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Spectroscopic analysis of the role of extractives on heat-induced discoloration of black locust (*Robinia pseudoacacia*)

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Abstract
To investigate the role of extractives on heat-induced discoloration of wood, samples of black locust (*Robinia pseudoacacia*) wood flour were extracted with various solvents prior to heat-treatment. Analysis of their color parameters and chromophoric structures showed that the chroma value of the unextracted sample decreased while that of the extracted sample increased after heat-treatment. Both samples showed broad diffuse reflectance UV-Vis (DRUV) absorption bands with maxima around 360–380 nm after heat-treatment due to the formation of conjugated double bonds, carbonyl functionalities, and quinoid structures. Compared with the unextracted sample, the dominant chromaticity of the extracted samples hypochromatically shifted and the peak became narrower. This result showed that extractives contribute mostly to the reduction in the light reflection on heat-treated wood. In addition to extractives, lignin and hemicellulose also contributed to the formation of color substances upon heat-treatment. The increase in C_3/C_2 ratio in X-ray photoelectron spectroscopy (XPS) spectra signified the oxidation reactions in the heating process. The increase in O_1/O_2 for extracted sample after heat-treatment and changes in DRUV and Fourier transform infrared spectroscopy (FTIR) spectra support the hypothesis that discoloration can also arise from the degradation of hemicellulose and the condensation reactions of lignin.

Keywords: *Color space, discoloration, diffuse reflectance UV-Vis (DRUV), attenuated total reflectance-Fourier transform infrared (ATR-FTIR), heat-treatment, X-ray photoelectron spectroscopy (XPS).*

Introduction

A major problem with the process of drying wood is the tendency of the wood to discolor (darkening and reddening) upon exposure to high temperature. There is general agreement that the discoloration is due mainly to extractives constituents in wood and hemicelluloses degradation (Sundqvist and Morén 2002, Mehrotra *et al.* 2010). However, neither the precise nature of the chromophores responsible for the discoloration nor the exact mechanism for their formation has been conclusively established.

Reactions which involve phenolic extractives have been considered as the main source of the discoloration that occurs in timber during drying. The oxidation products of phenol, such as quinones, are often implicated as an important contribution for color changes (Mitsui *et al.* 2001, Bekhta and Niemz 2003). The color originates from phenolic deposits located in ray and axial parenchyma cells, where extractives are situated (Luostarinen 2006). Proanthocyanidins are one example of compounds that could form such colored deposits by oxidation or polymerization during drying (Luostarinen and Möttönen 2004a,b, Möttönen and Luostarinen 2005). The Brauns lignin has been identified as another potential cause for the discoloration of vacuum-dried silver birch (Hiltunen *et al.* 2006a). Discolorations of European oaks (*Quercus robur and Quercus petraea*) and sugar maple (*Acer saccharum Marsh.*) have been linked to polymerization or oxidation of phenolic extractives during kiln drying (Miller *et al.* 1990, Charrier *et al.* 1995). In oak wood, temperature and oxygen evoke polymerization of ellagitannins. However, the compositions of wood extractives vary with wood species. The discoloration mechanisms can be different for various wood species.

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Black locust (*Robinia pseudoacacia*) is a dark color wood which contains high amounts of extractives in its heartwood and several phenolic extractives have been isolated from the wood of *R. pseudoacacia* (Fan *et al.* 2010). In the current work, the role of the extractives on the discoloration of black locust wood (*R. pseudoacacia*) under heat-treatment was investigated. Most of the extractives can be removed with solvents, such as ethanol, water, benzene, dichloromethane, chloroform, or a combination of ethanol/cyclohexane (Maldas and Kamdem 1999). The unextracted and the extracted samples of *R. pseudoacacia* wood flour were analyzed, when subjected to the heat-treatment, and their color changes, chromophoric structures, *Attenuated total reflectance-Fourier transform infrared* (ATR-FTIR), diffuse reflectance UV-Vis (DRUV) spectra, and X-ray photoelectron spectroscopy (XPS) were compared.

