

Influences of Thermo-Vacuum Treatment on Colors and Chemical Compositions of Alder Birch Wood

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With high temperature-heat treatment, the dimensional stability and durability of wood is improved and wood color is darkened as well. In this paper, alder birch wood (*Betula alnoides*) was treated by the Thermo-Vacuum Treatment (TVT). The changes of wood color parameters and the chemical composition were determined by the CIE1976 $L^*a^*b^*$ method and the chemical analysis method, respectively. The results were revealed as follows: (1) A lower value of lightness, L^* , and a higher value of total color difference, ΔE^* , were obtained at the higher heat-treatment temperatures and longer treatment time. (2) The higher the heat-treatment temperatures and the longer the heat-treatment times were, the lower the contents of hemicellulose and cellulose were and the higher the content of lignin was. Moreover, Fourier Transform infrared spectroscopy (FTIR) analysis demonstrated that the characteristic absorption peaks of cellulose, hemicellulose, and lignin diminished. The acetylation reaction of hemicellulose and the degradation reaction of groups of lignin side chain occurred during TVT. (3) TVT degraded the chemical composition of cell walls, which resulted in further changes of the wood color. A significant correlation existed between the differences of color indices and the differences of the chemical composition after TVT.

Keywords: Alder Birch; Thermo-Vacuum Treatment (TVT); Wood color; Chemical composition

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INTRODUCTION

Alder birch wood (*Betula alnoides*) is a fast-growing species found in the tropical zone, south subtropical zone, and part of the middle subtropical zone, mainly distributed in the southern Gaoligong Mountains, Wuliang Mountain, Ailao Mountains, and Lancang River, Red River Basin in the regions of southern Yunnan Province, China. Although the production yield is large, the drawbacks of low dimensional stability and poor durability limit the application of alder birch.

A high temperature heat-treatment method has been found to reduce wood hygroscopicity (Olek *et al.* 2013), improve dimensional stability (Esteves *et al.* 2008; Gunduz *et al.* 2009), and improve biological durability (Calonego *et al.* 2010). However, wood color is always greatly changed (Aksoy *et al.* 2011; Akgül and Korkut 2012; Allegretti *et al.* 2012; Srinivas and Pandey 2012; Kamperidou *et al.* 2013), and chemical composition is degraded (Akgül and Korkut 2012) after the heat treatment. Most previous studies have used the convection of nitrogen, saturated steam, or superheated steam in the treatment chamber during the high temperature heat-treatment. As a result, the mechanical

strength of the wood was reduced according to different heat-treatment conditions (Surini *et al.* 2012; Rautkari *et al.* 2014). Due to the processing environment of the thermo-vacuum treatment (TVT) without oxygen or little oxygen, almost no oxidation reaction in wood occurred. In addition, since the water boiling point is reduced under vacuum conditions, much evaporation occurs at lower temperatures, leading to less water within wood participating in hydrolysis. Less weight loss occurs under vacuum conditions (Allegretti *et al.* 2012; Srinivas and Pandey 2012).

In this study, alder birch wood was treated by TVT under the relative vacuum of -0.08 MPa, with different temperatures (160 to 200 °C) and different treatment times (1 to 4 h). The wood colors and chemical compositions were measured before and after TVT, and the relationships between the changes of color and chemical compositions were explored. The aim was to use the changes of color to predict the changes chemical compositions, and further to predict the dimensional stability and mechanical strength properties, ultimately achieving to control the quality of heat-treated woods.

EXPERIMENTAL

Material

Six alder birch trees were obtained from Jinghan Town, Longchuan County, Dehong City, Yunnan Province, China, in December 2008. The average height and breast height diameter of these trees were 10 m and 20 to 25 cm, respectively. The trunks of trees, 1.3 to 5.3 m above the ground were selected and sawed into plates 40 mm thick in the radial direction. After having been air-dried, these plates were cut down to 150 mm (L) × 50 mm (T) × 20 mm (R) for TVT. The initial moisture content and density were 9.8% and 0.49 kg/m³, respectively.

