

Physical and Chemical Properties of *Castanopsis fargesii* Wood after Heat Treatment in Sand or Vacuum Media

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Castanopsis fargesii is among the most prevalent hardwood species in South China. To improve the poor dimensional stability of *C. fargesii* wood, heat treatments were performed using vacuum or sand as the medium at four temperatures from 170 °C to 215 °C for 4 h. As a medium, vacuum or sand can create a low oxygen environment. The results showed that, as the temperature increased, the oven-dry density decreased, whereas the dimensional stability and the total color change (ΔE^*) increased with both media, two different changing patterns of a^* and b^* were observed, the lignin content increased, and the holocellulose content decreased. The oven-dry density decreased 9.4% and 25.5%, volume shrinkage ratio decreased 27.8% and 37.7%, and the ΔE^* was 19.63 and 45.52, the lignin contents increased from 17.62% to 28.62% and 42.87%, and the holocellulose contents decreased from 80.49% to 69.43% and 51.04% when *C. fargesii* wood was heated under vacuum and with sand at 215 °C, respectively. Overall, sand heat treatment affected wood physical and chemical properties more than vacuum heat treatment. The analysis of functional groups and crystallinity also showed that there were severe changes in *C. fargesii* wood under sand heat treatment.

Keywords: *Castanopsis fargesii*; Heat treatment; Shrinkage; Color; Chemical properties

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INTRODUCTION

Wood is the only natural polymer of the four main construction materials (steel, cement, plastic, and wood) and it has good environmental properties, such as visual characteristics, tactile characteristics, audio characteristics, and temperature and moisture control characteristics. In addition, wood is renewable and environmentally friendly, which has made wood one of the most popular materials in the world. Further, wood has outstanding advantages in energy consumption and environmental protection (Li *et al.* 2017). However, some species of wood have defects, such as low dimensional stability and decay resistance. Due to the loss of forests (Lin *et al.* 2019) and increased wood demand, wood must be modified prior to use to improve its lifespan. Among all modification methods, heat treatment is favorable because it requires no additional chemicals, meanwhile it produces a beautiful color similar to a tropical style (Fan *et al.* 2010; Candelier *et al.* 2013; Okon *et al.* 2017). Further, heat treatment improves wood stability and service time, which may be caused by changes in chemical components (Özlem *et al.* 2016) and micro-structures (Wang *et al.* 2011; Guo *et al.* 2015; Altgen *et al.* 2018). Different media, such as steam, oil, and vacuum, are used (Esteves *et al.* 2009). When wood is heat-treated in a vacuum medium, it shows less degradation than that in a N₂ medium at the same temperature (Candelier *et al.* 2012). However, the mechanical

properties of wood might be better after treatment with N₂ or vacuum than after treatment with steam or air (Rautkari *et al.* 2014; Yang *et al.* 2016; Lee *et al.* 2018).

The use of sand or vacuum as media creates a hypoxic environment. Several experiments have used vacuum in heat treatment. Sun *et al.* (2013) found that vacuum could protect the wood from oxygen and remove the volatile compounds that contribute to the degradation of the polysaccharides, which causes less degradation than other media; thus, the degree of change is less than other media. As sand is an easily obtained, fire protective, and cheap material, it has been widely used in construction. In addition, sand is used as an energy-transfer medium for cooking in several areas. Sand heat treatment works by transferring thermal energy *via* thermal conduction. When wood is heated, sand builds a relatively closed system that forms organic acids formed; hence, it can catalyze hydrolysis, while the volatile products are taken away in other media of the heat treatment process, such as vacuum, N₂, or steam (Stamm 1956).

Castanopsis fargesii Franch is one of the most prevalent species middle subtropical evergreen broadleaved trees. It belongs to the Fagaceae family and is an important commercial timber in southern China. Sources of wood of the Fagaceae family are abundant. In Fujian Province alone, the forest savings area of Fagaceae wood exceeds 20,000 hm² (Liu 2010). Wood in the Fagaceae family, such as *C. fargesii* is usually used for furniture, flooring, and agricultural tools. However, *C. fargesii* wood has low dimensional stability and resistance to fungi decay. Therefore, *C. fargesii* must be heat-treated to improve its quality, which results in improved stability and a beautiful color. The heat treatment of wood in a sand medium has rarely been reported. In this study, the physical properties (oven-dry density, color, and shrinkage) and chemical content of *C. fargesii* wood during heat treatment were tested. To reveal the influence of sand and vacuum media, *C. fargesii* wood was treated at the same temperature and duration for both sand and vacuum media.

EXPERIMENTAL

Materials

The *C. fargesii* wood was obtained from DaTian county in FuJian province (China). Nine trees that were 35 years old were cut from a *C. fargesii* plantation. The wood was sawn into boards of 25 mm in thickness and then dried in an oven at 60 °C to reach a moisture content (MC) of 10 ± 1%. The samples used for tests were cut along the tangential (T), radial (R), and longitudinal (L) directions. The dimensions of the samples were 20 mm × 20 mm × 20 mm (T × R × L). The samples were divided into 8 treatment groups and 1 reference group, each groups contained 25 samples.

