

**STUDY ON COLOR AND SURFACE CHEMICAL  
PROPERTIES OF *EUCALYPTUS PELLITA* WOOD  
SUBJECTED TO THERMO-VACUUM TREATMENT**

BAILING SUN, ZHE WANG, JUNLIANG LIU  
CHINESE ACADEMY OF FORESTRY, RESEARCH INSTITUTE OF WOOD INDUSTRY  
P. R. CHINA

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**ABSTRACT**

The objective of this study was to investigate the color and surface chemical properties of *Eucalyptus pellita* wood subjected to thermo-vacuum treatment. Specimens were thermally modified in a vacuum at various temperatures for 4 h. The color parameters of untreated and heat-treated samples were measured using the CIE Lab method. Surface chemical properties were evaluated by UV-Vis spectroscopy, <sup>13</sup>C NMR spectroscopy and X-ray photoelectron spectroscopy. The results showed that eucalypt wood became darker uniformly throughout with the increase of treatment temperature, and the total color variation  $\Delta E^*$  obviously increased at higher temperature. The spectral changes indicated that degradation and oxidation of hemicellulose, lignin and extractives contributed to the formation of color substances during thermo-vacuum treatment. Crystalline content of carbohydrates increased. The decrease in O/C ratio signified the increase of the relative content of lignin and extractives on the wood surfaces in the heating process.

**KEYWORDS:** *Eucalyptus pellita*, thermo-vacuum treatment, color, surface chemical properties.

**INTRODUCTION**

Thermal modification is considered to be an effective and eco-friendly technique to improve wood stability and durability as well as obtain desirable color. Several thermal modification processes have been industrialized and widely described in literatures (Esteves and Pereira 2009). In recent years, thermal wood modification in relatively vacuum was developed as an alternative to prevent influence of oxygen during the treatment process (Yang et al. 2010, Ferrari et al. 2013b, Sun et al. 2017). Compared to other methods, this process has several advantages, such as high energy efficiency, less corrosion problems, and a lower rate of wood thermal degradation (Allegretti et al. 2012, Candelier et al. 2013a).

Thermal modification causes the chemical degradation of wood cell wall polymers and extractives. The degradation starts through deacetylation of hemicelluloses and the released acetic acid acts as a depolymerization catalyst that further increases polysaccharide and lignin decomposition (Tjeerdsma et al. 1998, Sivonen et al. 2002, Nuopponen et al. 2004). Amorphous cellulose is degraded resulting in an increase of cellulose crystallinity (Bhuiyan et al. 2000, Özgenç et al. 2017). In lignin, the cleavage of ether linkages and a reduction of methoxyl content lead to a more condensed structure (Nuopponen et al. 2004, Wikberg and Maunu 2004). As for extractives, most disappear during the process, but new ones appear resulting from polysaccharide degradation simultaneously (Esteves et al. 2008a, Candelier et al. 2013b).

Wood color also changes during thermal treatments, which is esthetically important and affects the commercial value of wood. The degree of color change depends on the heating process, the timber species, and wood density. Previous study demonstrates that oxidative and hydrolytic reactions are the main cause for production of chromophores during the process (Fengel and Wegener 1989). The color change is mainly ascribed to the colored degradation products from hemicelluloses and lignin resulting from thermal treatment and extractives joining in the color formation of heat-treated wood (McDonald et al. 1997, Sundqvist and Morén 2002, Sundqvist 2004, Sehlstedt-Persson 2003). With thermo-vacuum treatment, some researchers have examined the effects of factors affected by heating processes such as temperature, duration, and moisture (Srinivas and Pandey 2012, Ferrari et al. 2013a, Wang et al. 2016). However, the discoloration mechanisms of heat-treated wood under vacuum are still unclearly explained and need to be further explored.

*Eucalyptus pellita* is a fast-growing tree species and preferred for industrial plantation in China. For its main shortcomings, one previous study has reported that thermo-vacuum treatment can effectively improve its dimensional stability with a slight loss of mechanical properties (Sun et al. 2013). However, during the process, its color change behavior has not been comprehensively investigated. *Eucalyptus* wood is reddish in the sapwood and gradually become darker to the heartwood. Therefore, in this study, thermo-vacuum treatment as an alternative heat-treatment to improve its color homogeneous throughout was explored to obtain more desirable wood color. Meanwhile the chemical changes due to heat treatment were also comprehensively evaluated to reveal the discoloration mechanisms. Different surface chemical analyzing methods were used, such as diffuse reflectance UV-Vis, NMR and XPS.

