

The Role of Phenolic Extractives in Color Changes of Locust Wood (*Robinia pseudoacacia*) during Heat Treatment

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To investigate the effects of phenolic extractives on the discoloration of black locust wood (*Robinia pseudoacacia*) during heat treatment, phenolic compounds were extracted using an accelerated solvent extraction. The main components of the phenolic extractives were analyzed. The phenolic compounds were heat treated at 120 and 140 °C in nitrogen, oxygen, and saturated steam. The results showed that the a^* values shifted toward red and the b^* values shifted toward yellow after the heat treatment. The changes in the color parameters were more pronounced when the samples were treated at 140 °C in saturated steam compared with treatment at 120 °C in oxygen or nitrogen atmosphere. During heat treatment, hydroxyl groups in the phenolic components were oxidized to form carbonyl groups, or the adjacent hydroxyl groups formed quinoid structures. It was possible that the sample underwent condensation reactions to produce conjugated double-bond structures that led to the increase in color parameters.

Keywords: Phenolic extractives; Heat treatment; Wood color; Discoloration; Chemical changes

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INTRODUCTION

Wood color is one of the most important factors when wood is used as an interior material for houses or furniture. As trees age, they form an interior xylem core, known as heartwood. Heartwood usually shows a deeper color than the sapwood, but the specific tone varies among different wood species. Heartwood with a rare and peculiar color is valuable, as it is favored for use as interior materials. Wood color is modulated by the composition and structure of the extractives (Gierlinger *et al.* 2004; Sandor *et al.* 2009). There are many chromophoric groups in wood extraction components, such as organic acids, alkaloids, polyphenol compounds, anthraquinone compounds, and coumarins. Polyphenols can be divided into two types: (1) phenols, including flavonoid compounds, chlorogenic acids, gallic acids, ellagic acids, and polyphenol compounds with glycoside groups; and (2) oligomers or polymers polymerized by monomers, which are also called tannins (Manach *et al.* 2004; Sreerama *et al.* 2010; Hmid *et al.* 2013; Machu *et al.* 2015).

Changes in wood color during heat treatment are mainly the product of condensation and oxidation reactions of phenolic/polyphenolic compounds. The discoloration of some European wood species is also linked to the polymerization or oxidation of phenolic extractives (Hiltunen *et al.* 2008). The accumulation of phenolic compounds turns the wood surface yellow (Hiltunen *et al.* 2008; Moya *et al.* 2012). Wood

extractives that play a role on the color changes of heat-treated wood vary depending on the wood species, part of the tree, and environmental conditions (Alañón *et al.* 2011; Zanuncio *et al.* 2014). Other factors, such as the difference between the radial and longitudinal sections, species, and treatment conditions, also influence the color of heat-treated wood (Pincelli *et al.* 2012; Gonzalez de Cademartori *et al.* 2013).

Black locust (*Robinia pseudoacacia* L.) is an important, fast-growing species. The valuable trait in stiffness, wear resistance, and high basic density make it widely used in industry. However, the difference in color of sapwood and heartwood limits its decorative application. The sapwood of black locust is yellowish. Most parts of the cross-sectional area are heartwood, and the color is dark green or olive drab.

There is a lack of sufficient information on the chemical properties of this kind of wood species. Color change is caused primarily by changes in the chemical structures of the polar extractives (Fan *et al.* 2010). The flavanonol dihydrorobinetin (DHR) is present in the younger sapwood of *R. pseudoacacia*, although the content is low in comparison to the heartwood, where it is abundant (Sergent *et al.* 2014). Higher amounts of DHR and the hydroxyl cinnamic acid derivative (HCA) were found in the sapwood–heartwood transition zone. The content of HCA increased towards the heartwood and decreased again in the inner heartwood parts. The appearance of flavonol robinetin (ROB) in the older parts of the heartwood reached maximum, and it decreased gradually along the wood ray until the disappearance in the sapwood (Dünisch *et al.* 2010).

The effects of extractives on the color change during the heat treatment of wood are complex and not completely understood. Previous studies have focused on the effect of the overall extractives on wood color changes and did not determine the role of phenolic compounds (Sundqvist and Morén 2002; Zanuncio *et al.* 2015). It is of fundamental importance to investigate the changes to the phenolic extractives during heat treatment and to develop new heat treatment techniques for producing high-quality wood products.

The objective of this study was to evaluate the influence of phenolic extractives on the color change of black locust wood during heat treatment. The phenolic extractives were extracted in acetone/water (9:1, v/v). The chemical and color changes of the phenolic extractives were investigated.

EXPERIMENTAL

Materials

Fifteen-year old black locust wood was harvested from Guangxi province in southwest China. The logs were debarked and then dried at ambient conditions. The heartwood was used in this study. After being ground and screened, the 40 to 60 mesh-sized (250 to 425 μm) wood flour was selected and sealed in a polyethylene (PE) bag at room temperature and 13% relative humidity (RH) until it was required for further experimentation.

Extraction of Phenolic Compounds

Phenolic compounds were extracted using an accelerated solvent extraction (ASE 200, Dionex, Bannockburn, USA). In preliminary studies, extraction procedures with different solvents (acetone/water 9:1, toluene/ethanol 2:1, methanol/water 3:1) were tested. Extraction with acetone/water 9:1 at room temperature and a constant pressure of 10 atm was determined to be the most suitable method for the extraction of phenolic compounds

from black locust wood. The extraction was performed for 12 h. The solvent was removed by rotary evaporation under vacuum at 40 °C. The condensed extractive was washed using ether to remove fat-soluble extractives. The extractive content was measured gravimetrically after being dried in a vacuum oven at 40 °C for 48 h. The dried extractive was dissolved in methanol (CH₃OH) and then subjected to reversed-phase high-performance liquid chromatography/mass spectrometry (HPLC/MS) analysis.