Heat Treatment

The samples of *C. fargesii* wood were heated with the media of vacuum and sand. The sand heat treatment was performed in a Model 30-1060 oven (Memmert, Schwabach, Freistaat Bayern, Germany). Sand was sieved in meshes of 0.42 mm and 0.85 mm (20-mesh to 40-mesh). The samples were entirely and separately buried between sand. Vacuum heat treatment was performed in a DZF-6090 vacuum drying oven (Yiheng, Shanghai, China), in which the relative pressure ranged between -0.02 MPa and 0.01 MPa. The samples were treated with the same process, in which they were heated at a rate at 10 °C/h, and a staged heating process was adopted to ease the internal stress and avoid distortion

and cracking. The heat treatment was applied at four temperatures (170, 185, 200, and 215 °C) for 4 h with sand and vacuum media.

Physical Properties

Oven-dry density testing method

According to GB/T 1933 Method for determination of density of wood (2009). The samples were placed at 60 °C for 4 h, and the temperature was raised to 103 °C for 8 h. Then, the samples were measured every 2 h. Between the two measurements, if the change did not exceed 0.5% of its own weight, it was considered as stable and having reached oven-dry condition.

To determine the density of samples, the oven-dry dimensions and weight of untreated and sand or vacuum treated samples were measured to 0.01 mm and 0.001 g sensitivity. The density of samples was calculated according to Eq. 1,

$$\rho_0 = M_0 / V_0 \quad (1)$$

where ρ_0 (g/cm³) is oven-dry density; M_0 (g) is oven-dry mass of each sample, and V_0 (m³) is oven-dry volume of samples.

Dimensional stability testing method

According to GB/T 1932 Method for determination of shrinkage of wood (2009), the dimensions and weight of the samples were determined in three states, which included the saturated state, the air-dry state, and the oven-dry state.

First, the samples were soaked in distilled water, which was measured with a digital vernier caliper, and the water was changed every 3 d until the tangential dimension changes of the tested samples were less than 0.02 mm between tests.

Then, the air-dry dimensions of 3 directions were detected when the samples were put into a 20 °C and 65% relative humidity (RH) environment, and they were measured with a digital vernier caliper every 6 h.

Finally, the samples were placed at 60 °C for 6 h, and the temperature was raised to 103 °C for 8 h. Then, the samples were measured every 2 h. Between the two measurements, if the change did not exceed 0.5% of its own weight, it was considered as stable and having reached oven-dry condition. The shrinkage ratio was calculated according to Eq. 2,

$$\beta_{\max} = (L_{\max} - L_0) / L_{\max} \times 100 \quad (2)$$

where β_{\max} is the shrinkage ratio, L_{\max} is the data from the saturated state condition, and L_0 is the data from oven-dry condition.

Color testing method

Color measurements were taken on the surface of the wood specimens *via* an X-rite spectrophotometer (Model Color i7, Grand Rapids, Michigan, USA) before and after heat treatment. Each group had 25 samples, and each sample was measured two times. The conditions were adjusted to 20 °C and 65% RH until the specimens reached equilibrium MC before color measurements. The CIE $L^*a^*b^*$ system is characterized by three parameters; L^* describes the lightness from black (0%) to white (100%), a^* represents green (- a) to red (+ a), b^* represents the blue (- b) to yellow (+ b), and ΔE^* means the total color difference. The data were calculated with Eq. 3:

$$\Delta E^* = \left((L^*_{treated} - L^*_{reference})^2 + (a^*_{treated} - a^*_{reference})^2 + (b^*_{treated} - b^*_{reference})^2 \right)^{1/2} \quad (3)$$

All the parameters tested were subjected to analysis of variance (ANOVA), and significant differences between the mean values of reference by Statistical Product and Service Solutions (SPSS IBM Version 24, Chicago, American) and the samples were determined by multiple comparison test at $p < 0.05$.

Chemical Properties Characterization

Chemical composition analysis method

The treated and reference samples were chopped into small pieces and milled with a Wiley mill (Moling 800Y Wuyi Haina Electric Appliance Co., Ltd, Jinhua, China) into a homogenous meal, which would be sieved in 0.25 mm and 0.42 mm (40-mesh to 60-mesh) of standard particle dimensions to chemical analysis and in meshes of 200 for chemical structure analysis. Klason lignin content was measured according to GB/T 2677.8 Fiber raw material - Determination of acid-insoluble lignin (1994), α -cellulose was measured according to GB/T 774 Fiber raw material - Determination of acid-insoluble lignin (1989), and the holocellulose content was measured according to GB/T 2677.10 Fiber raw material - Determination of holocellulose (1995).