## MATERIAL AND METHODS

### Materials

*Eucalyptus pellita* F. Muell. was obtained from China Eucalypt Research Centre in Guangdong Province, China. *Eucalyptus pellita* wood blocks, 330×40×40 mm, were cut from defect free wood and air-dried. Six samples were prepared for each treatment. The samples were oven dried at (103 ± 2)°C until a constant weight.

### Thermo-vacuum treatment

Thermo-vacuum treatment was carried out at 160, 180, 200, 220, and 240°C for 4 h under vacuum (0.02 to 0.08 MPa) in a laboratory vacuum pressure furnace. The samples were kept inside the furnace during the heat treatment process, and removed at the end of each heat treatment when the temperature fell to 40°C. The untreated wood blocks were used as control samples.

## Color measurement

Color was measured at three locations on each sample before and after the treatment, and six replicates were used. The surface color of samples was quantified using a Minolta CM-2600d spectrophotometer (Konica Minolta, Inc., Japan) through the CIE Lab system. The diameter of measured circle on the radial surface of samples was 8 mm. The light source was the Standard Illuminant D 65 and 10° standard observer.

The color system is characterized by three parameters,  $L^*$ ,  $a^*$ , and  $b^*$  coordinates. The total color variation ( $\Delta E^*$ ) was calculated from lightness ( $L^*$ ) and two color coordinates of  $a^*$  and  $b^*$  according to the following equation:

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

where:  $L^*$  - the brightness ranging from black (0) to white (100),  
 $a^*$  - the color coordinate from red (positive) to green (negative),  
 $b^*$  - the color coordinate from yellow (positive) to blue (negative).

## UV-Vis spectroscopic analysis

The wood samples were ground (Wiley mill) and sieved with 100-120 mesh sieves. The diffuse reflectance UV-Vis (DRUV) spectra from wood samples before and after thermo-vacuum treatment were recorded over the wavelength range 240-800 nm on a Cary 5000 UV-Vis spectrophotometer equipped with an integrating sphere.

## CP/MAS $^{13}\text{C}$ NMR analysis

The wood samples were ground into powder and sieved ( $\geq 200$  mesh). The wood powder was analyzed by Solid-state CP/MAS  $^{13}\text{C}$  NMR. The spectra were recorded on a Bruker AV 400 spectrometer at a frequency of 75.5 MHz. Chemical shifts were calculated relative to tetramethyl silane (TMS), which was used as the control. Acquisition time is 0.026 s with number of transients of about 1600. All the spectra are run with a relaxation delay of 2 s, contact time of 1 ms and spectral width of 300 Hz. Spinning rates are 5 kHz. Chemical shifts are expressed in parts per million.

## XPS analysis

Small wood chips of size 5×5×1 mm were cut with a cutter blade from untreated and heat-treated wood radial surface. X-ray photoelectron spectroscopy (XPS) measurements were performed on Thermo Scientific ESCALAB 250Xi spectrometer using a monochromatic Al  $K\alpha$  X-ray source ( $h\nu = 1486.6$  eV) with a power of 150W. The high-resolution spectra were collected at pass energy of 20 eV with a step of 0.1 eV using for quantitative measurements of binding energy and atomic concentration. XPS peak software (Vision 4.1) was utilized in the data processing. Chemical bond analysis of the carbon and oxygen was accomplished by fitting the C1s and O1s peaks, and then de-convoluting them into four and two sub-peaks, respectively.

# RESULTS AND DISCUSSION

## Color changes

Changes in color parameters of untreated and heat-treated eucalypt wood are presented in Tab. 1. Eucalypt wood became darker when exposed to heat treatment in vacuum. Lightness of heat-treated eucalypt wood decreased with treatment temperature.

Tab. 1: Color CIE Lab parameters and color difference between untreated and heat-treated eucalypt wood.