Separation and Characterization of the Major Phenolic Compounds

The separation and characterization of the major phenolic compounds was conducted using reversed-phase HPLC/MS. This analysis was carried out with liquid chromatography coupled with mass spectrometry (LC/MS) on a ThermoFisher system in which a HPLC (Surveyor) system was equipped with a linear ESI-Ion Trap (LTQ XL) Mass Spectrometer (ThermoFisher Scientific, San Jose, CA, USA). Five microliters of the extractives were directly injected *via* an autosampler (Surveyor autosampler plus, Rolla Biotech, CA, USA) into the HPLC system equipped with a reverse phase C-18 column (Phenomenex 250 mm, 5 mm particle size, CA, USA). The column temperature was set to 30 °C. Solvent A (1% CH₂O₂) and solvent B (CH₃OH) were used as the mobile phase in the gradient mode (100% A from 0 to 5 min, 0% to 30% B from 5 to 30 min, 30% to 33% B from 30 to 40 min, 33% to 35% B from 40 to 50 min, 35% to 45% B from 50 to 60 min, 45% to 60% B from 60 to 70 min, 60% to 80% B from 70 to 80 min) at a flow rate of 1 mL/min. The separated compounds were detected with an ultraviolet (UV) spectrophotometer. The detection wavelength was adjusted to 280 nm and the UV spectra from 200 to 600 nm were recorded for peak identification. Peak identification was performed through the comparison of the retention times, UV spectra, and mass spectra with that of the purchased standards (Sigma Aldrich, Darmstadt, Germany).

The prominent peaks were analyzed with a mass spectrometer (LTQ XL ThermoFisher Scientific, Waltham, USA) using an atmospheric pressure electrospray ionization (ESI) probe in the negative ion mode. The temperature and voltage of the capillary was 120 °C and 0.42 V, respectively, and the vaporizer temperature was 288 °C. The identification of the phenols was conducted under the full scan mode in the range of 260 to 1000 m/z, and was processed using X-calibur 1.4 software.

Heat Treatment

The selected phenolic extractives were heat-treated for 24 h at either 120 or 140 °C under atmospheric conditions. The phenolic extractives were placed in a sealed stainless steel reaction kettle with a Teflon vessel in either oxygen, nitrogen, or saturated steam, and heated in an electric oven. The heat-treated samples were cooled and vacuum-dried for over 24 h at room temperature to ensure that the moisture content was less than 5%. Each trial had three replicates. The treated and untreated samples were stored in desiccators until further study.

Color Measurements

The dried extractives collected before and after heat treatment were pressed into pieces with a mould of 13-mm diameter using a hydraulic press. The color was measured at three locations on each sample. A Konica Minolta CM-2300d Chroma Meter (Konica Minolta Holdings, Inc., Tokyo, Japan) was used to measure the optical properties with a C standard illuminant and 8° standard observer according to the CIEL*a*b* color system. The CIEL*a*b* color system is a three-dimensional color space that defines the lightness

(L^*) of the sample, as well as the color coordinates (a^* and b^*). L^* represents the reflectance of a sample that ranges between 0 and 100, which are black and white, respectively. An increase in the L^* indicates that the color has faded or become lighter ($+\Delta L^*$ = lightening). A decrease in the L^* indicates that the color has darkened ($-\Delta L^*$ = darkening). The color coordinate a^* is the red/green ($+a^*/-a^*$) coordinate, while b^* is the yellow/blue ($+b^*/-b^*$) coordinate. Chroma C^* is derived from a^* and b^* (Eq. 1), and corresponds to the color saturation, which ranges from dull (low value) to vivid (high value).

$$C^* = \sqrt{a^{*2} + b^{*2}} \quad (1)$$

In this study, the ΔL^* , Δa^* , Δb^* , and ΔC^* were calculated according to Eqs. 2 through 5. A positive value signified an increase, while a negative value signified a decrease.

$$\Delta L^* = L^*_{\text{treated}} - L^*_{\text{untreated}} \quad (2)$$

$$\Delta a^* = a^*_{\text{treated}} - a^*_{\text{untreated}} \quad (3)$$

$$\Delta b^* = b^*_{\text{treated}} - b^*_{\text{untreated}} \quad (4)$$

$$\Delta C^* = C^*_{\text{treated}} - C^*_{\text{untreated}} \quad (5)$$

where ΔL^* , Δa^* , Δb^* , and ΔC^* are the change in the lightness, red/green coordinate, yellow/blue coordinate, and color saturation, respectively. L^*_{treated} , a^*_{treated} , b^*_{treated} , and C^*_{treated} represents the heat-treated sample, and $L^*_{\text{untreated}}$, $a^*_{\text{untreated}}$, $b^*_{\text{untreated}}$, and $C^*_{\text{untreated}}$ represents the untreated sample. The corresponding total color difference (ΔE^*) was calculated according to Eq. 6,

$$\Delta E^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (6)$$

Attenuated Total Reflection/Fourier Transform Infrared (ATR-FTIR) Spectra

The attenuated total reflection/Fourier transform infrared (ATR-FTIR) spectra of the phenolic extractives before and after the heat treatment were performed on a Tensor 27 spectrophotometer (Bruker, Karlsruhe, Germany) in order to reveal the functional groups present in the extractives. The spectra were acquired by accumulating 64 scans at a resolution of 4 cm^{-1} in the absorbance mode from 4000 to 400 cm^{-1} . The peaks were normalized with respect to the peak at 1599 cm^{-1} (aromatic skeletal vibrations in the benzene ring), which acted as the internal standard.