Fourier Transform Infrared (FTIR) Analysis

The changes in chemical structure between the samples of different treatment conditions and the reference samples were analyzed *via* infrared spectroscopy. The meal samples were heated to 103 °C for oven drying and then blended with KBr and pressed into thin pellets, which were scanned with FTIR spectrometer (Bruker Vertex 70, Leipzig, Germany) in the range of 4000 to 500 cm^{-1} with a resolution of 4 cm^{-1} .

X-ray Diffraction (XRD) Analysis

The crystalline structure of the untreated and treated *C. fargesii* wood samples were analyzed by X-ray diffraction. The X-ray diffraction measurement was performed *via* an X-ray diffractometer (Rigaku Ultima IV, Tokyo, Japan) with a diffractogram range of 5° to 50° (2θ) with a scanning of 2 °/min. The CrI of the samples were calculated according to Eq. 3 the method developed by Segal *et al.* (1959),

$$\text{CrI}(\%) = (I_{002} - I_{am}) / I_{002} \times 100\% \quad (3)$$

where I_{002} is the maximum intensity of the lattice diffraction angle ($2\theta = 22^\circ$) and I_{am} is the scattering intensity of diffraction from an amorphous background ($2\theta = 18^\circ$).

Thermogravimetric (TGA) Analysis

The thermogravimetric analysis was performed under nitrogen atmosphere with thermal analyzer (NETZSCH STA449F3, Selb, Germany) in order to study the degradation of the untreated, vacuum and sand treated samples. Specimens weighing 4 to 6 mg of reference, sand (200 °C, 4 h) and vacuum (200 °C, 4 h) heat-treated *C. fargesii* wood were put in aluminum crucibles and temperature was heated to 800 °C from 30 °C, at a heating rate of 10 °C/min and a flow rate of 30 mL/min.

RESULTS AND DISCUSSION

Physical Properties of Heat-treated *C. fargesii* Wood Oven-dry Density Analysis

The oven-dry density of the heat-treated *C. fargesii* wood at different temperatures and with different media is presented in Fig. 1. With the media of vacuum and sand, the oven-dry density of the heat-treated *C. fargesii* wood gradually decreased as temperature increased, and the decline in the oven-dry density of the *C. fargesii* wood after sand heat treatment was much higher than that after vacuum heat treatment under the same process. A marked drop in the oven-dry density of *C. fargesii* wood appeared after 200 °C for the sand medium, whereas it did not appear in the vacuum medium. The oven-dry density of the heat-treated *C. fargesii* wood in the sand and vacuum media decreased 3.1% to 25.5% and 2.0% to 9.4%, respectively, compared to reference group. This change pattern was similar to the findings of other research (Kuboijima *et al.* 2000), in which density decreased as heating temperature increased. Wang *et al.* (2011) found that the oven-dry density only decreased 16.6% after treatment at 280 °C under vacuum. The main causes of this phenomenon were the depolymerization reactions of wood polymers. Changes in wood density depend on changes in both mass and volume. The ANOVA showed that temperature, medium, and the interaction had an insignificant effect ($p < 0.05$) on the oven-dry density of *C. fargesii* wood.

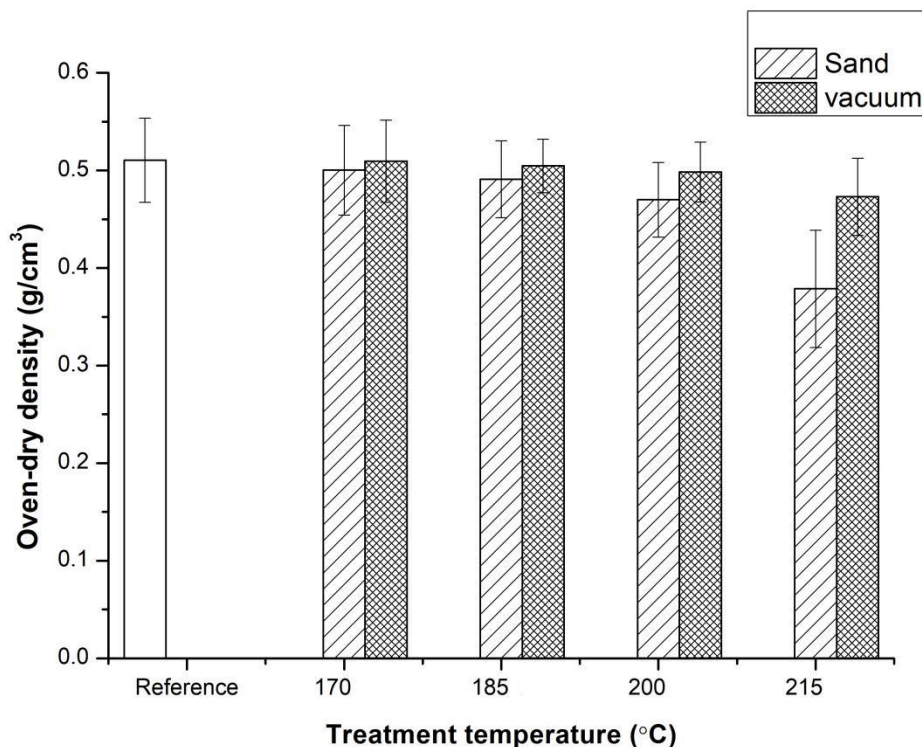


Fig. 1. The oven-dry density of heat-treated *C. fargesii* wood under different temperatures and with different media