Heat-treatment (°C)	Color CIE Lab parameters			Color difference			
	$L^*$	$a^*$	$b^*$	$\Delta L^*$	$\Delta a^*$	$\Delta b^*$	$\Delta E^*$
Control	72.66	11.83	23.55	0	0	0	—
160	69.67	11.85	21.38	-2.99	0.02	-2.17	3.69
180	66.85	11.68	20.68	-5.80	-0.15	-2.87	6.48
200	57.81	11.67	20.56	-14.85	-0.14	-2.99	15.15
220	48.62	11.51	20.13	-24.03	-0.31	-3.43	24.28
240	33.55	10.70	19.10	-39.11	-1.13	-4.46	39.38

For instance, compared with untreated eucalypt wood, lightness ( $L^*$ ) decreased 4.1 and 8.0% within 4 h of treatment at 160 and 180°C, respectively. The maximum reduction (53.8%) was obtained for 4 h at 240°C. The parameter  $a^*$  increased at 160°C, but decreased afterwards reaching 9.5% for wood treated at 240°C for 4 h. Parameter  $b^*$  decreased with treatment temperature with a maximum decrease of 18.9% at 240°C for 4 h. A similar trend was noted by Esteves et al. (2008b). Compared with  $\Delta a^*$ , the changes of  $\Delta b^*$  is greater. But these changes were smaller than the change of parameter  $\Delta L^*$ . This was in consistent with previous studies (Wang et al. 2016, Dubey et al. 2011, Jin et al. 2011).

Total color variation  $\Delta E^*$  between the untreated and heat-treated samples increased slightly for less intensive treatments and then significantly at higher temperature. Maximum change in  $\Delta E^*$  increased from 15.15 to 39.38 with increase in temperature from 200 to 240°C. According to some previous studies, the color changes can be attributed to degradation of hemicelluloses and lignin, formation of oxidation products such as quinones and phenolic substances etc., and extractives dissolution, oxidation, decomposition or migration (Sundqvist 2004, Jin et al. 2011, Sen et al. 2012, Esteves et al. 2011, Chen et al. 2014). Therefore, to better understand the changes in eucalypt wood color upon heating, it is necessary to qualitatively and quantitatively analyze the wood chemical composition.

### UV-Vis spectroscopic analysis

Diffuse reflectance UV-Vis spectroscopy was used to characterize the wood chromophores and changes in their concentration relating to the discoloration of wood during heat treatment. As shown in Fig. 1, it is clear that the absorptions within the UV region (280-380 nm) increased with the temperature increasing and were significantly enhanced at 240°C for 4 h.

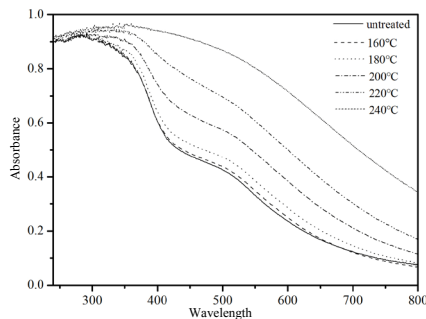


Fig. 1: UV-Vis diffuse reflectance spectra of untreated and heat-treated eucalypt wood.

The absorption at 280 nm indicates the augmentation of  $\beta$ -5, unsaturated  $C_\alpha$ ,  $C_\beta$  bond and  $\beta$ -C=O structure in lignin (Chen et al. 2012a). The broad absorption bands with peaks at about 330–380 nm can be attributed to the conjugated structures, such as double bonds, conjugated carbonyl functionalities, and quinoid structures from breakdown products of lignin, hemicellulose and extractives (Polcin and Rapson 1969, Chen et al. 2012b). In the visible region (400–760 nm), the absorptions in the 400 to 500 nm region relating to quinines also increased with the temperature increasing, which originate from degradation and oxidation of the aromatic hydroxyl groups of lignin and aromatic extractives during treatment process (Chen et al. 2012a).

### CP/MAS $^{13}\text{C}$ NMR analysis

CP/MAS  $^{13}\text{C}$  NMR spectra of untreated and heat-treated eucalypt wood at different temperatures are shown in Fig. 2. Evolution of NMR spectra recorded the changes in polymeric structural constituents of wood before and after heat treatment. Signals between 72 and 75 ppm are assigned to carbohydrates C2, C3 and C5 carbons.

