood are not only on surface, but also in the entire board. Therefore, wood flour could be more representative for the overall wood discoloration status. Results from this study can be used in developing suitable drying processes for producing black locust wood with a desirable surface color that can be controlled to closely resemble that of exotic hardwoods.

EXPERIMENTAL

Wood Sample Preparation

Black locust wood was harvested from Heilongjiang province in northeast China. The logs were debarked then dried in ambient conditions. The heartwood was employed. After being ground and screened, the 40 to 60 mesh (250 to 425 μm) wood flour was selected for testing and sealed in a polyethylene (PE) bag at room temperature and 13% relative humidity (RH) until required for further experimentation. The control was prepared by vacuum drying the extracted wood flour at room temperature for 7 days.

Extraction of Wood Flour

The extracted wood flour was obtained by successive extraction with 50% ethanol (ethanol/water 50/50 v/v), 75% ethanol (ethanol/water 75/25 v/v), absolute ethanol, acetone, benzene, and ether in a Soxhlet apparatus. To ensure complete removal of extractives, successive extractions were performed for more than 48 hours for each operation until the corresponding reflux extractant turned colorless. Finally, the extracted wood flour was dried in a vacuum at room temperature for more than 7 days (the moisture content of the wood flour was nearly 0%) and kept in sealed storage until further required for color and surface chemical test and heat treatment.

Heat Treatment

Extractive-free wood flour was conditioned with distilled water to a moisture content of 30% prior to heat treatment. The heat treatment was carried out in a sealed stainless steel autoclave with a Teflon vessel in either oxygen or nitrogen atmosphere in an electric oven. Samples of wood flour were put into an oven which heated to 120 $^{\circ}\text{C}$ previously. The heat treatment was carried out for 24 hours at 120 $^{\circ}\text{C}$ (The heat treatment condition employed is consistent with industrial wood drying process). The heat-treated samples were cooled and vacuum dried at room temperature for more than 7 days (the moisture content of the wood flour was nearly 0%) in the dark prior to color, DRUV, FTIR-ATR, CPMAS- ^{13}C -NMR, and CHN analyses.

Measurement of Color Parameters

The color change of extractive-free wood flour after heat treatment in either oxygen or nitrogen atmosphere was analyzed by a DF110 colorimeter (Guangzhou ABC Co., Ltd) with a D65 standard illuminant and 10° standard observer. The wood flour was pressed into pellets with a die of 30 mm in diameter. Color parameters were measured using five replicates of each treated and untreated sample and an average value was reported. The color parameters L^* , a^* , b^* , and C^* were determined by the CIELAB system, in which lightness (L^*) was recorded from black (0%) to white (100%), a^* from green (-a) to red (+a), and b^* from blue (-b) to yellow (+b). The corresponding variations ΔL^* , Δa^* , Δb^* , and ΔC^* with heat treatments were calculated using the unheated control as a reference (e.g. $\Delta L^* = L^*_{treated} - L^*_{ref}$). Total color difference (ΔE^*) between heat treated and unheated control was calculated using Equation 1.

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \quad (1)$$

CHN Elemental Analysis

CHN elemental analysis of the extractive-free samples before and after heat treatment was performed on a Vario El micro-analysis with a micro cube (Elementar Analysensysteme GmbH). Three replicate samples were analyzed.

CPMAS-¹³C-NMR

Solid state CP-MAS (cross-polarization/magic angle spinning) ¹³C NMR was performed on a Brüker MSL 300 spectrometer instrument. The resonance frequency for ¹³C was 75.47 MHz and the sample was spun at the magic angle with a speed of 6.0 kHz. The contact time was 3.0 ms and the relaxation delay was 1.5 s. The number of transients was 32,768.

FTIR-ATR Spectra

FTIR spectroscopy was performed on a Tensor 27 spectrophotometer (Brüker) to provide information about functional groups present in the wood flour. Spectra were obtained by attenuated total reflectance (ATR) spectroscopy. During analysis, the surface of the sample was in contact with a ZnSe crystal with a 45° angle of incidence. Scans were run at a resolution of 2 cm⁻¹. For each sample, 32 scans were recorded in absorbance units from 4000 to 700 cm⁻¹. The FTIR-ATR spectra were baseline-corrected using the Brüker OPUS software and normalized on the peak at 1050 cm⁻¹ as the internal standard (Windeisen and Wegener 2008). Five replicate samples were analyzed.