Table 1. ANOVA of Oven-dry Density for Heat-treated *C. fargesii* Wood under Different Temperatures and Media

| Factor | Tangential | |
|------------------------|------------|------|
| | F | Sig. |
| Medium | 2.235 | .111 |
| Temperature | 1.478 | .232 |
| Medium* Temperature | .012 | 1.00 |

Shrinkage Analysis

Figure 2 shows that the shrinkage of heat-treated *C. fargesii* wood decreased as temperature increased under both media, which indicated that the dimensional stability of the *C. fargesii* wood was improved. Other researchers found the same increase pattern in the process of heat treatment for various wood species (Esteves *et al.* 2007; Okon *et al.* 2017; Lee *et al.* 2018; Fu *et al.* 2019). The shrinkage in the tangential direction was higher than that in radial direction, whereas shrinkage in the radial direction was much higher than that in the longitudinal direction. The anisotropy was due to the wood structure and the arrangement of microfibrils in the cell wall (Gunduz *et al.* 2009; Dündar *et al.* 2012).

The lowest volume shrinkage ratio of the heat-treated *C. fargesii* wood at 215 °C with sand and vacuum media were 7.2% and 9.0%, respectively. This result represented decreases of 37.7% and 21.8% for the sand and vacuum media, respectively, compared to the reference group. When *C. fargesii* wood was treated at 215 °C, the volume shrinkage ratio with sand heat treatment was 20.5% lower than that with vacuum heat treatment, whereas the volume shrinkage ratio with sand heat treatment at 185 °C was slightly smaller than that with vacuum heat treatment at 215 °C. The ratio of shrinkage in the tangential direction to that in the radial direction was 2.7 for the *C. fargesii* wood of reference group, whereas it decreased to 2.0 and 2.2 after heat treatment at 215 °C in the sand and vacuum media, respectively. The decrease of this ratio showed that the anisotropy of the *C. fargesii* wood decreased as temperature increased. Overall, the heat-treated *C. fargesii* wood with the sand medium has higher dimensional stability than that with the vacuum medium under the same process. The increase of dimension stability was caused by holocellulose decomposition. The ANOVA (Table 2.) showed that temperature and medium had significant effects on the tangential, radial, and volume shrinkage of the heat-treated *C. fargesii* wood ($p < 0.05$).

Table 2. ANOVA of Shrinkage from Saturated State to Oven-dry State for Heat-treated *C. fargesii* Wood under Different Temperatures and Media

| Factor | Tangential | | Radial | | Longitudinal | | Volume | |
|------------------------|------------|------|--------|------|--------------|------|--------|------|
| | F | Sig. | F | Sig. | F | Sig. | F | Sig. |
| Medium | 60.437 | .000 | 27.289 | .000 | 16.193 | .000 | 46.842 | .000 |
| Temperature | 28.889 | .000 | 24.514 | .000 | .841 | .476 | 31.103 | .000 |
| Medium* Temperature | 1.544 | .209 | 2.958 | .037 | .255 | .857 | 2.388 | .074 |