TVT Process of Wood Specimens

Heat treatments were carried out at 160 °C, 170 °C, 180 °C, 190 °C, and 200 °C under -0.08 MPa vacuum for 1 h, 2 h, 3 h, and 4 h, respectively. Ten replicates were conducted at each treatment condition. Heat-treatment time was counted from the time when the wood surface layer reached the target temperature. After reaching the target treatment times, heating power was turned off and the samples were cooled to room temperature. The vacuum chamber was released and the samples were removed from the treatment chamber.

Determination of Color Changes

Using the CIE (1976) $L^*a^*b^*$ method, color changes before and after TVT were measured using an automatic color difference meter (SC-80C, Beijing Kangguang Instruments Co., China). Ten points were measured for each sample. The ΔL^* and ΔE^* values were calculated by Eqs. 1 and 2,

$$\Delta L^* = L^* - L_0^* \quad (1)$$

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

where L^* represents the lightness, a^* represents the red-green color coordinate, b^* represents the yellow-blue color coordinate, ΔL^* represents the lightness difference, Δa^*

represents the red-green color coordinate difference, Δb^* represents the yellow-blue color coordinate difference, and ΔE^* represents the overall color difference between the untreated and the heat-treated samples.

Determination of Wood Chemical Composition

The determination of holocellulose contents was according to the national standard of the People's Republic of China GB/T 2677.10-1995 (1995). The determination of cellulose content was according to the nitric acid-ethyl-alcohol method. The determination of lignin content was according to the national standard of the People's Republic of China GB/T 2677.8-94 (1994). The holocellulose, cellulose, and lignin contents were determined before and after TVT.

For FTIR analysis, the oven-dried wood flour and spectrum potassium bromide were fully mixed in a ratio of 1:150 and poured into the agate mortar to be ground into powder form (keeping the wood powder and potassium bromide staying in dried condition in the whole process). Using the powder tablet press machine (FW-4A, Uncommon Technology Development Co., China), the powder mixture was compressed into slice samples that were scanned by the FTIR (Scimitar 1000, Varian Inc., America) with an infrared absorption spectrum in the range 4000 to 400 cm^{-1} .

The $\Delta Hemicellulose$, $\Delta Cellulose$ and $\Delta Lignin$ were calculated by Eqs. 3 to 5,

$$\Delta Hemicellulose = Hemicellulose_T - Hemicellulose_0 \quad (3)$$

$$\Delta Cellulose = Cellulose_T - Cellulose_0 \quad (4)$$

$$\Delta Lignin = Lignin_T - Lignin_0 \quad (5)$$

where $\Delta Hemicellulose$, $\Delta Cellulose$, and $\Delta Lignin$ represent the hemicellulose content difference, the cellulose content difference, the lignin content difference between untreated and heat-treated samples, respectively. The subscript T represents the heat-treated samples, whereas the subscript 0 represents the untreated samples.

RESULTS AND DISCUSSION

Changes of Wood Color

Figure 1 provides examples of the macro images of alder birch wood before and after TVT. It can be seen that the color of alder birch wood changed from light white to dark brown and turned uniform after TVT. As a result of heat treatment, they clearly showed a darker tone for all the heat treatment conditions. The higher the heat-treatment temperature was and the longer the heat-treatment time was, the darker the color was shown. At the heat-treatment temperatures of 160 °C and 170 °C, slight color changes were found, and the color changes were greater when temperatures were at 180 °C or above. Compared to the effect of temperature, the treatment time was less effective on color changes.

Figure 2 presents the results of ΔL^* and ΔE^* of alder birch wood for different heat-treatment temperatures and times, where it can be seen that the higher the heat-treatment temperature was and the longer the heat-treatment time was, the lower the value of ΔL^* was and the higher the value of ΔE^* was. The value of L^* decreased from 76.812 to 52.272. The highest ΔE^* was 25.21 after heat treatment at 200 °C/4h.