Materials and methods

Wood specimen

The 16-year-old Black Locust (*R. pseudoacacia*) logs with diameter of 25–30 cm at breast high were harvested from Heilongjiang province, northeast China. The logs were debarked and dried in ambient conditions. Heart wood of black locust was employed in this study. The wood was kept in a humidity chamber at 20°C and 13% relative humidity until equilibration. Then the wood was milled and sieved; 40–60 mesh flour was obtained, and then stored in a sealed polyethylene bag at room temperature until required for further experimentation.

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, benzene, acetone, and ether in a Soxhlet apparatus. To ensure complete removal of extractives, 24 hours of each extraction process was performed till the reflux extractant turned colorless. Finally, the extracted wood flour was dried under vacuum at room temperature and kept under sealed storage until required for further experimentation.

Heat-treatment

Both the unextracted and the extracted samples were conditioned with distilled water to moisture content of 30% prior to heating in an autoclave. In a previous studies (Chen *et al.* 2012), it was observed that 30% moisture content for black locust wood had a greater effect on color and chemical changes compared with other moisture contents. The wood flour was heated in duplicate at 120°C for 24 h in a sealed cylindrical Teflon cell placed inside a stainless-steel autoclave. This temperature was chosen because it is commonly used in wood drying. The wood flour was vacuum-dried at room temperature prior to color measurement and spectroscopic analysis.

Attenuated total reflectance-Fourier transform infrared

Attenuated total reflectance-Fourier transform infrared spectroscopy was performed on a Tensor27 spectrophotometer (BRUKER) to provide knowledge of functional groups present at the wood flour samples. Spectra were obtained by using ATR. The surface of the samples analyzed 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. Five replicate samples were analyzed.

DRUV spectroscopic analysis

The DRUV spectra from unextracted and extracted samples 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 $BaSO_4$ as a white (R_∞) optical standard. Scans were performed over the wavelength range 240–800 nm. The reflectance spectra of the samples were converted into *K*/*S* spectra using the Kubelka–Munk equation:

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

where R (between 0 and 1) is the measured reflectance and K and S are the absorption and scattering coefficients, respectively. The *K*/*S* spectra as a function of wavelength, is used to identify the apparent absorption maxima. Typically, based on the Kubelka–Munk theory, we can assume that *K*/*S* is approximately linear to the variation of chromophores in this range of absorption values.

Color characteristics

Color changes on unextracted and extracted wood flour after heat-treatment were analyzed using a colorimeter. Color parameters were measured using five replicates of each sample and average value was reported. To develop a more understandable

relationship between color scale and reflectance at different wavelengths, the International Commission on Illumination (CIE) 1931 tristimulus values (*XYZ*) and the CIE-Yxy color space were employed (Ohno 2000). The tristimulus values X, Y, Z were calculated according to the following formulas (Equations (2), (3), and (4)) using the simulated daylight (D65) standard illuminant. Color changes due to heat-treatment were reported using reflectance and wavelength data. The reflectance measurements were taken between 380 and 780 nm.

$$X = K\int_{380}^{780} S(\lambda)\rho(\lambda)x(\lambda)d(\lambda) \tag{2}$$

$$Y = K\int_{380}^{780} S(\lambda)\rho(\lambda)y(\lambda)d(\lambda) \tag{3}$$

$$Z = K\int_{380}^{780} S(\lambda)\rho(\lambda)z(\lambda)d(\lambda) \tag{4}$$

where $S(\lambda)$ is the spectral power of the light source, $x(\lambda)$, $y(\lambda)$, and $z(\lambda)$ are the supplementary colorimetric system tristimulus values, and $\rho(\lambda)$ is the spectral reflectance factor of the sample surface, K is the normalizing factor which is determined by the formula (5):

$$K = 100/\int_{380}^{780} S(\lambda)y(\lambda)d(\lambda) \tag{5}$$

The chromaticity coordinates x and y based on the CIE-Yxy colorimetric spaces were obtained from the X, Y, Z tristimulus values according to Equations (6) and (7).