DRUV Spectra

The diffuse reflectance spectra of extractive-free samples before and after heat treatment were recorded at room temperature on a UV-3100 UV-Vis near-IR spectrophotometer equipped with an integrating sphere. The reflectance spectra were recorded against BaSO₄ as a white (R_∞) optical standard. The wood flour was pressed into pellets prior to DRUV analysis and the study was carried out over the wavelength range 240 to 800 nm. The reflectance spectra of wood samples were converted into K/S spectra using the Kubelka-Munk Equation (2) (Schmidt and Heitner 1999).

$$K/S = \frac{(1-R)^2}{2R} \quad (2)$$

where R is the measured reflectance, K and S are the absorption and scattering coefficients, respectively. Difference spectra were calculated by subtracting the K/S absorption spectrum of non-heated extractive-free samples from the heat treated samples (Equation 3), and plotted as a function of wavelength to identify the apparent absorption maxima. Based on the Kubelka-Munk Theory, it can be assumed that $\Delta(K/S)$ signifies appearance or formation of chromophores during heat treatment.

$$\Delta(K/S) = (K/S)_{after} - (K/S)_{before} \quad (3)$$

RESULTS AND DISCUSSION

Changes In Color Parameters After Heat Treatment

The changes in CIELAB parameters, ΔL^* , Δa^* , Δb^* , ΔC^* and total color difference (ΔE^*) of the extractive-free wood flour heat-treated in either oxygen or nitrogen atmospheres are shown in Table 1.

Table 1. ΔL^* , Δa^* , Δb^* , ΔC^* , and Total Color Difference (ΔE^*) of Samples Heat-Treated in Oxygen and in Nitrogen

	Heat-Treated in Oxygen Atmosphere	Heat-Treated in Nitrogen Atmosphere
ΔL^*	-24.6 (± 0.45)	-19.09 (± 0.38)
Δa^*	5.72 (± 0.23)	5.48 (± 0.19)
Δb^*	4.32 (± 0.31)	5.68 (± 0.32)
ΔC^*	6.05 (± 0.36)	7.18 (± 0.27)
ΔE^*	25.63 (± 0.29)	20.66 (± 0.22)
^a Numbers in parentheses represent the standard deviation of five replicates.		

After heat treatment in oxygen or nitrogen atmosphere, the wood flour changed their color behavior regarding ΔL^* , Δa^* , Δb^* , and ΔC^* values. According to ΔL^* values, decreasing brightening could be observed. The darkening was more severe when heat treated in oxygen ($\Delta L^* = -24.6$) compared to in nitrogen ($\Delta L^* = -19.09$). This indicates that more visible light-absorbing substances are formed upon heating in the presence of oxygen. In the case of Δa^* values, the wood flour showed a reddish behavior after heat treatment either in oxygen ($\Delta a^* = 5.72$) or nitrogen ($\Delta a^* = 5.48$) atmosphere. According to Δb^* values, the yellowish behavior of the wood flour increased after heat treatment in oxygen ($\Delta b^* = 4.32$) or in nitrogen ($\Delta b^* = 5.68$) atmosphere. This suggests that color substances absorbed in the violet-green region of the visible spectrum to produce a reddish and yellowish color were formed during heat treatment. These substances were

considered as quinone-like substances that formed through degradation and/or oxidation reactions (Sundqvist 2004). After heat treatment, the color of the wood flour became vivid (increase in C^* values). The yellowish behavior of the wood flour could be partly caused by low molecular weight phenolic substances, which have a pale yellow color (Hiltunen *et al.* 2006) and are formed during heat treatment. In the absence of extractives, the source of the phenolic substances could be predominantly lignin degradation and oxidation reactions. As expected, the total color difference (ΔE^*) of the heat-treated samples was greater in the presence of oxygen compared with nitrogen.