Fig. 1. Macro picture of Alder birch wood before and after TVT

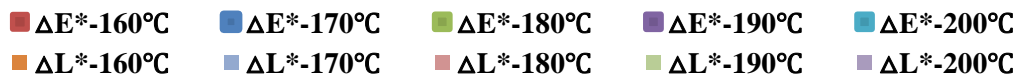


Fig. 2. Influences of TVT on ΔL^* and ΔE^* of Alder birch wood

Under the same heat-treatment time, the changing trends of ΔL^* and ΔE^* were slow when the temperature was under 180 °C but changed remarkably when the heat-treatment temperatures were 180 °C or above. Under the same heat-treatment temperature, the change trends of ΔL^* and ΔE^* were flattened off with the extension of heat-treatment time, which indicated that the influence of heat-treatment time on ΔL^* and ΔE^* was not as great as the heat-treated temperature. The results of this study were compatible with the literature findings (Liu *et al.* 1994; Shi *et al.* 2011). Through the result analysis of: ΔL^* and ΔE^* , it was found that the color change was mainly caused by ΔL^* , which was consistent with previous studies (Marcos *et al.* 2009; Allegretti *et al.* 2012).

A strong correlation between ΔE^* , the heat-treated temperature (t), and time duration (τ) was found, $\Delta E^*=0.2562t+1.33\tau-34.723$ ($R^2=0.8877$). So was the strong correlation between ΔL^* and the heat-treated temperature (t) and time duration (τ), $\Delta L^*=-0.2786t-1.346\tau+39.37$ ($R^2=0.9047$).

Changes of Wood Chemical Compositions

Figure 3 shows the relative content variations of hemicellulose, cellulose, and lignin of alder birch wood after TVT. It can be seen in Fig. 3 that the higher the heat-treatment temperature was and the longer the heat-treatment time was, the lower the relative contents of hemicellulose and cellulose and the higher the relative contents of lignin were found. The relative content of hemicellulose and cellulose decreased by 17.41% and 5.92%, respectively, while that of lignin increased by 36.49% under the condition of heat-treatment temperature of 200 °C, heat-treatment time of 4h, and relative vacuum of -0.08 MPa. The trend of changes of the three chemical constituents was consistent with the research results of Akgül and Korkut (2012) and Cao (2008). When the heat treatment temperature was 180 °C or below, the contents of hemicellulose tended to decrease and that of lignin increased flatly. When the temperature was over 180 °C, the contents of hemicellulose decreased quickly while that of lignin tended to increase, which indicated that most polysaccharide substances in the wood began to thermally degrade. It was found that the hemicellulose of alder birch wood was mostly degraded by TVT in this research. The result was consistent with the findings in literatures (Yildiz *et al.* 2005, 2006).