$$x = \frac{X}{X+Y+Z} \tag{6}$$

$$y = \frac{Y}{X+Y+Z} \tag{7}$$

In the x, y chromaticity diagram, horizontal axis x and vertical axis y represent reddish and greenish color, respectively and Y is the brightness measurement.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy analysis was performed on unextracted and extracted samples before and after heat-treatment with ThermoVG Scientific Sigma Probe using a microfocusing monochromatic AlKαX-ray source at an operating pressure between 10^{-9} and 10^{-8} mbar. A high-resolution scan was conducted on the C_{1S} peak from 280 to 300 eV and the O_{1S} peak from 530 to 535 eV for each sample. Chemical bond analysis of carbon was accomplished by fitting the C_{1S} peak and deconvoluting into four sub peaks for C–C/C = C, C–O, C = O–, COO– groups, with areas represented by C_1, C_2, C_3, C_4, respectively, and the O_{1S} signals were similarly deconvoluted into two sub peaks for C = O, C–O groups and represented by O_1 and O_2, respectively. The ratio of C_3/C_2 and O_1/O_2 was calculated.

Results and discussion

Changes of color chromaticity of unextracted and extracted samples after heat-treatment

As shown in Table I, after heat-treatment, the X, Y, Z values for both the unextracted and the extracted samples decreased substantially. X, Y, and Z represent the red, green, and blue part of the spectrum of sunlight, respectively. The heat-treated extracted sample showed slightly greater tristimulus values compared with the heat-treated unextracted sample. The changes in X and Y of the heated unextracted and the heated extracted samples are quite apparent, and this suggests that the extractives contributed mostly to the decrease in the reflection of the red color after heat-treatment. Meanwhile, the X, Y, Z tristimulus values for extracted samples decreased even more compared with the unextracted sample upon heat-treatment. This suggests that other factors beside extractives were responsible for the heat-induced discoloration. These factors are most likely structural changes in hemicelluloses and lignin, which were not removed by extraction. It can be inferred from the above results that in addition to extractives, both lignin and hemicellulose play an important role in the formation of color substances during heat-treatment, and that chromophoric groups, such as the quinoid and conjugated double-bond structures, which absorb UV-Vis light in the range 300–650 nm. These chromophores are believed to be formed by condensation and oxidation reactions.

In an attempt to develop a more understandable color scale, the CIE Chromaticity Coordinates x, y were calculated from the CIE Tristimulus Values

Table I. Average tristimulus values X, Y, Z of the samples before and after heat-treatment.

Sample description	*X*	*Y*	*Z*
Unextracted	27.59 (±0.03)[a]	27.32 (±0.11)	16.37 (±0.05)
Heated unextracted	15.15 (±0.01)	14.52 (±0.09)	9.95 (±0.02)
Extracted	46.41 (±0.12)	47.40 (±0.08)	36.72 (±0.15)
Heated extracted	18.39 (±0.06)	17.51 (±0.04)	10.94 (±0.07)

[a]Numbers in parentheses represent the standard deviation of five replicates.

(*XYZ*) (HunterLab 2008) and are shown in the 1931CIE-Yxy color space (Figure 1).

It can be seen from Figure 1 that the dominant chromaticity of the unextracted samples moved to a longer wavelength after heat-treatment and the chroma value decreased. The dominant chromaticity of the extracted samples also shifted to a longer wavelength, but the chroma value increased upon heat-treatment. After heat-treatment the chromaticity of the extracted samples increased to a level that was similar to the unextracted samples. The extracted samples showed a higher chroma value compared with the unextracted after heat-treatment, which suggested that the removal of extractives made the wood brighter.

DRUV spectroscopic analysis

The *K*/*S* spectra of the unextracted and extracted samples before and after heat-treatment are presented in Figure 2.

It is clear from these spectra that extraction resulted in a decrease in the absorbance of the samples. It is reasonable to conclude that decrease in absorbance was due to the removal of components with conjugated double-bond structures (280–380 nm), including quinoid structures (380 nm). This would cause the color of wood to become brighter as stated above.

It can be easily seen that, heat-treatment results in red shift and broadening of the absorption bands. After heat-treatment, there were broad absorption bands with peaks around 360–380 nm for both the unextracted and the extracted samples. These absorption bands are far too broad to represent a single chromophore. Hence they can be ascribed to the extensive types of conjugated double bonds, carbonyl functionalities, and quinoid structures (Hiltunen *et al.* 2006b) formed from the breakdown products of lignin and other components due to heat-treatment. When comparing the *K*/*S* spectra of the unextracted and extracted samples after heat-treatment, one can also see that the unextracted samples absorbed more in both the UV and visible regions of the spectra with an absorption maximum around 380 nm. This suggests that discoloration of the unextracted sample was predominantly the result of breakdown products of extractives. However, the discoloration of the extracted sample appeared to result from breakdown products of other components other than extractives, and most likely lignin and some hemicellulose. The absorption around 500–570 nm, which corresponds to green light, increased upon heat-treatment. This explains the increase in the reddish color of wood specimen after heat-treatment.