Diffuse Reflectance Ultraviolet-Visible (DRUV) Spectra

The diffuse reflectance UV-visible (UV-Vis) spectra of the phenolic extractives before and after the heat treatment were recorded at room temperature on a UV-3100 UV-Vis near-IR spectrophotometer (Shanghai Mapada Instruments Co., Ltd, Shanghai, China) that was equipped with an integrating sphere. As a white (R_∞) optical standard, the reflectance spectra were recorded against BaSO_4 . The study was carried out over the wavelength range of 200 to 700 nm. The reflectance spectra of the tested samples were converted into a K/S spectra using the Kubelka-Munk equation (Eq. 7),

$$K/S = \frac{(1-R)^2}{2R} \quad (7)$$

where R (0 to 1) is the measured reflectance, and K and S are the absorption and scattering coefficients, respectively.

The difference spectra were calculated by subtracting the K/S absorption spectrum of the non-heated phenolic extractives from that of the heat-treated samples (Eq. 8). This was plotted as a function of the wavelength to identify the apparent absorption maxima. Based on the Kubelka-Munk Theory, it was assumed that K/S spectra signifies the appearance or formation of chromophores during the heat treatment.

$$\Delta(K/S) = (K/S)_{\text{after}} - (K/S)_{\text{before}} \quad (8)$$

Cross Polarization/Magic Angle Spinning-Carbon Nuclear Magnetic Resonance (CPMAS- ^{13}C -NMR) Analysis

Solid state cross polarization/magic angle spinning (CPMAS) and carbon nuclear magnetic resonance (^{13}C -NMR) were performed on a 400 MHz WB Solid-State NMR Spectrometer (JEOL, Tokyo, Japan). The resonance frequency for ^{13}C was 100.65 MHz, and the speed of spinning at the magic angle was 5.0 kHz. The contact time and relaxation delay were 2500 μs and 2 s, respectively. The number of transients was 1024.

RESULTS AND DISCUSSION

Characterization of the Major Phenolic Extractives

Six major phenolic extractives were detected in the acetone/water extracts of *R. pseudoacacia* heartwood by HPLC (Fig. 1), which were (+)-catechin, flavonones naringenin, 4'-methoxynaringenin, flavonols taxifolin, dihydrochalcone, and 4,2',4'-trihydroxylchalcone. However, no compounds with a molecular mass above 750 m/z were detected.

Changes in the Color Parameters Before and After the Heat Treatment

Figure 2 displays the changes in the color parameters a^* , b^* , and C^* of the phenolic extractives before (C) and after the heat treatment at 120 and 140 °C in nitrogen, oxygen, and saturated steam. The iso- C^* (chroma) lines were drawn based on Eq. 1. As can be seen from Fig. 2, the heat treatment was responsible for remarkable changes in all of the parameters of the CIEL $^*a^*b^*$ evaluation. The values of a^* , b^* , and C^* increased remarkably upon heating. This indicated that the a^* values shifted toward red and the b^* values shifted toward yellow after the heat treatment. The color of the phenolic components became vivid after heating. The red and yellow shifts and vivid color were more pronounced for the samples heated at 140 °C. However, the atmosphere played an important role in the increase of the a^* , b^* , and C^* values. The increase in the a^* , b^* , and C^* values was more pronounced when the phenolic components were subjected to a heat treatment in saturated steam atmospheric conditions than the samples that were treated in the oxygen and nitrogen atmospheres. The presence of water molecular could promote the oxidation or condensation of the products. The increase in a^* , b^* , and C^* values suggested that the phenolic components were susceptible to changes in the chemical structure and color when heated. Water and oxygen also played a very important role in the chemical and color changes of the phenolic components when exposed to heat. New chromophoric groups formed in the phenolic components during the heat treatment. It was concluded that

quinone-type structures were produced through oxidation and condensation reactions of the phenolic compounds during heating (Chen *et al.* 2012).

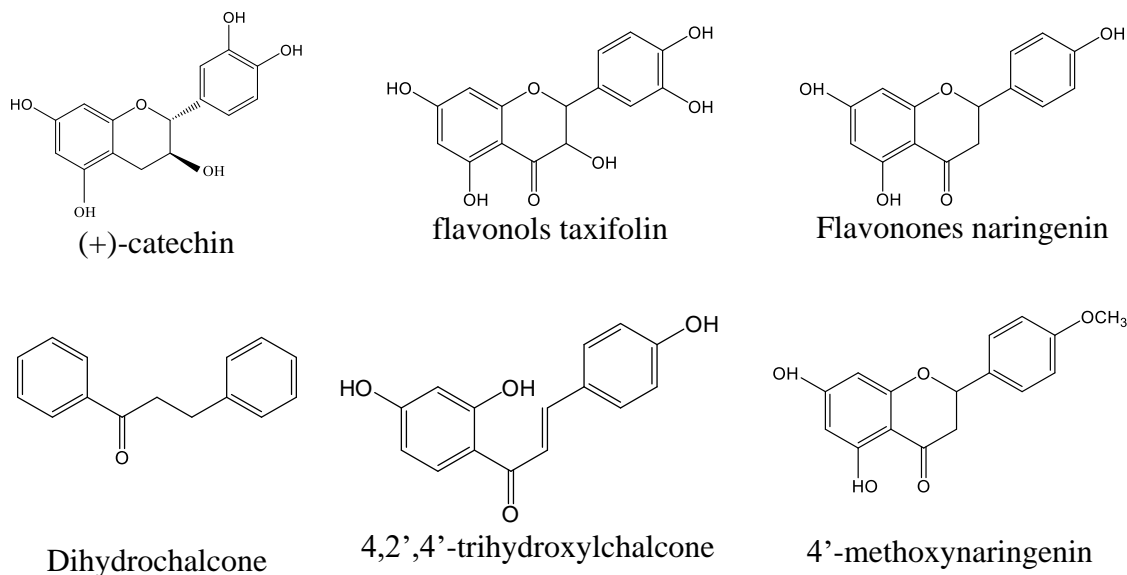


Fig. 1. Chemical structures of the compounds identified in the acetone/water extracts of black locust wood