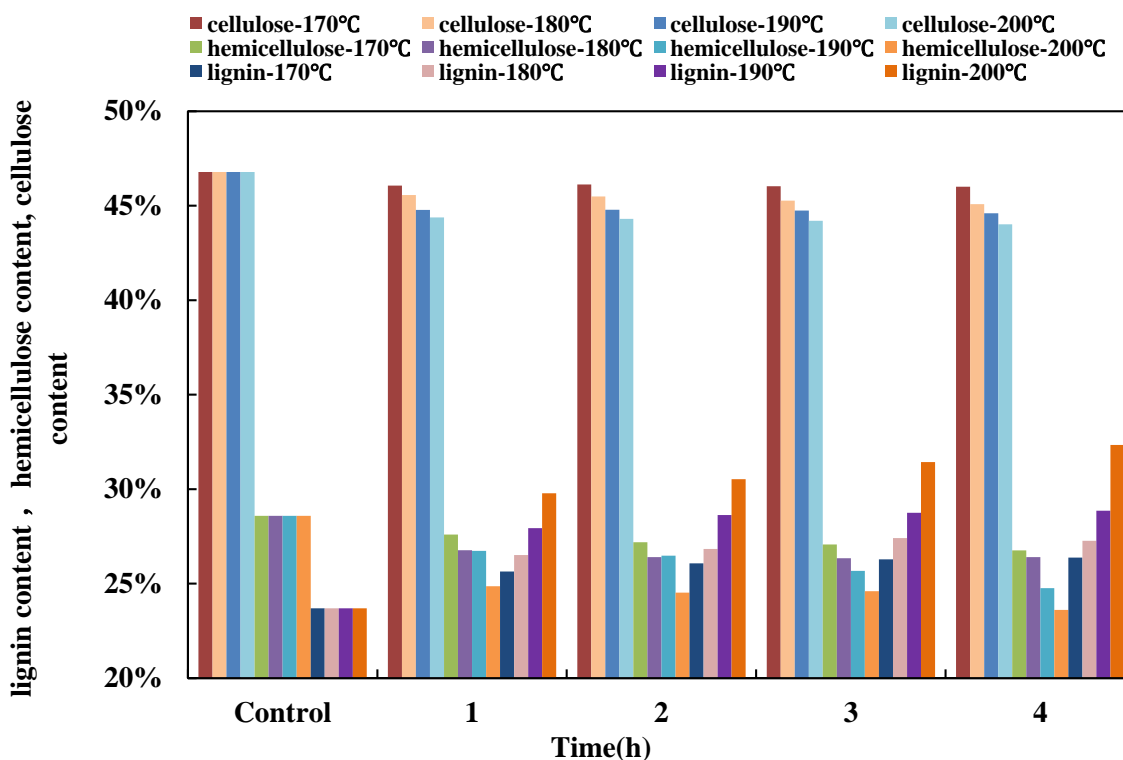


Fig. 3. Influences of TVT on hemicellulose content, cellulose content, and lignin content of alder birch wood

Heat-treatment resulted in changes of wood chemical constituents, mainly the degradation of hemicelluloses. Hemicelluloses are the least thermally stable wood

polymers, mainly owing to their low molecular weight, amorphous nature, and branched structure, which facilitate a rapid degradation as compared to other wood components (Akgül and Korkut 2012). The acetyl groups in hemicelluloses are thermally unstable and lead to the formation of acetic acid which is auto-catalyzed by the degradation of polysaccharides, in particular the hemicelluloses (Tjeerdma *et al.* 1998).

A strong correlation between $\Delta Hemicellulose$ and the heat-treated temperature (t), time duration (τ) was found, $\Delta Hemicellulose = -0.00086t - 0.0035\tau + 0.1416$ ($R^2=0.8679$). So was the strong correlation between $\Delta Cellulose$ (or $\Delta Lignin$) and the heat-treated temperature (t), time duration (τ), $\Delta Cellulose = -0.0005852t - 0.001145\tau + 0.09429$ ($R^2=0.9737$), $\Delta Lignin = 0.001522t + 0.004804\tau - 0.2492$ ($R^2=0.9236$).

Figure 4 illustrates the comparison diagram of alder birch wood infrared spectra before and after TVT.