ATR-FTIR spectra analysis

Figure 3 shows the ATR-FTIR spectra (normalized at 1050 cm^{-1}) of unextracted and extracted samples before and after heat-treatment. It can be observed that the absorbance in the 1800–1100 cm^{-1} region decreased with the removal of the extractives. The conjugated carbonyl groups (peak 1600–1680 cm^{-1}) decreased after extraction, which was consistent with

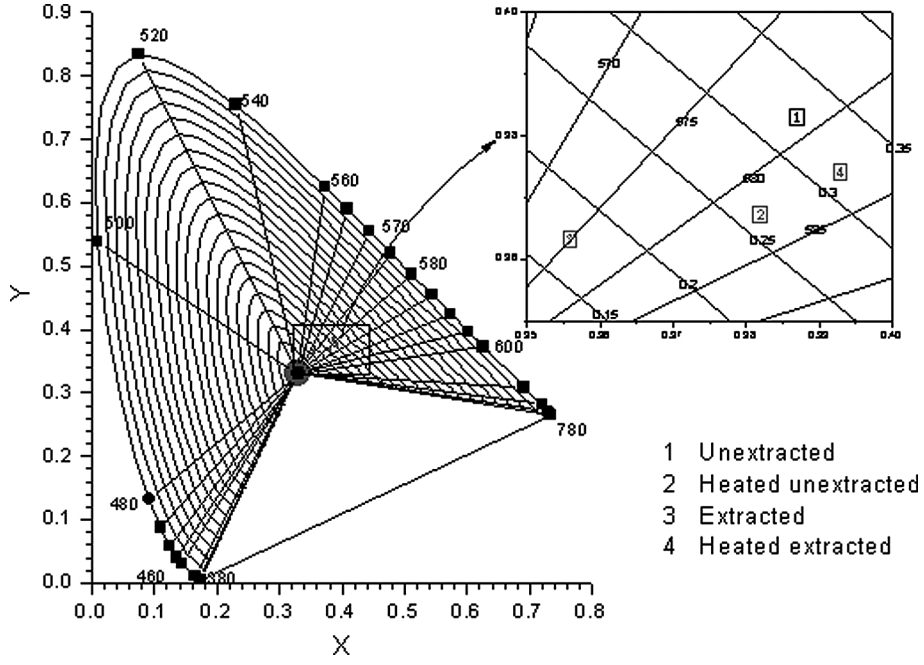

Figure 1. The CIE-Yxy color space of the samples before and after heat-treatment.

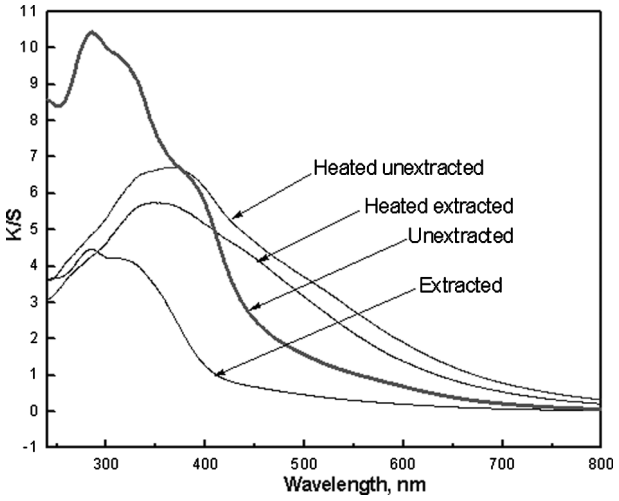

Figure 2. The *K/S* spectra of the unextracted and extracted samples before and after heat-treatment.

the result of the DRUV spectroscopic analysis. After heat-treatment, the peak at 1660–1680 cm^{-1} intensified, which can be attributed to the formation of quinone structures (Yamauchi *et al.* 2005). The formation of new quinone structures contributed considerably to the decrease of the tristimulus values *XYZ*.