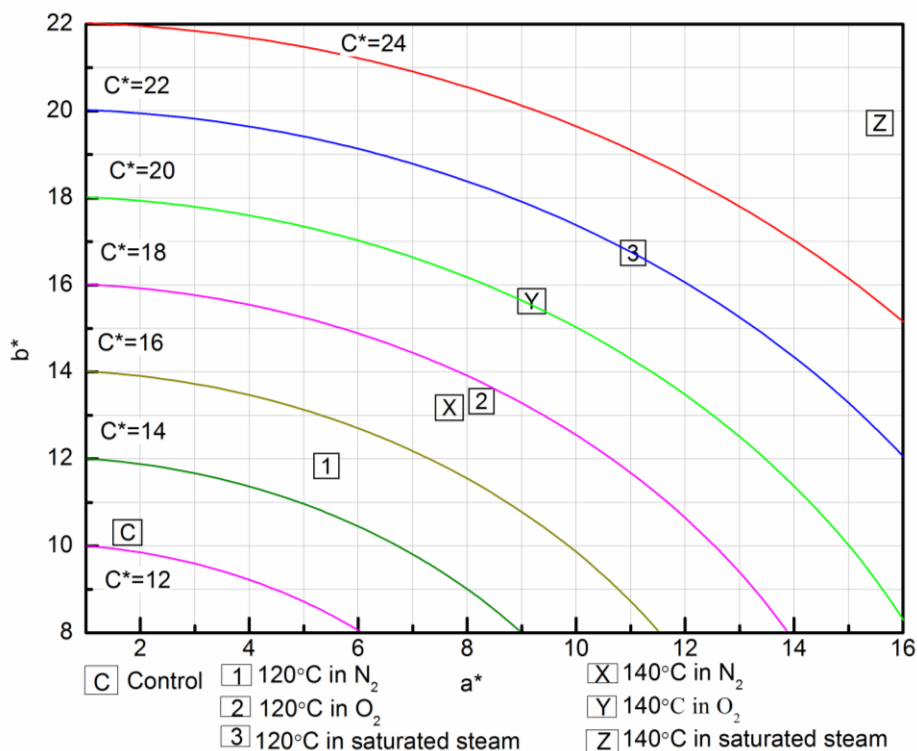


Fig. 2. Color parameters a^* , b^* , and C^* before and after the heat treatment

The changes in the lightness and color difference of the phenolic extractives after the heat treatment are shown in Table 1. Positive values represented an increase, while negative values represented a decrease in the parameters after the heat treatment. The

lightness, which corresponded to the brightness of the samples, decreased remarkably with an increased temperature; the phenolic components became darker after the heat treatment. The phenolic components of the samples that were heat-treated in the saturated steam atmosphere were darker than those treated in O₂ and N₂. The darkening was more severe for the heat treatment at 140 °C. The samples treated at 140 °C in the saturated steam atmosphere showed a reduction in the L^* values of more than 60%. This indicated that more visible light-absorbing substances were produced from the phenolic components during the heat treatment. It was concluded that the phenolic components were very sensitive to higher temperatures, oxygen, and water. The combined action of the temperature, oxygen, and water may have catalyzed a thermochemical condensation and/or oxidation reactions of the phenolic substances, which in turn influenced the wood color. The smallest color change was observed when the samples were treated at 120 °C in a N₂ atmosphere. As was expected, the color difference increased as a function of the temperature. The color difference showed the same behavior as the ΔL^* values.

Table 1. Changes in the Lightness (ΔL^*) and Color Difference (ΔE^*) of the Phenolic Extractives

		L^*	ΔL^*	ΔE^*
	Control	95.02 (± 1.03)	-	-
120 °C	in N ₂	82.08 (± 1.24)	-12.94 (± 1.21)	13.53 (± 0.08)
	in O ₂	73.36 (± 1.16)	-21.66 (± 1.37)	22.81 (± 1.64)
	in saturated steam	63.97 (± 1.09)	-31.05 (± 1.33)	31.05 (± 1.17)
140 °C	in N ₂	54.93 (± 1.67)	-40.09 (± 1.95)	40.09 (± 1.12)
	in O ₂	44.59 (± 1.53)	-50.43 (± 1.77)	53.13 (± 1.83)
	in saturated steam	36.94 (± 1.31)	-58.08 (± 1.06)	58.79 (± 1.49)