Results from this study showed that, oxygen plays a very important role in the chemical changes of extractive-free wood flour when exposed to heat. New chromophoric groups produced from lignin by way of oxidation and condensation. Although the degradation and oxidation of polysaccharides such as hemicellulose can be a contributing factor in the formation of color substances, polysaccharides are comparatively stable in heat treatment at such low temperatures due to their saturated structure (Sehistedt-Persson 2003; Sundqvist 2004). Therefore, the effect of degradation of hemicellulose on color change should be relatively small compared with lignin.

CHN Elemental Analysis

Chemical structure modifications are usually associated with an elemental change of the molecules. Therefore, elemental analysis can further the understanding of these changes related to heat treatment. The contents of C, H, N, and O in extractive-free wood flour before and after heat treatment in both oxygen and nitrogen atmospheres are shown in Table 2.

Table 2. C, H, N, and O Ratios Before and After Heat Treatment in Oxygen and Nitrogen Atmospheres

Sample	Percentage of Dry Weight			
	N	C	H	O
Control	0.174 (± 0.006) ^a	46.039 (± 0.022)	6.260 (± 0.003)	47.527 (± 0.015)
Heated in N ₂ Atmosphere	0.219 (± 0.004)	47.825 (± 0.023)	6.171 (± 0.001)	45.785 (± 0.028)
Heated in O ₂ Atmosphere	0.251 (± 0.002)	48.260 (± 0.001)	6.050 (± 0.002)	45.439 (± 0.004)

^a Values in parentheses represent the standard deviation of three replicates.

There was a slight decrease in hydrogen and oxygen content, which resulted in a relatively higher carbon content after heating in oxygen or nitrogen atmosphere, and the changes were slightly greater in oxygen compared with nitrogen. Figure 1 shows the O/C and H/C ratios in the extractive-free samples after heat treatment in the presence of nitrogen and oxygen. It can be seen that O/C and H/C ratios after heat treatment were slightly lower compared with the control non-heated samples. This decrease in the O/C ratio suggests that there was a loss of hydroxyl groups in the form of water as suggested by Abatzoglou *et al.* (1990), who observed that heat treatment of wood results in the elimination of water due to dehydration reactions, which in turn result in a decrease in both hydrogen and oxygen content.

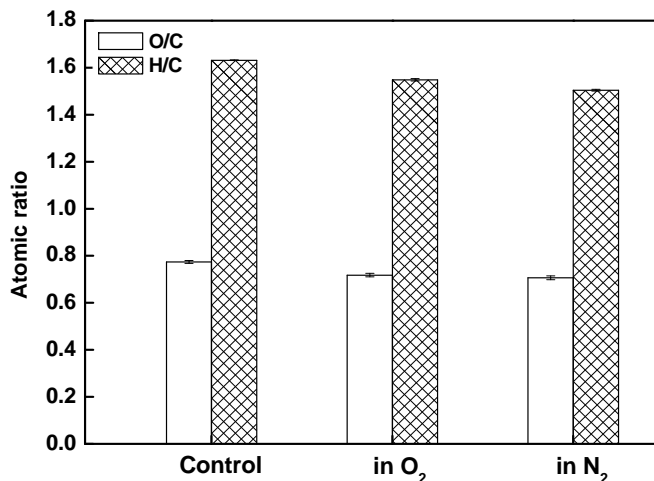


Fig. 1. O/C and H/C ratio in the extractive-free samples heat-treated in nitrogen and oxygen, respectively.

It is known that during the heat treatment of wood under moist conditions, carbonic acids, mainly acetic acid, are produced as a result of cleavage of the acetyl groups in hemicelluloses (Bourgois and Guyonnet 1988). Hemicellulose can undergo acid hydrolysis to form oligomeric and monomeric structures (Carrasco and Roy 1992), which can be transformed to furans and their condensation products (Ellis and Paszner 1994). Such reactions can contribute to a decrease of the hydrogen and oxygen content in the form of water molecules.

CPMAS-¹³C-NMR

Figure 2 shows the CPMAS-¹³C NMR spectra of the extractive-free samples before and after heat treatment in both oxygen and nitrogen atmospheres. The spectra were normalized to cellulose C1 signal at 105 ppm, which changes least upon heating.