The carboxyl groups (1736, 1235, and 900 cm^{-1}) increased and the absorption at 1736 cm^{-1} shifted to lower wave numbers after heat-treatment, which suggested the production of acid substances by the degradation of hemicellulose. The production of acidic substance can also catalyze the condensation reactions of lignin (Nuopponen *et al.* 2004). The oxidation and polymerization can also contribute to the darkening of the samples and the increase of the chromaticity parameters.

X-ray photoelectron spectroscopy

Figure 4 shows the high-resolution spectra of C_{1S} carbon and O_{1S} oxygen. Table II presents the binding energies of C_1, C_2, C_3, C_4, and the C_3/C_2 ratios. Table III presents the binding energies of O_1 and O_2 as well as the O_1/O_2 ratios.

It can be seen from Table II that the C_1 decreased and C_2, C_3, C_4 increased after extraction. This is consistent with the removal of the carbon-rich extractives and some aromatic substances, as observed with ATR-FTIR spectra. Since the ratio of C_3/C_2 decreased after extraction, largely due to increase in C_2, it can be inferred that the components with carbonyl structure in extractives contributing to the dark color of wood were removed. The carbonyl structure increased after heat-treatment for both the extracted and unextracted samples, as demonstrated by increase in the ratios, C_3/C_2 and O_1/O_2. It can also be seen that there was an increase in the relative area of C_4, which suggests an increase in carboxylic functionalities. This signifies the occurrence of oxidation reactions in the heating process. The increase in C_4 and the ratio of C_3/C_2, O_1/O_2 after heat-treatment was higher for unextracted samples compared with that for extracted samples, which suggested that carbonyl structure and carboxylic functionalities can be produced from extractives during heat-treatment. This is quite consistent

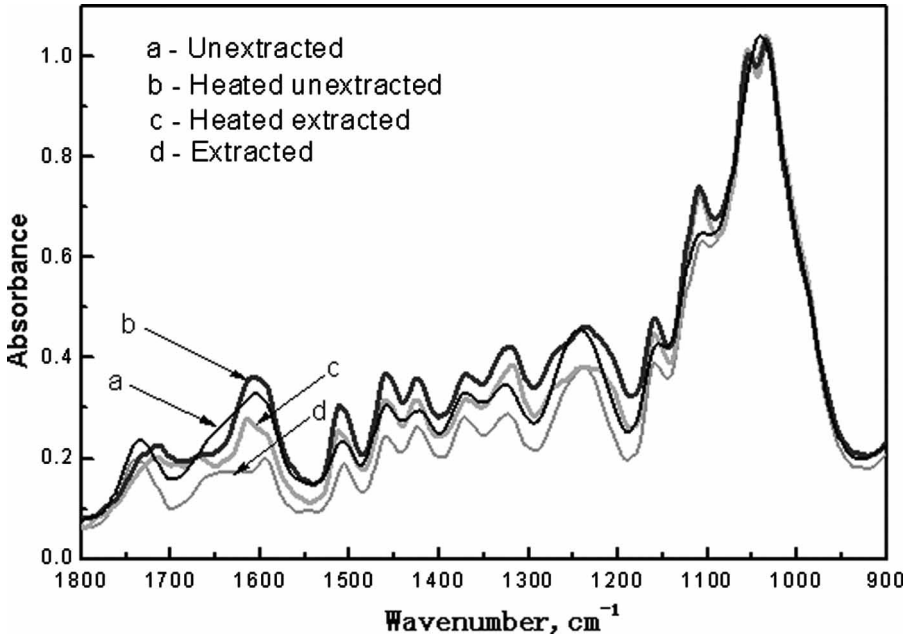

Figure 3. ATR-FTIR spectra of unextracted and extracted samples before and after heat-treatment.