Note: Numbers in parentheses represent the deviation of five replicates

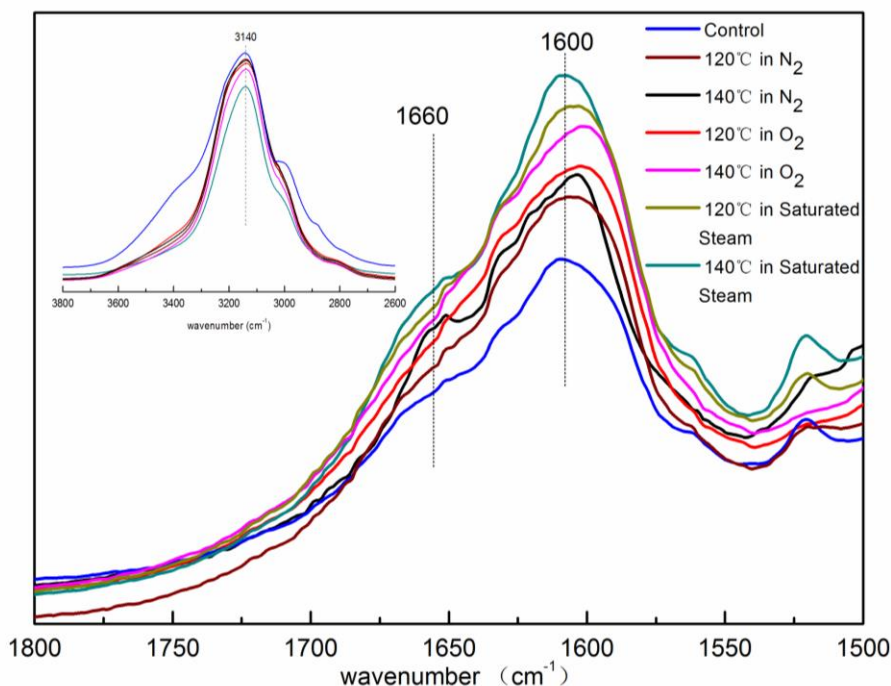


Fig. 3. ATR-FTIR spectra of the polyphenols before and after the heat treatment

ATR-FTIR Spectral Analysis

Figure 3 shows the ATR-FTIR spectra of the phenolic substances before and after the heat treatment. The absorption peak at 1660 cm^{-1} , which was assigned to conjugated carbonyls, increased, while the absorption intensity at 3200 cm^{-1} , which was hydroxyl groups in the phenolic components, decreased upon heating. This indicated that the hydroxyl groups in the phenolic components were oxidized to form carbonyl groups or the adjacent hydroxyl groups formed quinoid structures during the heat treatment. The absorption peak at 1600 cm^{-1} , which corresponded to the characteristic absorption peak of the aromatic skeletal vibrations with C=C stretching vibrations, became narrower and increased in intensity after the heat treatment. This indicated the formation and increase in conjugated structures in the phenolic components during heating. The changes in intensity of those peaks were more obvious when the samples were treated in saturated steam and oxygen at $140\text{ }^{\circ}\text{C}$.

2D-FTIR Spectral Analysis

Figure 4 shows the correlation spectra of the two-dimensional infrared (2D-FTIR) spectra of the polyphenols after the heat treatment in nitrogen, oxygen, and saturated steam. The 2D-FTIR spectroscopy provides higher resolution of the spectra (Popescu *et al.* 2011). The signals on the diagonal represented changes in the functional groups caused by the heat treatment (Huang *et al.* 2008; Li *et al.* 2015).

The darker color represented a higher sensitivity of the groups to the heat treatment. It was seen from Fig. 4c that the correlation strength of the C=O vibration at 1740 cm^{-1} was higher when treated in saturated steam than when treated in oxygen and nitrogen. The amount of double bonds between carbon and oxygen (C=O) increased. This was because of autocondensation and condensation reactions of the phenolic components during the thermal treatments (Kim *et al.* 2014).

The conjugated carbonyl bonds, which appeared at approximately 1680 cm^{-1} , may have been overlapped by a peak related to unconjugated carbonyls (Kim *et al.* 2014). The auto-peaks at 1400 to 1600 cm^{-1} that represented aromatic skeletal vibrations increased in the saturated steam. It was inferred that the groups linked to the aromatic ring skeleton were sensitive to water and oxygen during heating.

The intensity of the auto-peak at 1050 cm^{-1} , attributed to the C-O stretching vibrations, increased when the phenolic compounds were heated in saturated steam. This indicated that water was more effective for the condensation reactions of the phenolic compounds. This conclusion was also supported by the higher sensitivity in the region of 1000 to 1800 cm^{-1} when the samples were subjected to the heat treatment in saturated steam. The correlation strength of the -OH groups at approximately 3200 to 3400 cm^{-1} decreased upon heating.

The area of the hydroxyl peak became small when the samples were heated in the saturated steam atmosphere. This suggested that a portion of the -OH groups were replaced upon heating. With regards to the increase in the sensitivity of the peak at 1740 cm^{-1} , it was inferred that conjugated carbonyl groups formed through oxidation or condensation reactions.