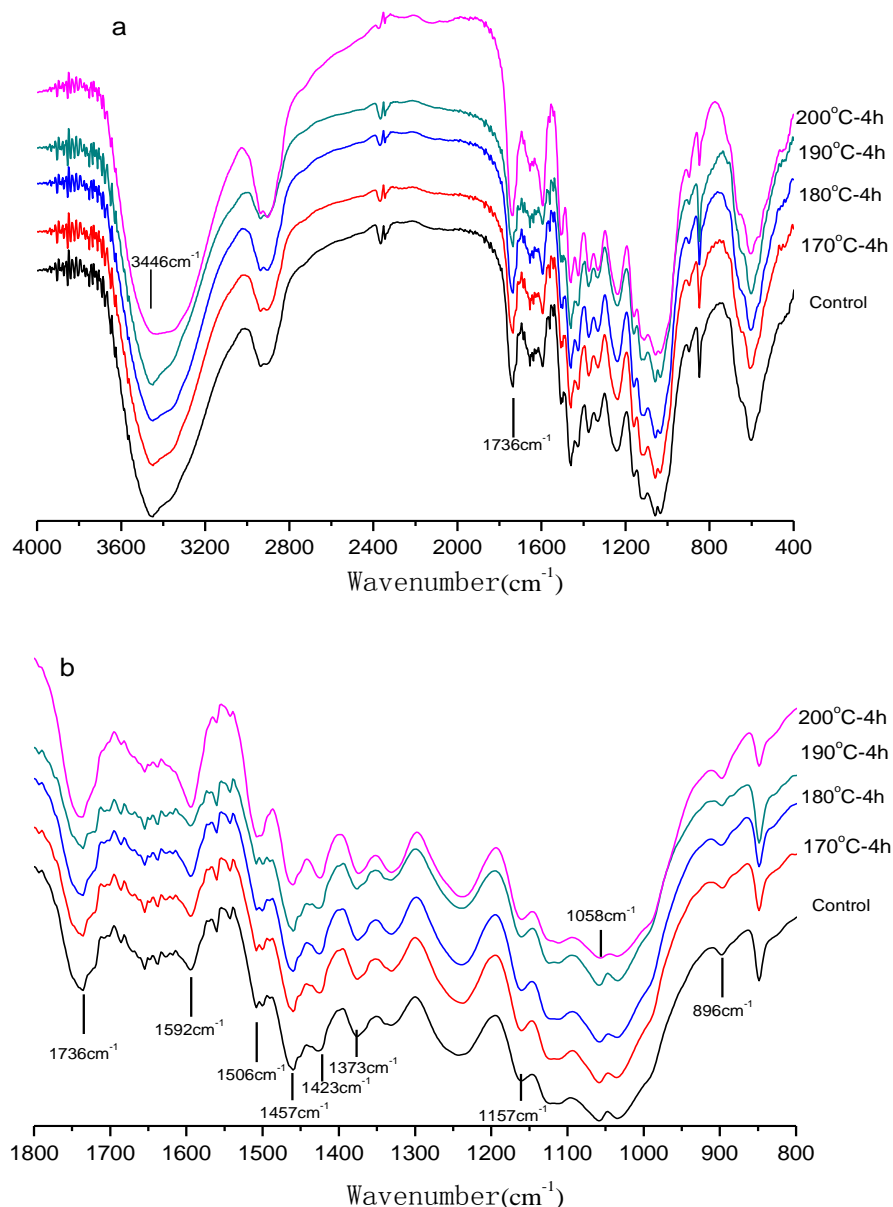


Fig. 4. Infrared spectrum of heat treatment of alder birch wood : a. 4000 to 400 cm⁻¹, b. magnification of 1800 to 800 cm⁻¹

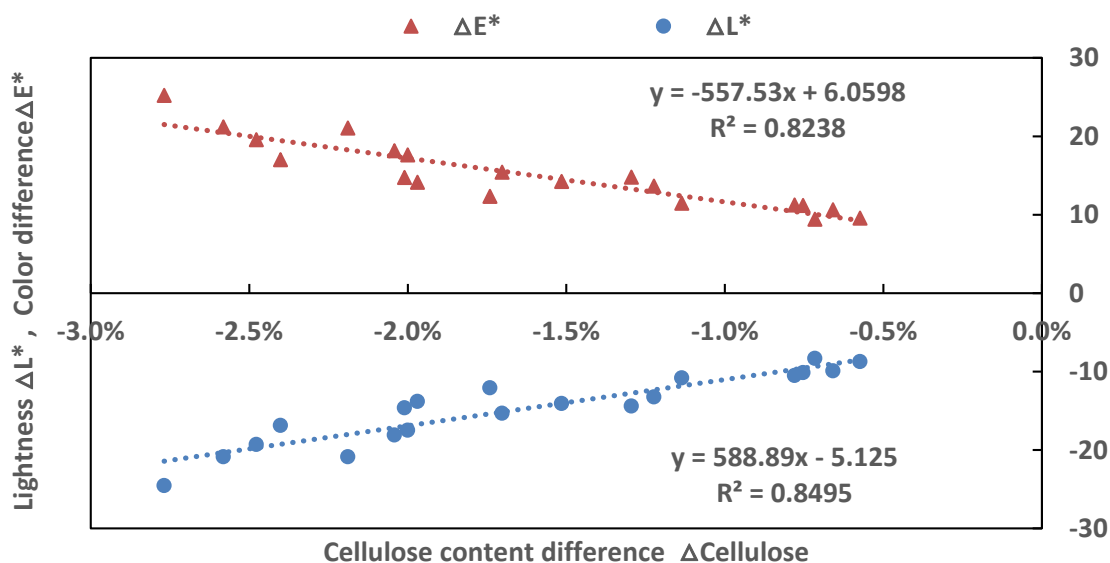
It can be seen in Fig. 4 that the -OH absorption peak at 3446 cm^{-1} may be attributed to cellulose. As the heat-treatment temperature was increased, the absorption peak intensity was reduced significantly. The C=O stretching vibration absorption peak of acetyl or carboxylic acid (xylan acetyl $\text{CH}_3\text{C}=\text{O}$) at 1736 cm^{-1} may be attributed to hemicellulose. With the higher heat-treatment temperature, hemicellulose started to undergo the deacetylation action, and acetyl hydrolysis generated acetic acid by hydrolysis, which decreased the number of C=O and gradually weakened the absorption peak intensity of hemicellulose, leading to the decrease in hemicellulose contents.