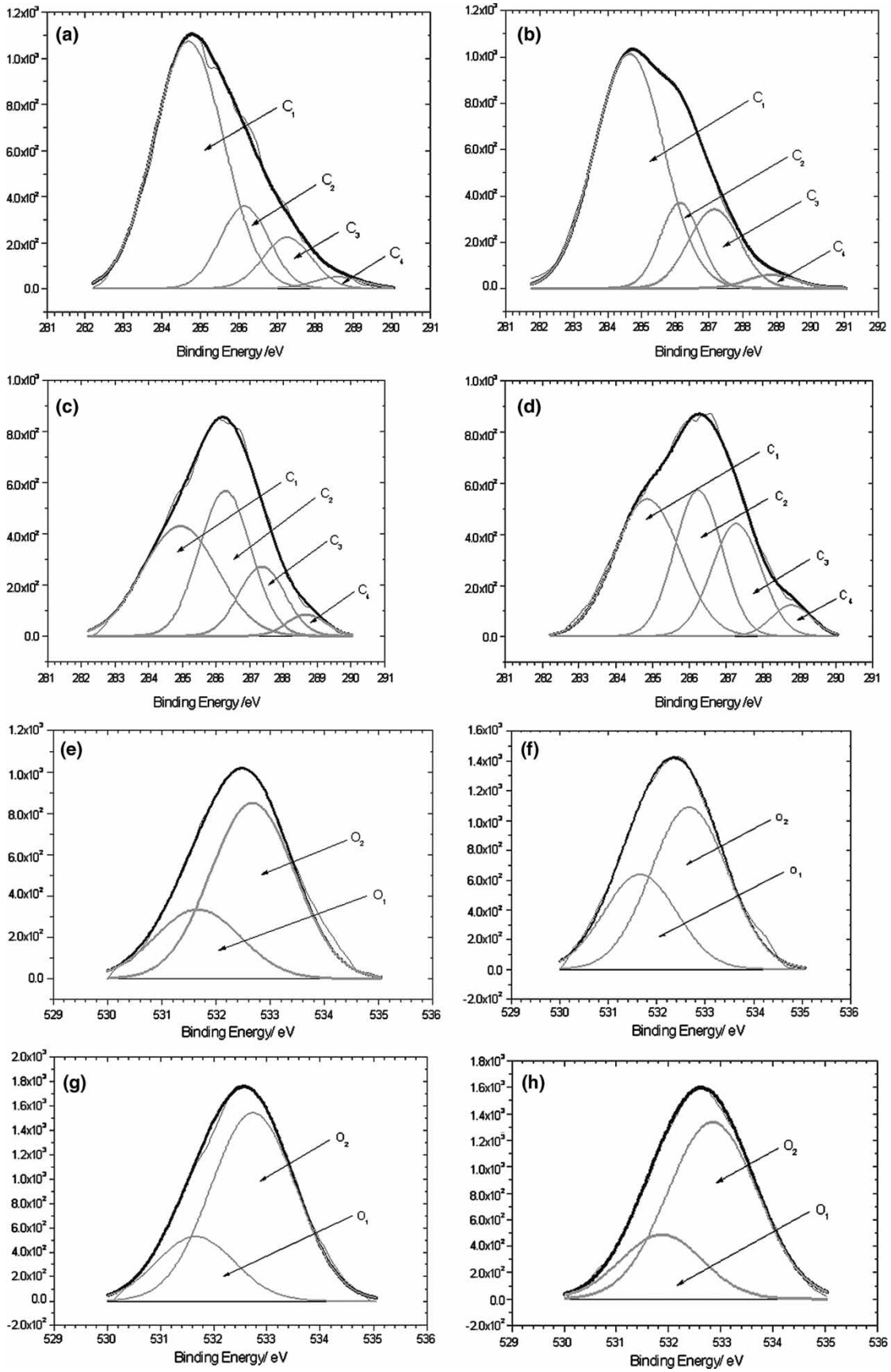

Figure 4. X-ray photoelectron spectroscopy scan of C_{1S} and O_{1S} of unextracted and extracted sample before and after heat-treatment.

Table II. Subpeak area fractions of C_{1S} and ratio of C_3/C_2.