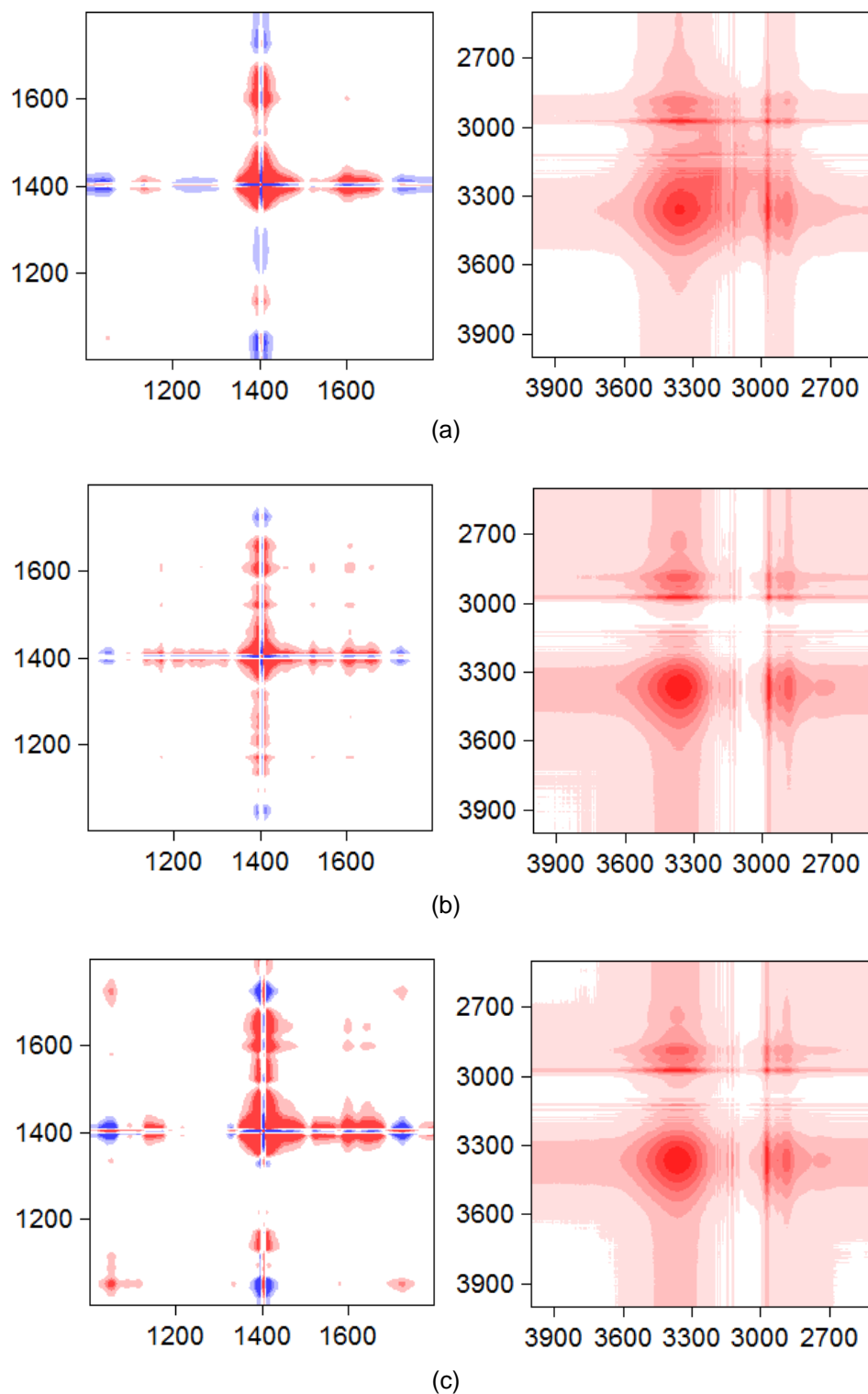


Fig. 4. 2D-FTIR spectra of the polyphenols after the heat treatment in (a) nitrogen, (b) oxygen, and (c) saturated steam

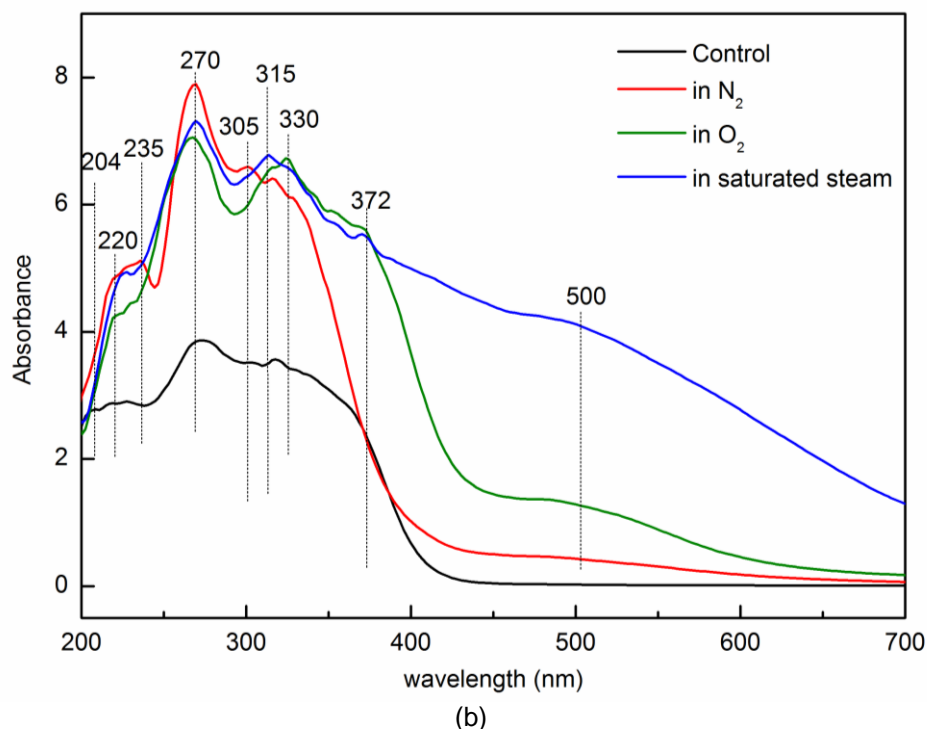
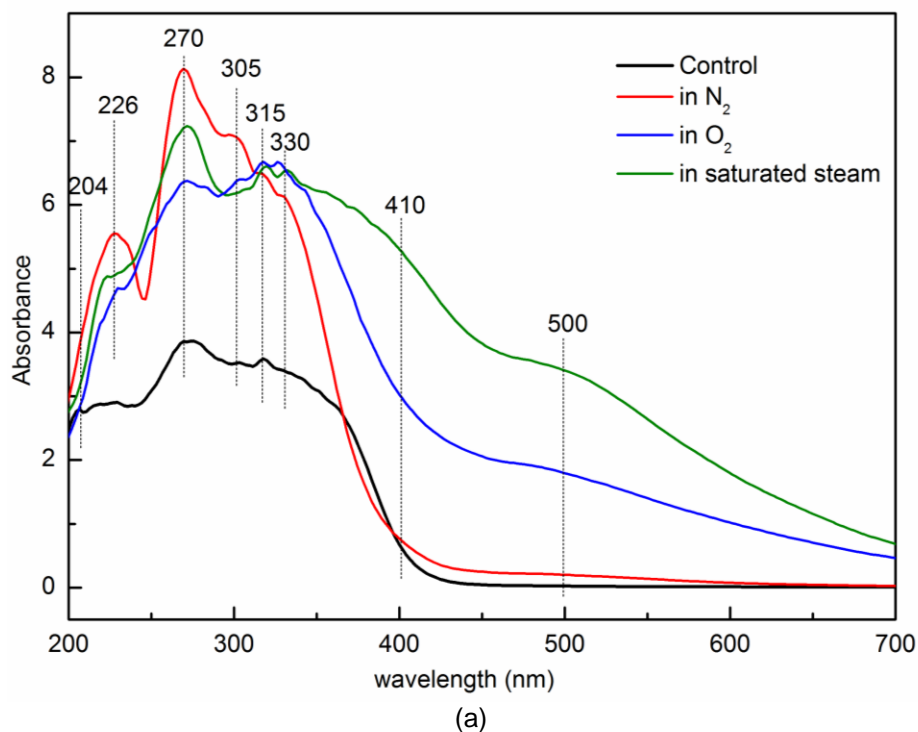