Absorption peaks of CH_2 scissoring vibration, CH bending vibration, C-O-C stretching vibration, C-O stretching vibration peak, and anomeric carbon (C_1) vibration at 1423 cm^{-1} , 1373 cm^{-1} , 1157 cm^{-1} , 1058 cm^{-1} , and 896 cm^{-1} , respectively, may be attributed to cellulose and hemicellulose. They weakened to different levels, which indicated that the carbohydrates started to undergo the degradation reaction, leading to the decreases of their contents.

The absorption peaks of benzene ring carbon skeleton vibration, aromatic ring carbon skeleton vibration, C-H bending vibration (lignin, CH_2 in glycan), and carbon skeleton vibration of benzene ring (lignin) at 1592 cm^{-1} , 1506 cm^{-1} , and 1457 cm^{-1} , respectively, may be attributed to lignin. Their intensities decreased to different extents, which indicated that, although some of the lignin were degraded by the thermal degradation, the degradation rate was much smaller than that of the hemicellulose.

Relationships between Color Differences and Chemical Composition Differences

Figure 5 shows the relationships of color index differences and chemical composition differences of the heat-treated Alder birch wood. It was revealed that the correlations between ΔL^* and $\Delta\text{Hemicellulose}$, $\Delta\text{Cellulose}$, ΔLignin , respectively, were strong, so were strong the correlations between ΔE^* and $\Delta\text{Hemicellulose}$, $\Delta\text{Cellulose}$, ΔLignin , respectively.