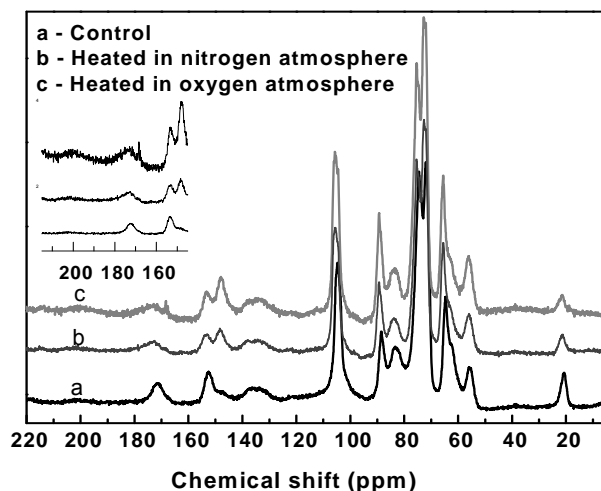


Fig. 2. CPMAS-¹³C-NMR spectra of the samples before and after heat treatment in N₂ and O₂

It can be seen that the signals at 173 ppm and 21 ppm, which correspond to acetyl groups in hemicelluloses (Gil and Neto 1999), decreased after heat treatment. Deacetylation of hemicelluloses results in the formation of acetic acid, which can further catalyze the depolymerization of polysaccharides. The signal at 136 ppm, assigned to C-1 and C-4 of etherified syringyl (S) and guaiacyl (G) units, is stable during heat treatment. The signal at 153 ppm decreased, while the signal at 148 ppm increased substantially after heat treatment. These changes were more obvious when the sample was heated under oxygen atmosphere. The signal at 153 ppm is assigned to the structure of etherified syringyl (S) units at C-3 and C-5 (Maunu 2002), and the signal at 148 ppm is assigned to phenolic syringyl (S) units and guaiacyl (G) units. Change in the relative intensities of 153 ppm and 148 ppm suggests cleavage of the β -O-4 linkage, which results in an increase in phenolic structure and a decrease in the etherified lignin structures during heat treatment. The second contribution to the marked growth of the band at 148 ppm is also due to the well-known reaction producing furfural from hemicelluloses under acid conditions (Gfeller *et al.* 2003), here due to the liberation of acetic acid from the acetyl groups of the hemicelluloses. The signal near 200 ppm assigned to the carboxylic groups in quinone structures intensified a little after heat treatment in the presence of oxygen. This signifies that the phenolic groups can be readily oxidized to quinone structures in the presence of oxygen, which would make the wood intensely colored.

FTIR-ATR Spectra

Figure 3 presents the FTIR-ATR spectra (normalized at $1,050\text{ cm}^{-1}$) of the extractive-free samples before and after heat treatment in both oxygen and nitrogen atmospheres.