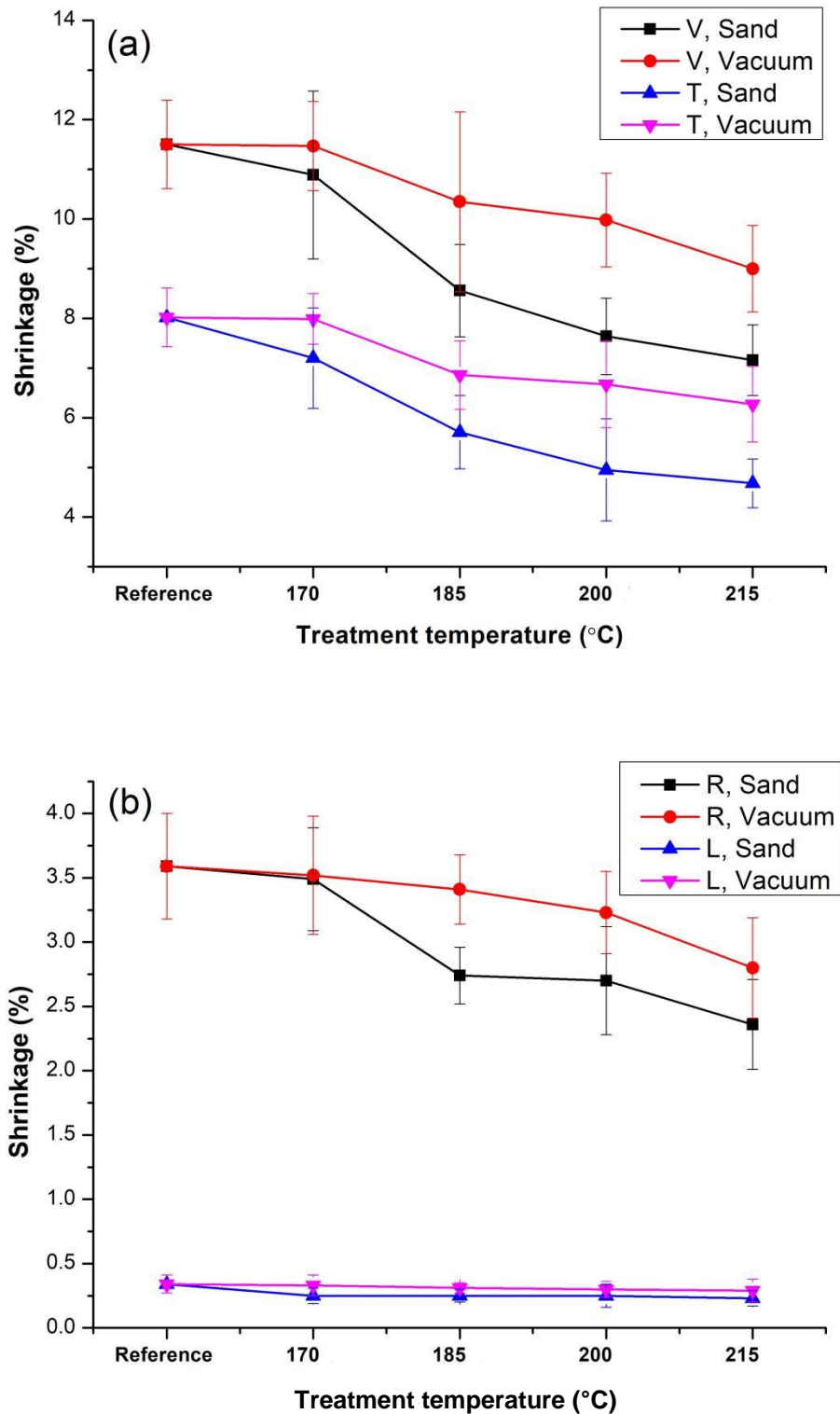


Fig. 2. Shrinkage from Saturated State to Oven-dry State of Heat-treated *C. fargesii* Wood under Different Temperatures and Media (a is Shrinkage of Tangential (T) and Volume (V); b is Shrinkage of Radial (R) and Longitudinal (L))

Color Analysis

The change pattern of the heat-treated *C. fargesii* wood color traits (L^* , a^* , b^* , and ΔE^*) with temperature under different media is presented in Fig. 3. The lightness value (L^*) of the heat-treated *C. fargesii* gradually decreased in both media as the temperature increased. At the same temperature, the lightness of the heat-treated wood was much smaller in the sand medium than the vacuum medium. The lightness of the *C. fargesii* before heat treatment was 74.8. After heat treatment at 215 °C for 4 h, the lightness in the vacuum and sand media decreased to 19.45 and 43.88, respectively. The change pattern was similar to that reported by other researchers (Fan *et al.* 2010), wherein the L^* value of wood decreased after heat treatment. According to the results of the variance analysis, the effects of heat treatment temperature and medium on L^* were significant ($p < 0.05$).

Figure 3 shows that there were two change patterns in the chroma (a^* , b^*) for the heat-treated *C. fargesii* wood as temperature increased. Pattern 1 increased at first, which was followed by a decline. Pattern 2 was a consistent increase. In this study, the change pattern of a^* and b^* were in line with pattern 1 with sand heat treatment and pattern 2 with vacuum heat treatment. Both change patterns were previously reported (Bekhta and Niemz 2003; Mehmet *et al.* 2007; Fan *et al.* 2010; Okon *et al.* 2017). Before heat treatment, the a^* value of the *C. fargesii* wood was 4.91, and the b^* value was 18.84. Compared to the untreated wood, the increase ranges of a^* and b^* were 17% to 40% and 8.7% to 14.3% after vacuum heat treatment. The variation range of b^* was 12% to 98%, the increase range of a^* was 8.5% to 9.2%, and the decrease range of a^* was 25.6% to 62.1% after sand heat treatment. The inflection point of chroma for the sand-heat-treated *C. fargesii* wood appeared at 185 °C. The oxidation products, such as quinones, were produced during the heating process, and they absorbed the supplementary light of red. As the amount of such substances increased, the value of a^* gradually increased. The increase of b^* could be partly caused by the low-molecular-weight phenolic substances, which are pale yellow and formed during heat treatment (Yao *et al.* 2010). In addition, as the amount of these substances increased, the values of a^* and b^* gradually increased (Fan *et al.* 2010). According to Table 3, the effects of heat treatment temperature, medium, and the interaction on chroma value were significant ($p < 0.05$).