Fig. 5. K/S spectra of the polyphenols before and after the heat treatment at 120 (a) and 140 °C (b)

DRUV Spectra Analysis

Figure 5 shows the *K/S* spectra of the polyphenols before and after heating at 120 and 140 °C in oxygen, nitrogen, and saturated steam. The absorption intensity in the spectral region from 200 to 700 nm increased after the heat treatment, which was attributed to the formation of conjugated double-bond structures, including quinoid structures (370

to 550 nm). This led to an increase in the a^* parameter, which gave the phenolic substances a reddish color.

The peak at 204 nm was assigned to the E2 absorption band of benzene rings, which shifted to red (210 to 230 nm) when the auxochromes increased on the benzene ring. It was inferred that chemical reactions occurred in the phenolic substances and the number of chromophore groups on the benzene rings increased during heating. The absorption peak at 270 nm, which was attributed to the C=O groups conjugated to the benzene ring, increased sharply with the heat treatment. The increase was more severe when the samples were treated in nitrogen than when treated in oxygen and saturated steam. This was related to the formation of conjugated carbonyl groups. It was possible that the sample underwent a condensation reaction to produce the conjugated structures. An increase in absorption was observed at 320 to 350 nm after the heat treatment in oxygen and saturated steam. This was related to the formation of conjugated carbonyl groups, aromatic ketones, and alpha- and beta-unsaturated ketone structures (Chen *et al.* 2012; Koch *et al.* 2006). The increase in those groups was more obvious when the samples were treated at 140 °C. This may have resulted in the formation of quinoid structures and other chromophores in the phenolic compounds upon heating. The absorption at 410 nm after the heat treatment in all conditions at 140 °C may have caused the formation of polymeric quinine in the samples. This contributed to the yellowing of the phenolic components. However, stronger absorption was seen from 390 to 650 nm when the phenolic components were treated in saturated steam, which indicated that conjugated structures were formed during the heat treatment in saturated steam, and this resulted in the increase in the a^* and b^* values.

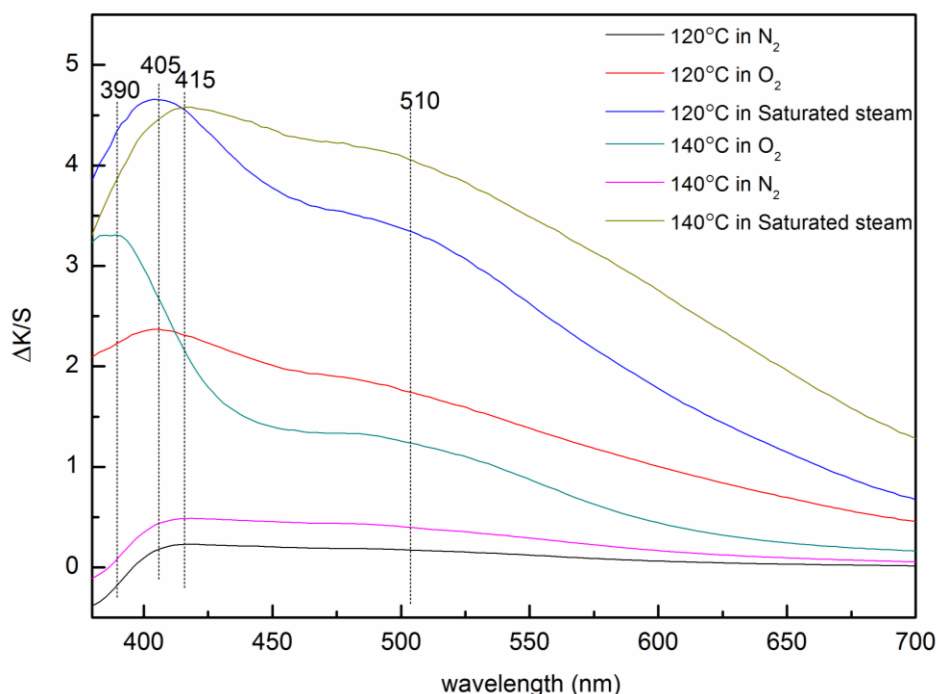


Fig. 6. $\Delta K/S$ spectra of the polyphenols before and after the heat treatment

Figure 6 shows the difference in the absorption spectra ($\Delta K/S$) at 380 to 700 nm of the polyphenols before and after the heat treatment. The absorption intensity increased strongly in the visual light area when the polyphenolic substances were heat-treated in the

saturated steam atmosphere, while there was no obvious increase in the absorption intensity when the samples were subjected to heating in the nitrogen atmosphere. It was concluded that the temperature was more effective in discoloring the phenolic components than other factors, such as the moisture and oxygen contents. The temperature was also effective at forming structures in the polyphenols that absorbed visual light during the heat treatment. This indicated that more conjugated structures were produced through oxidation or condensation reactions in the presence of saturated steam and oxygen. The increase in the light absorption at longer wavelengths contributed to the higher a^* , b^* , and C^* values.