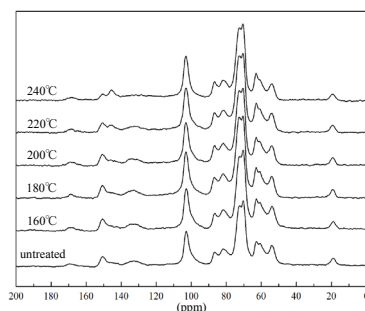


Fig. 2:  $^{13}\text{C}$  NMR spectra of untreated and heat-treated eucalypt wood.

The signals were unchanged with heat treatment, meaning there was no pyranose ring opening (Boonstra et al. 2006a). The crystalline carbohydrates C4 and C6 signals at 89 and 65 ppm increased for 4 h at 240°C, and meanwhile the amorphous carbohydrates C4 and C6 signals at 82 and 62 ppm decreased obviously. That can be mainly attributed to the degradation reaction of less stable polysaccharidic components at higher temperature (Hakkou et al. 2005, Boonstra et al. 2006b). Degradation of hemicellulose was particularly obvious at temperatures above 200°C. The shoulder at 102 ppm appearing on the C1 signal of carbohydrates and at 105 ppm is attributed to hemiacetal carbon of hemicellulose, which decreased after heat treatment. The signals of acetyl groups at 173 ppm also significantly decreased with increasing temperature indicating deacetylation of the hemicellulose. Regarding the lignin, methoxyl groups of syringyl and guaiacyl lignin units are detected at 56 ppm, while aromatic carbons appear between 120 and 160 ppm. Aliphatic carbons of phenylpropane units of lignin are partially masked by polysaccharide signals (Inari et al. 2007). The appearance of signals between 125 and 135 ppm can be ascribable to thermal crosslinking of lignin (Tjeerdsma et al. 1998, Wikberg and Maunu 2004). The signal at 132 ppm attributed to ArC-H or  $C_\gamma$  disappeared at 240°C. This indicates a certain proportion of lignin skeleton cleavage and a decrease in the molecular weight. The rise in the intensity of signal at 148 ppm related to C3, C5 in syringyl unetherified and the fall in the intensity of signal at 153 ppm associated with C3, C5 in syringyl  $\beta$ -O-4 showed an increase in the proportion of unetherified aromatic fragment (particularly in structures of the syringyl type) (Rokhin et al. 1995, Chen and Robert 1988, Li et al. 2003).

## XPS analysis

The typical XPS survey spectra of untreated and heat-treated eucalypt wood are shown in Fig. 3.

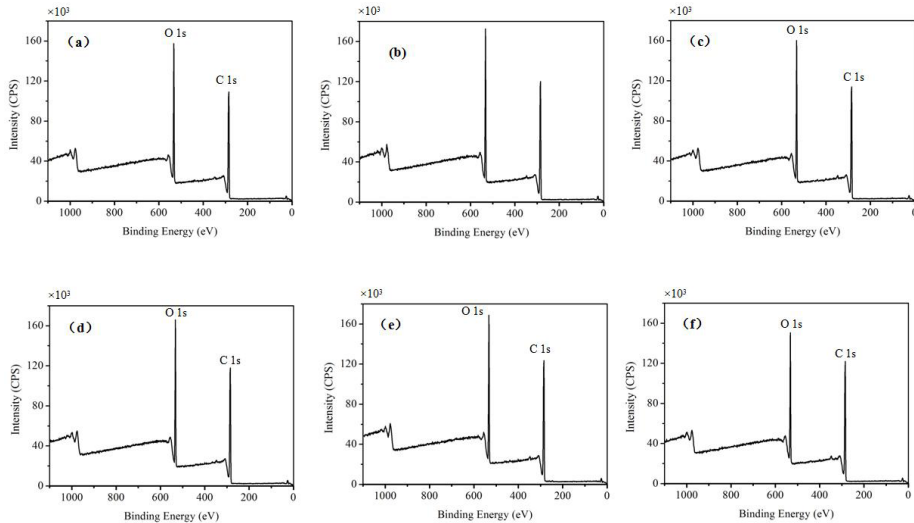


Fig. 3: XPS survey spectra of untreated and heat-treated eucalypt wood: (a) untreated; (b) heat treated at 160 °C for 4 h; (c) heat treated at 180 °C for 4 h; (d) heat treated at 200 °C for 4 h; (e) heat treated at 220 °C for 4 h; (f) heat treated at 240 °C for 4 h.