The degree of color change of *C. fargesii* wood after heat treatment was characterized by the total color difference (ΔE^*). Figure 3 shows that ΔE^* increased as temperature increased with both media. The ΔE^* of the *C. fargesii* wood heat-treated in sand was larger than that treated in vacuum when the treatment process was same. After heat treatment at 215 °C for 4 h, the ΔE^* of *C. fargesii* wood was 45.52 and 19.63 with the sand and vacuum media, respectively. Notably, the ΔE^* of the heat-treated *C. fargesii* wood in vacuum at 215 °C was the same as that treated in sand at 170 °C (21.33). Vacuum heat treatment always resulted in lower changes in color than sand heat treatment did in the same process. The darker color of heat-treated wood was mainly caused by the formation of degradation products from amorphous carbohydrates, changes in extractions, and the formation of oxygen products (Kačíková *et al.* 2013; Barčík *et al.* 2015). According to the ANOVA results, the effects of heat treatment temperature, medium, and the interaction on ΔE^* were extremely significant.

Overall, the effects of vacuum heat treatment at 215 °C on the ΔE^* and L^* of *C. fargesii* wood were similar to that of sand heat treatment at 170 °C. The maximum values of a^* and b^* in the vacuum medium were close to those in the sand medium, which showed that the degradation of wood that was heat-treated in the vacuum medium was less severe

than the sand medium. The temperature and medium had significant effects on the color characteristics of the heat-treated *C. fargesii* wood ($p < 0.05$).

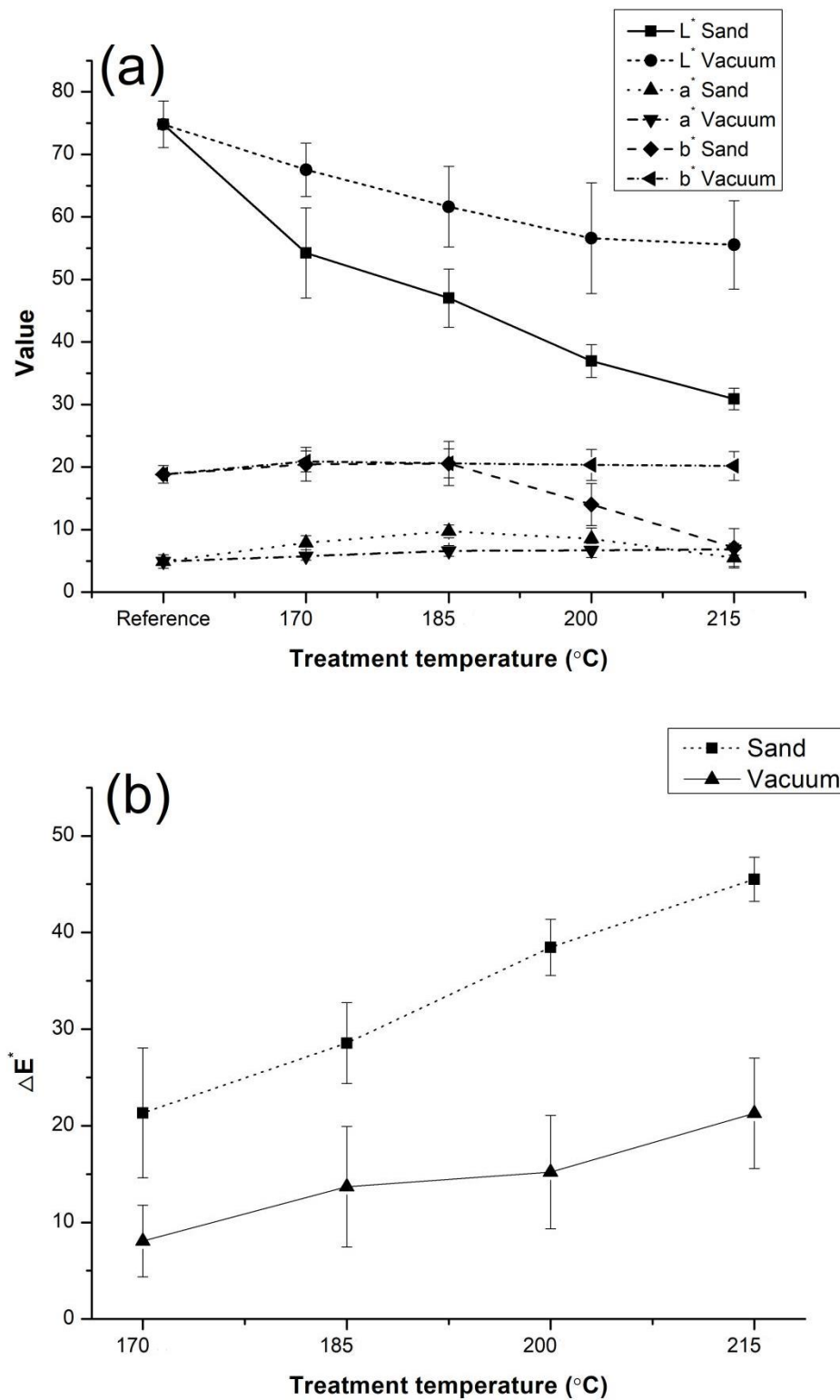


Fig. 3. L^* , a^* , b^* (a) and ΔE^* (b) of the *C. fargesii* wood under different heat treatment temperatures and media