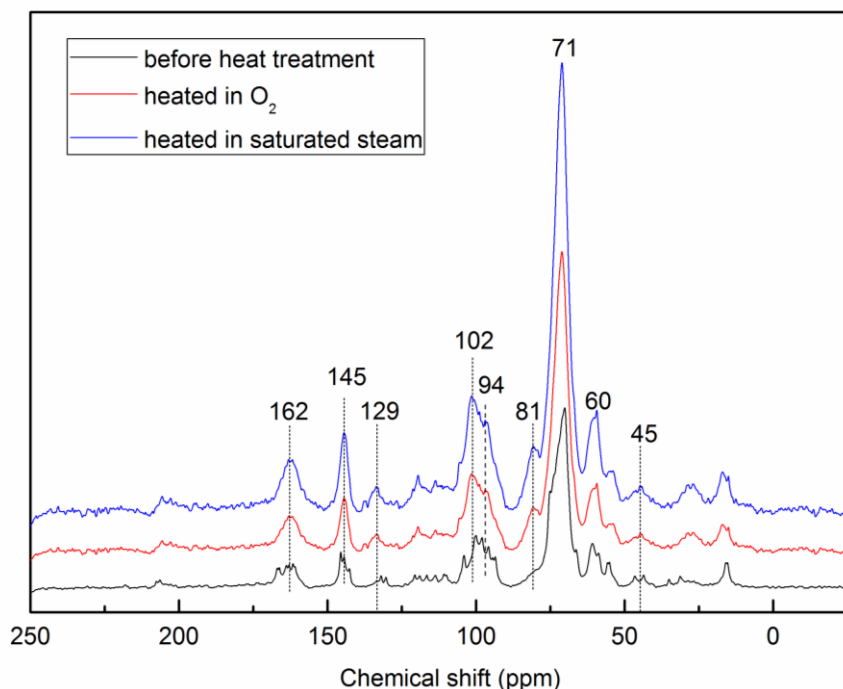


Fig. 7. CPMAS- ^{13}C -NMR spectra of the polyphenols before and after the heat treatment

CPMAS- ^{13}C -NMR Analysis

The CPMAS- ^{13}C -NMR spectra of the polyphenols before and after the heat treatment at 140 °C in the oxygen and saturated steam atmospheres are shown in Fig. 7. The intensity of the signals clearly increased after the heat treatment in oxygen and saturated steam. The intensity was stronger when heated in the saturated steam than in the oxygen atmosphere. The signals at 31 and 45 ppm, which corresponded to methylene groups (Chen *et al.* 2009), increased after the heat treatment. The intensity of the signal at 60 ppm also increased, which was assigned to methoxyl groups. Additionally, the intensities of the peaks at 94 and 129 ppm increased, which suggested that there was an increase in the conjugated carbonyls bonded in the benzene ring of the phenolic components. The chemical shifts at 162 ppm, which was assigned to C5, C7, and C9 in ring A of the phenolic compounds, and 145 ppm, which was assigned to C3' and C4' in the B ring of the phenolic compounds (Navarrete *et al.* 2011), increased upon heating. The increase in these signals may have corresponded to the oxidation of phenol groups during heating. After the heat treatment, there was also an increase at 200 to 225 ppm, which was assigned to carbonyl groups (Chen *et al.* 2014). This demonstrated that the phenolic

components were oxidized and generated carbonyl groups in the presence of oxygen and saturated steam, which made the color more vivid.

CONCLUSIONS

1. The color change and its mechanism of the phenolic extractives of black locust wood (*R. pseudoacacia*) during heat treatment were examined in this study. The chemical structures of the phenolic extractives changed during the heat treatment, which resulted in a more reddish and yellowish color. The changes in the color parameters were more noticeable when the samples were treated in the saturated steam or oxygen atmospheres at 140 °C. The effect of saturated steam heat treatment is most pronounced when heated at the same temperature and time. The oxygen and moisture contents had greater effects on the darkening of the phenolic extractives color.
2. The chemical changes of the phenolic extractives followed the same trend and degree as was seen for the color changes. Components that absorbed visible light were formed during the heat treatment. Conjugated systems were produced and enhanced through oxidation and condensation reactions during heating. The hydroxyl groups in the phenolic components were oxidized to form carbonyl groups or the adjacent hydroxyl groups formed quinoid structures during the heat treatment. The formation of conjugated C=O structures was consistent with the increase in the a^* , b^* , and C^* parameters.

ACKNOWLEDGEMENTS

The financial support from the National Natural Science Foundation of China (series project No. 31400498) and the Scientific Research Foundation for the Overseas Returned Scholars, Ministry of Education of China (No. 14JIX-01) is gratefully acknowledged.

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Article submitted: April 26, 2017; Peer review completed: July 15, 2017; Revised version received: July 21, 2017; Accepted: July 22, 2017; Published: August 8, 2017.
DOI: 10.15376/biores.12.4.7041-7055