The XPS spectra reveal that carbon and oxygen are the major elements in the untreated and heat-treated samples, which occur at about 284 and 532 eV, respectively. In addition, a small amount of silicon was detected on the surface of samples through characteristic emission peaks at about 98 eV. The detail atomic percentages of eucalypt wood subjected to different treatments are reported in Tab. 2.

Tab. 2: Summary of XPS spectral parameters of untreated and heat-treated eucalypt wood.

Heat-treatment (°C)	O (%)	C (%)	Si (%)	O/C	C1 (%)	C2 (%)	C3 (%)	C4 (%)	O1 (%)	O2 (%)
Control	30.43	69.19	0.37	0.44	32.22	30.25	3.71	3.00	1.45	28.97
160	30.44	69.35	0.21	0.44	33.17	29.51	3.84	2.82	1.02	29.42
180	30.11	69.53	0.36	0.43	34.09	28.86	4.43	2.15	1.63	28.48
200	29.87	69.91	0.22	0.43	34.92	27.96	3.49	3.53	1.33	28.53
220	29.75	69.93	0.32	0.42	36.10	26.37	3.97	3.48	1.79	27.96
240	28.48	71.17	0.35	0.40	37.88	26.26	3.47	3.57	2.53	25.95

As shown, the percentage of carbon atoms increased with treatment temperature increasing, while the percentage of oxygen atoms decreased. In comparison with untreated wood, the oxygen to carbon (O/C) ratios decreased from 0.44 to 0.40 during heat treatment. This finding agrees with the results obtained by previous studies (Wang et al. 2016, Gérardin et al. 2007). The degradation of wood can be detected through a change in the O/C atomic ratio (Inari et al. 2006). In principle, the O/C ratio of cellulose, which is made up of  $\beta$ -D-glucopyranose units,

is calculated as 0.83. Hemicellulose, which is mainly represented by glucuronoxylans, has an O/C of approximately 0.8. The contribution of lignin is more complex due to its complicated molecular structure. The theoretical value of O/C for lignin is approximately 0.33 (Inari et al. 2006, Kocaefe et al. 2013). The O/C ratio of extractives, which are mainly composed of lipophilic compounds, is estimated to be 0.1 (Inari et al. 2011). Therefore, the high polysaccharide content can be reflected by high O/C ratio, while the presence of more lignin and extractives on wood surfaces can be indicated by a low O/C ratio. Therefore, in this study the decrease in O/C ratio could be attributed to the increase of the relative content of lignin resulting from the degradation of hemicellulose. Dehydration of polymers initially present in wood or the formation of new components leading to the formation of volatile by-products with low oxygen content could be a cause of the decrease in O/C ratio after heat treatment (Tuong and Li 2011).

In order to further investigate the surface chemical structures of heat-treated wood, the high-resolution XPS spectra of C1s and O1s were processed. The assignment of the high-resolution C1s XPS spectra may correspond to four types of carbon atoms expressed as C1-C4 (Kamdern et al. 2001, Nzokou and Kamdem 2005, Xu et al. 2013). The C1 component corresponding to carbon atoms bonded only with carbon or hydrogen atoms, which mainly arises from lignin and wood extractives (Kamdern et al. 1991). The C2 component corresponding to carbon atoms bonded with one oxygen atom, which has been shown to be mainly derived from cellulose and hemicelluloses (Kamdern et al. 1991, Wang et al. 2009, Meng et al. 2016). The C3 peak represents carbon atoms bonded to a carbonyl or two non-carbonyl oxygen atoms, which is assigned to cellulose (Popescu et al. 2009). The C4 represents carbon atoms linked to one carbonyl and one non-carbonyl oxygen atoms (Inari et al. 2006).