Table 3. Variance Analysis of Color Characters for Heat-treated *C. fargesii* Wood under Different Temperatures and Media

| Factor | <i>L</i> * | | <i>a</i> * | | <i>b</i> * | | ΔE^* | |
|---------------------------|------------|------|------------|------|------------|------|--------------|------|
| | F | Sig. | F | Sig. | F | Sig. | F | Sig. |
| Treatment | 252.503 | .000 | 40.713 | .000 | 74.616 | .000 | 360.073 | .000 |
| Temperature | 44.521 | .000 | 15.636 | .000 | 30.165 | .000 | 57.419 | .000 |
| Treatment* Temperature | 4.629 | .004 | 16.56 | .000 | 25.424 | .000 | 7.878 | .000 |

Chemical Properties of Thermally Modified Wood

Chemical composition analysis

The changes in the holocellulose, cellulose, and lignin of the heat-treated *C. fargesii* wood at different temperatures and media are presented in Table 4. As temperature increased, the lignin content increased and the content of holocellulose decreased. The chemical differences of the heat-treated *C. fargesii* wood in the sand and vacuum media were the degrees of holocellulose degradation and the change patterns of cellulose.

The holocellulose contents in the heat-treated *C. fargesii* wood in both the sand and vacuum media decreased as the temperature increased, and the decreased degree of holocellulose in the sand medium was much higher than that with the vacuum medium. The decrease in holocellulose was mainly caused by the degradation of hemicellulose. Hemicellulose is the first part of degradation due to its lower thermal stability, as hemicellulose has no crystal region (Mburu *et al.* 2008). Acetyl groups are an important factor, since they facilitate thermal degradation of hemicellulose. They are thermally labile and lead to the formation of acetic acid, thereby causing acid-catalysed degradation of the polysaccharides. Acid-catalysed reactions result in the formation of formaldehyde, 2-furaldehyde, and other aldehydes (Okon *et al.*, 2017). Acetic acid and other small molecular volatiles produced during heat treatment can further promote the degradation of hemicellulose. However, in the process of vacuum heat treatment, these substances were extracted, while in the process of sand heat treatment, these volatiles were released slowly, which further promoted the degradation of hemicellulose.

The cellulose content in the heat-treated *C. fargesii* wood decreased compared to the reference group when it was heated to 170 °C in both media. This may have occurred because the non-crystalline region of cellulose was degraded. However, as the temperature continued to increase, the crystalline region in cellulose provided stability to the cellulose chains and protected them against acid attack during hydrolysis. However, hemicellulose continued to degrade, so the cellulose content increased a small amount. The relative cellulose content has been shown to increase after heat treatment (Severo *et al.* 2012). Brito *et al.* (2008) studied the heat treatment of eucalyptus and *Pinus* and observed that the content of glucose as the cellulose constituent slightly increased, which reflected an increase in cellulose content. When the *C. fargesii* wood was heated in the sand medium at 215 °C, the cellulose content decreased, which was consistent with the decrease in cellulose crystallinity observed in the XRD analysis. At high heat treatment temperature, depolymerization occurs in both the crystalline and noncrystalline regions, the degradation of cellulose is intense, so the relative content of cellulose decreased.

The acid-insoluble lignin content in the heat-treated *C. fargesii* wood in both the sand and vacuum media increased as temperature increased. Compared with the reference group, the lignin content of the heat-treated *C. fargesii* wood increased from 17.2% to 42.7% and 28.62% in the sand and vacuum media, respectively, at 215°C. This occurred because the reduction in polysaccharides was higher than that in lignin. In addition, hemicellulose degrades thermally approximately four times faster than wood, whereas lignin degrades approximately half as fast as wood (Stamm 1956; Kačíková *et al.* 2013). Alternatively, this increase may have come from the condensation reactions of carbohydrates, which would have increased the amount of acid-insoluble material in heat-treated wood.