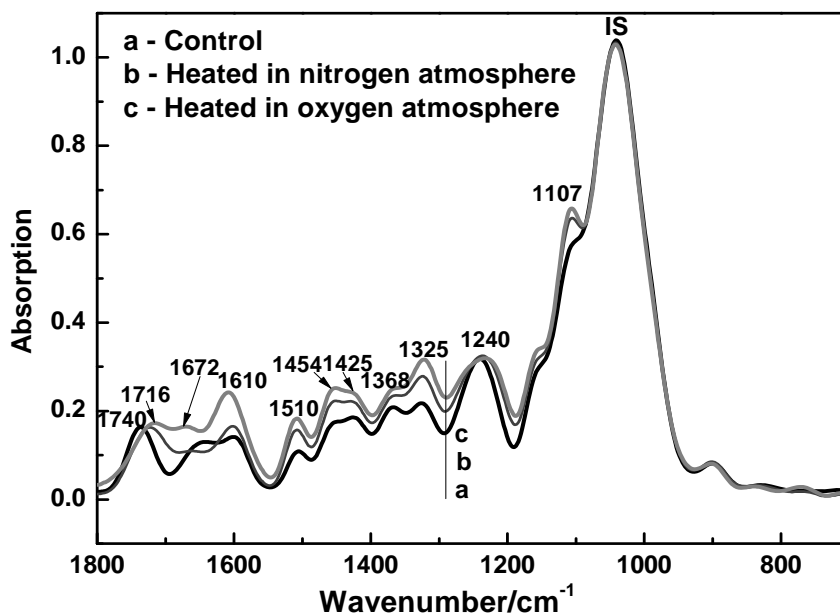


Fig. 3. FTIR-ATR spectra of the samples before and after heat treatment in nitrogen and in oxygen

It can be seen that the absorptions in the spectral region 1100 to 1800 cm^{-1} increased after heat treatment. The increased intensity of the aromatic skeletal vibration at 1602 cm^{-1} and 1505 cm^{-1} , and the shift from 1602 cm^{-1} to 1610 cm^{-1} after heat treatment could be caused by cleavage of the propyl groups in lignin (Ucar *et al.* 2005), such as the abundant β -O-4 structure in lignin, which is consistent with the results from ^{13}C NMR spectral analysis. After heat treatment, the peak at 1325 cm^{-1} also increased, which suggests the existence of products of condensation reactions in lignin according to Faix (1992). The intensified peak at 1454 cm^{-1} signifies the formation of new conjugated double bonds due to heat treatment. These results are also consistent with those obtained from ^{13}C NMR spectral analysis. The peak at 1740 cm^{-1} shifted to a lower wavenumber of 1716 cm^{-1} ; this suggests the decrease in ester structures and carboxyl groups and the formation of α , β -unsaturated ketone, and α -C=O in lignin structure. These will contribute to the darkening of heat-treated samples. In addition, the bands that are associated with the aromatic rings (1510 cm^{-1} and 1425 cm^{-1}), asymmetric bending of methyl groups (1454 cm^{-1}) increased after heat treatment, and the intensity of these bands was greater when heat treated in oxygen compared to nitrogen. The increase in the intensity of the peak at 1510 cm^{-1} indicates splitting of the aliphatic side chains in lignin and cross-linking formation by condensation reactions of lignin (Colom *et al.* 2003; Muller *et al.* 2003; Pandey and Pitman 2003).

The new peak at 1672 cm^{-1} after heat treatment in the presence of oxygen can be attributed to the formation of a quinone structure (Yao and Sun 1988) in the extractive-free wood fiber, which is in agreement with the results from NMR analysis and can cause discoloration. The increase in the C-O peak at 1107 cm^{-1} can be the result of a different reaction taking place in the extractive-free wood flour during heat treatment. This might indicate the formation of new alcohols and esters.

Diffuse Reflectance UV-Vis Spectra Analysis

The K/S and the difference (heated minus unheated sample) spectra ($\Delta(K/S)$) obtained from the extractive-free samples heat-treated in either oxygen or nitrogen atmosphere are plotted in Fig. 4a and 4b, respectively. It can be seen that the absorptions in the spectral region 290 to 800 nm clearly increased after heat treatment, which suggests the formation of conjugated structures due to heat treatment, even in absence of oxygen. A relatively stronger absorption could be observed when the sample was heat-treated in the presence of oxygen. This suggests that oxidation reactions can contribute to the further formation of conjugated structures during heat treatment. An absorption maximum was observed at 340 nm after heat treatment under nitrogen atmosphere, and the absorption maximum became stronger and shifted to red at 350 nm when heat-treated under oxygen atmosphere. The intensified band near 340 to 350 nm is consistent with the formation of extensive conjugated structures, such as the $\text{C}_\alpha=\text{C}_\beta$ double bond, β -C=O structure, and the conjugated carbonyl group in side chains of lignin such as coniferyl aldehyde (Polcin and Rapson 1969). An increase in those peaks signified that condensation and oxidation, as well as elimination reactions occurred during the heating process. Figure 4b shows the increase in the intensity of the band at 405 nm. The intensification of this peak should be attributed to the formation of quinone structures, α,β -unsaturated ketone, and α -C=O in lignin, which resulted from radical oxidation of

aromatic hydroxyl groups of lignin during heat treatment. This is consistent with the increase in a^* and b^* values after heat treatment.