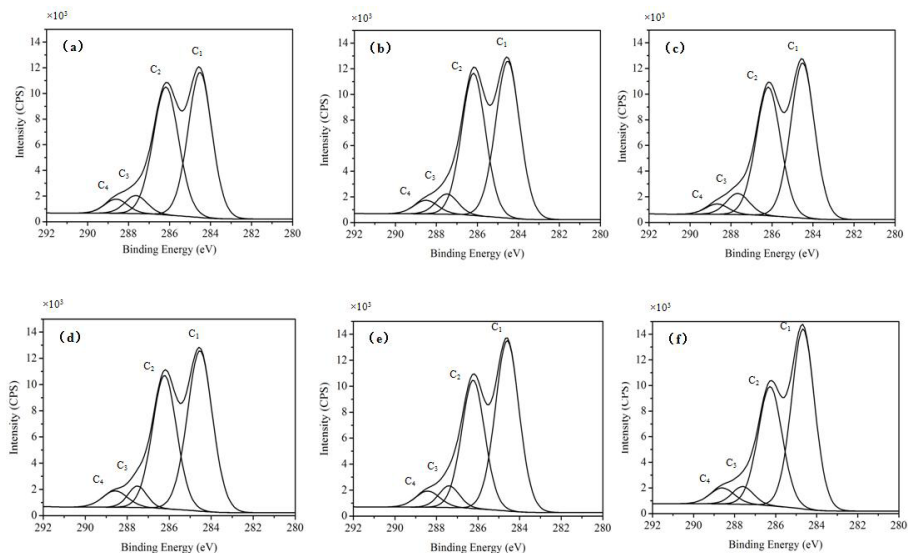


Fig. 4: C1s spectra of untreated and heat-treated eucalypt wood: (a) untreated; (b) heat treated at 160 °C for 4 h; (c) heat treated at 180 °C for 4 h; (d) heat treated at 200 °C for 4 h; (e) heat treated at 220 °C for 4 h; (f) heat treated at 240 °C for 4 h.

As shown in Tab. 2 and Fig. 4, C1 and C2 components are the major constituents of C1s on the surfaces of untreated and heat-treated wood samples. The C1 component had the most important contribution for the eucalypt wood surface before and after heat treatment. The C1

contribution increased whereas the C2 contribution decreased with the increase of treatment temperature, which indicated that the degradation of polysaccharides occurred and the contents of lignin and extractives increased during heat treatment. The changes in the contribution of C1 and C2 peak of wood samples show that wood surfaces are richer in lignin and poorer in polysaccharides after heat treatment.

The lack of research on the O1s peak of woody materials is attributed to the complex shift in behavior of the O1s peak compared with that of the C1s peak (Meng et al. 2016). As shown in Tab. 2, the contribution of oxygen atoms presented two components: O1 and O2. According to the literature, the O1 peak corresponds to oxygen atoms bonded to carbon with a double bond, and the O2 peak corresponds to oxygen atoms bonded to carbon with a single bond (Kamdem et al. 1991, Hua et al. 1993). At the higher treatment temperatures, the increase of O1 component is maybe an indication of oxidation reaction.

## CONCLUSIONS

The color of thermally modified eucalypt wood became darker uniformly throughout with treatment temperature increasing. The values of lightness  $L^*$  and  $b^*$  decreased with thermo-vacuum treatment, while  $a^*$  increased first and decreased later on. The results of UV-Vis spectroscopy indicated that oxidation products and phenolic substances such as the quinines from lignin were formed during thermo-vacuum treatment. In addition, both hemicellulose and extractives also played an important role in the formation of color substances in the heating process. The results obtained from NMR showed degradation of hemicellulose occurred by deacetylation releasing acetic acid, which further increased the degradation of lignin. The decrease in O/C ratio signified the increase of the relative content of lignin and extractives on the wood surfaces after thermo-vacuum treatment. The increase in O1 indicated the occurrence of oxidation reactions during heat treatment. According to these results, thermo-vacuum treatment can effectively change the overall color of eucalypt wood through altering its chemical components.

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BAILING SUN\*1, ZHE WANG, JUNLIANG LIU\*  
CHINESE ACADEMY OF FORESTRY  
RESEARCH INSTITUTE OF WOOD INDUSTRY  
BEIJING 100091  
P. R. CHINA

Corresponding author: liujunliang@caf.ac.cn  
PHONE: +86-010- 62889477

\*ISUNBLING@126.COM, SUN\_BAI\_LING@163.COM