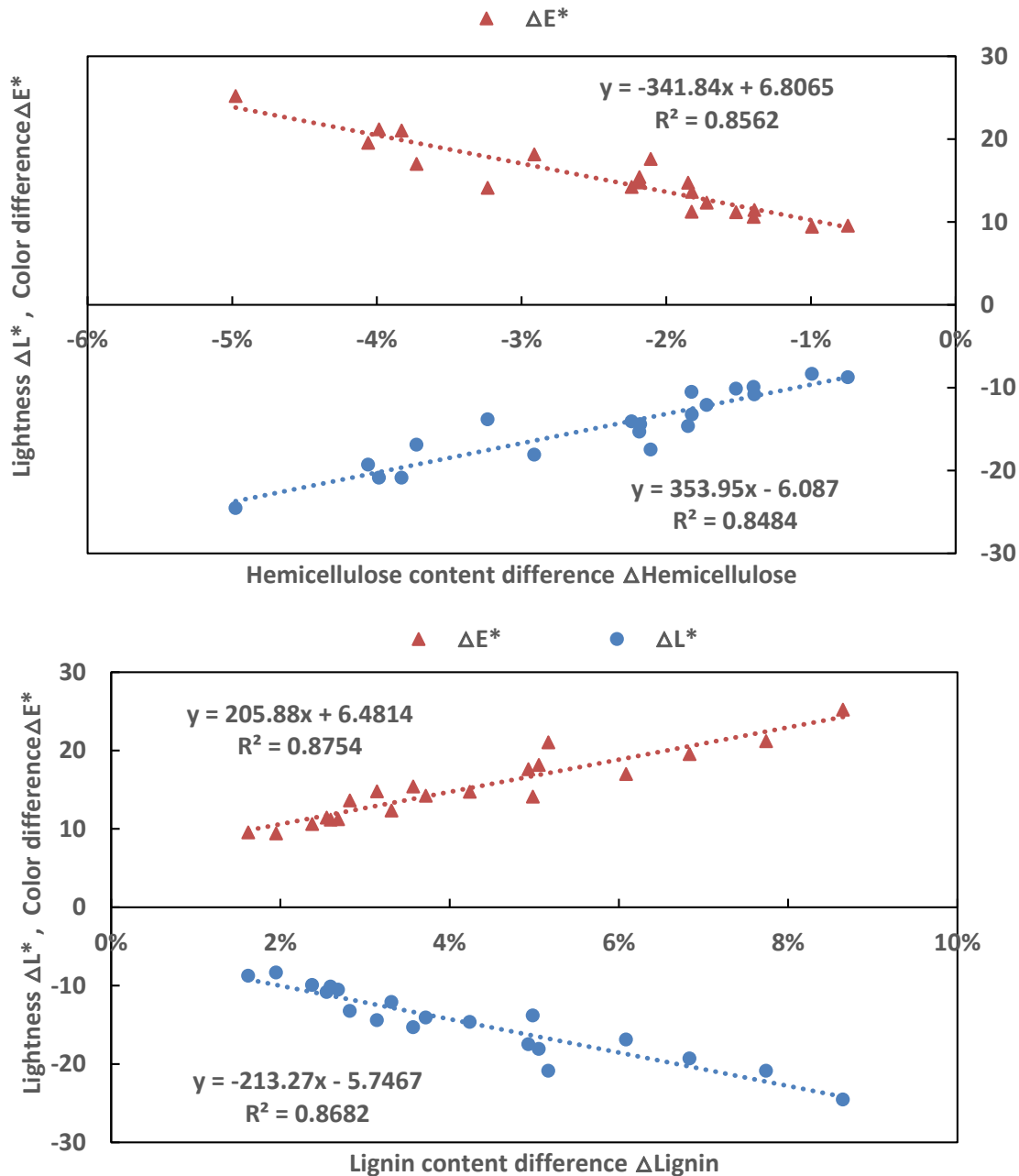


Fig. 5. Relationships between color index differences and chemical composition differences

Some of the colored products, furfural, for instance, formed after the thermal degradation of hemicelluloses. These colored components lead to wood color change. These heat-degraded compounds, along with wood extractives and other compounds such as low molecular weight sugars and amino acids, migrate towards the wood surface during the heat-treatment process (Dubey 2010). Furthermore, lignin contains many chromophoric groups, for example, the benzene ring, carbonyl, ethenyl, and coniferyl aldehyde groups. Their color changes also may cause wood color changes (Bourgeois *et al.* 1991; Marcos *et al.* 2009; Dubey 2010). It may be concluded that the degradations of hemicellulose and lignin caused the formations of color products, resulting in the strong correlation between the color change and chemical composition.

CONCLUSIONS

1. On the whole, the wood color became uniform after TVT. The higher the heat-treatment temperature was and the longer the treatment time was, the lower the value of L^* was and the higher the value of ΔE^* was.
2. The higher the heat-treatment temperature was and the longer the heat-treatment time was, the lower the cellulose content and hemicellulose content was and the higher the lignin content was. The FTIR analysis found that the intensity of functional group characteristic absorption peaks of cellulose, hemicellulose, and lignin weakened.
3. The degradation of cell wall composition led to the changes of the chemical structure, which further caused wood color changes. This paper analyzed the relationships between wood color changes and chemical composition changes, finding that the correlations between ΔL^* and $\Delta Hemicellulose$, $\Delta Cellulose$, and $\Delta Lignin$, respectively, were strong, so were strong the correlations between ΔE^* and $\Delta Hemicellulose$, $\Delta Cellulose$, $\Delta Lignin$, respectively.

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