Sample description	Relative area of C_{1s} peaks (%)				
	C_1 (284.7eV)	C_2 (286.3eV)	C_3 (287.5eV)	C_4 (288.7eV)	C_3/C_2
Unextracted	70.8	16.6	10.3	2.3	0.62
Heated unextracted	66.6	14.2	16.5	2.7	1.16
Extracted	41.42	37.97	16.35	4.26	0.43
Heated extracted	36.98	34.90	23.64	4.48	0.68

with the decrease in chroma value for unextracted samples after heat-treatment. There was a slight increase in carbonyl structure and carboxylic functionalities for heated extracted sample. If we assume that all of the extractives were removed during extraction, then it is reasonable to hypothesize that discoloration in this case was a result of lignin or hemicellulose degradation products. It has been reported that hemicelluloses are thermally unstable wood components, due to the presence of acetyl groups (Bourgois *et al.* 1989). Lignin degrades partly over a wide temperature range, starting at relatively low temperatures (Nassar and Mackay 1984). It is generally accepted that O_1 represents C = O in lignin, and O_2 represents C–O in carbohydrate (Tshabalala 2005). The increase in O_1/O_2 after heat-treatment, combined with the intensified peak at 1660–1680 cm^{-1}, 1736 cm^{-1}, 1235 cm^{-1}, and 900 cm^{-1} in ATR-FTIR spectra support the hypothesis that discoloration can also arise from the degradation of hemicellulose and the condensation reactions of lignin. Acetic acid released (1736 cm^{-1}, 1235 cm^{-1}, and 900 cm^{-1}) by thermal deacetylation of hemicelluloses acts as a catalyst, which increases the condensation reactions of lignin (1660–1680 cm^{-1}) and further contributes to the wood darkening. The XPS results are in good agreement with the ATR-FTIR and DRUV spectroscopy and also with the wood color changes induced by heat-treatment.

Conclusion

The role of extractives in heat-induced discoloration of *R. pseudoacacia* has been elucidated by a combination of colorimetric and spectroscopic analysis. The removal of the extractives can make the wood brighter due to the decrease of components with chromophoric groups such as conjugated double-bonds structures. After heat-treatment, the dominant chromaticity of wood moved to longer wavelength due to the formation of various types of conjugated double bonds, carbonyl functionalities and quinoid structures. Compared with the unextracted samples, the dominant chromaticity of the extracted samples moved to a shorter wavelength and the UV-Vis absorption peak became narrower. Extractives contribute mostly to the reduction in the light reflection on heat-treated wood. In addition to extractives, both lignin and hemicellulose play an important role in the formation of color substances during heat-treatment.

The CIE chromaticity coordinates is a useful tool which permitted the development of a more understandable color scale. The DRUV spectra of the wood flour before and after extraction and heat-treatment identified UV-Vis absorption bands, that are characteristic of the chromophoric products formed. The results obtained from DRUV correlate quite well with the results obtained by the chromaticity coordinates system. After heat-treatment, the formation of new quinone structures was identified by the increased UV-Vis absorption around 500–570 nm. As shown by the decrease in the tristimulus values *XYZ*, it is evident that these structures contribute considerably to the wood reddish color. The formation of new quinone structures also can be confirmed by the intensified peak at 1660–1680 cm^{-1} in FTIR spectra. XPS has been found useful to study the concentration of different types of bonds between carbons and oxygen atoms and to determine the types of reactions caused by heat-treatment. The carbonyl structure increased after heat-treatment for both the extracted and unextracted samples. The increase in C_3, C_4 and O_1 and C_3/C_2 signified the occurrence of oxidation reactions in the heating process. It is also reasonable to conclude that the increase in O_1/O_2 for extracted sample after heat-treatment supports the hypothesis of the degradation

Table III. Subpeak area fractions of O_{1S} and ratio of O_1/O_2.

Sample description	Area of O_{1S} peaks (%)		
	O_1(C = O) (531.7 eV)	O_2(C–O) (532.8 eV)	O_1/O_2
Unextracted	28.24	71.76	0.39
Heated unextracted	35.46	64.53	0.55
Extracted	23.84	76.16	0.31
Heated extracted	26.7	73.3	0.36

of hemicellulose by deacetylation and the possible formation of acetic acid. The acetic acid released can act as a catalyst, which further increases the condensation reactions of lignin. The XPS results are consistent with the observed IR absorption peaks in the range 1736–1690 cm^{-1} and the intensified peak at 1660–1680 cm^{-1}, which suggest the formation of carboxylic groups. Results from this study can provide reference for the processing of black locust wood in the control or inducing of surface color.

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