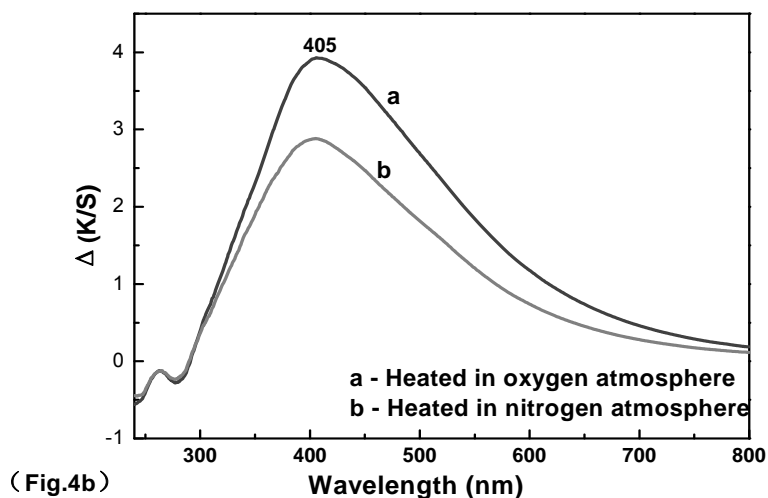
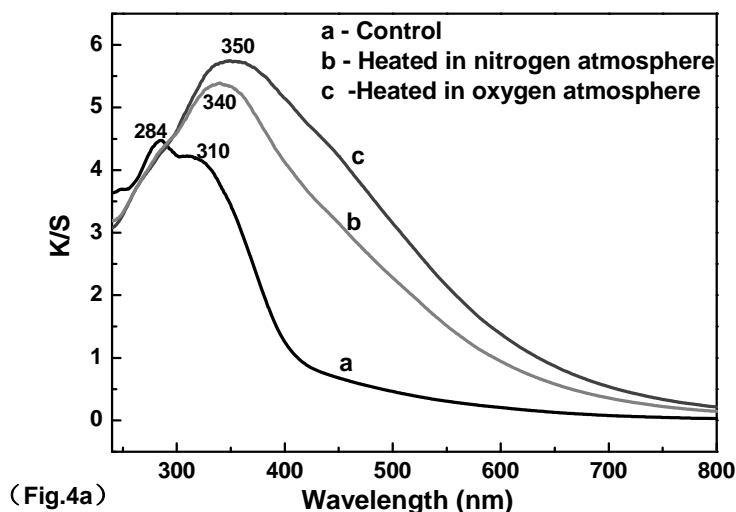


Fig. 4. DRUV spectra of the samples before and after heat treatment in nitrogen and in oxygen.

CONCLUSIONS

Heat treatment resulted in a decrease in lightness and an increase in the other chromaticity indexes (a^* and b^*) and chroma (C^*). There was a greater color difference (ΔE^*) in the samples heated in the presence of oxygen compared with nitrogen. The increase in a^* can be attributed to the formation of quinones, and the increase in b^* can be attributed to the formation of low molecular weight phenolic substances from lignin thermal degradation reactions. The decrease in the O/C ratio after heat treatment suggests

the loss of functional groups containing oxygen, such as hydroxyl groups. The β -O-4 structure in lignin appears to be cleaved by heat treatment. This results in a decrease in etherified and an increase in phenolic structures. The occurrence of condensation and oxidation reactions in lignin structures are characterized by FTIR-ATR spectra. New conjugated double bonds, such as α,β -unsaturated ketone, and α -C=O produced during heat treatment. The new absorbance peak at 1672 cm^{-1} after heat treatment in the presence of oxygen signifies the formation of a quinone structure. DRUV spectra showed an increase in the absorbance band at 340 to 350 nm and 405 nm, which suggests the formation of extensive conjugated structures, such as $C_{\alpha}=C_{\beta}$ double bond, α -C=O, β -C=O, and quinone structures.

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