Table 4. The Components of the *C. fargesii* Wood under Different Heat Treatment Temperatures and Media

| Heat Condition | | Holocellulose (%) | | Cellulose (%) | | Lignin (%) | |
|----------------|--------|-------------------|------|---------------|------|------------|------|
| | | Mean | SD | Mean | SD | Mean | SD |
| Reference | | 80.49 | 0.48 | 48.0 | 0.49 | 17.62 | 0.72 |
| Sand | 170 °C | 72.36 | 0.60 | 45.7 | 0.08 | 24.83 | 1.63 |
| | 185 °C | 63.38 | 0.09 | 46.2 | 0.92 | 25.20 | 0.75 |
| | 200 °C | 57.18 | 2.4 | 48.8 | 0.84 | 31.44 | 0.81 |
| | 215 °C | 51.04 | 0.05 | 44.8 | 0.03 | 42.87 | 0.30 |
| Vacuum | 170 °C | 72.98 | 0.16 | 45.38 | 1.49 | 25.20 | 3.26 |
| | 185 °C | 72.11 | 0.30 | 46.4 | 0.42 | 26.19 | 0.20 |
| | 200 °C | 69.97 | 0.99 | 46.77 | 0.39 | 28.16 | 1.05 |
| | 215 °C | 69.43 | 0.79 | 51.12 | 0.79 | 28.62 | 0.14 |

FTIR Analysis

The FTIR spectra of the heat-treated *C. fargesii* wood in both media and the reference group are presented in Fig. 4. The peak at 1737 cm^{-1} was attributed to the stretch vibration of C=O, which belongs to carbonyl, carboxyl, and acetyl. The decrease at this peak indicates a decrease in hemicellulose content. The increase in the intensity of the band at 1510 cm^{-1} was assigned to the C=C stretching of the aromatic skeletal components in lignin with both media. This indicated an increase in the amount of lignin in the wood, and the degradation of amorphous carbohydrates occurred. The peak at 1232 cm^{-1} was assigned to the C-O stretching vibration coupled with the aromatic ring vibration in lignin and the C-O stretching vibration in xyloglucan.

The increase in the intensity of the band at 1054 cm^{-1} , which was assigned to the C-O stretching vibrations in cellulose and hemicellulose, indicated the formation of aliphatic alcohols during heat treatment. This may have led to the percentage increase in crystalline cellulose, which indicated that dehydration occurred, and a large number of hydroxyl groups were lost in cellulose and hemicellulose during heat treatment. The band at 1033 cm^{-1} , which was assigned to the C-O ester stretching vibrations in methoxy and the β -O-4 linkages in lignin, increased. This indicated that the cleavage of β -O-4 linkages and splitting of the methoxy groups from the lignin structure occurred. The degradation

reaction of the cleavage of β -O-4 linkages in lignin is catalyzed by acetic acid, which is formed and released from the degradation of acetyl groups in hemicellulose. The acetic acid can also catalyze other degradation reactions in the wood components (Li *et al.* 2015; Özgenç *et al.* 2016; Liu *et al.* 2017; Hoseinzadeh *et al.* 2019). The peaks at 1724, 1372, and other peaks related to holocellulose groups decreased or disappeared, while the peaks at 1510, 1033 cm^{-1} and other peaks related to lignin groups increased. This result is the same as the result of chemical composition determination. After heat treatment, the holocellulose content of *C. fargesii* wood decreased while the lignin content of *C. fargesii* wood increased.

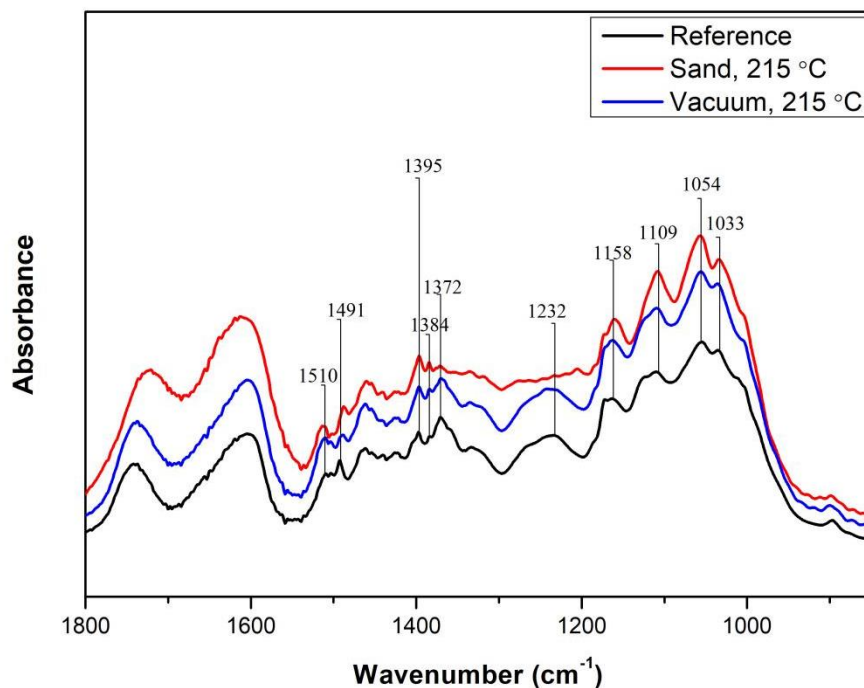


Fig. 4. FTIR spectra of *C. fargesii* wood under different heat treatment media

XRD Analysis

The CrI of the *C. fargesii* wood before and after heat treatment is shown in Table 5. As temperature increased, the CrI of the vacuum-heat-treated *C. fargesii* wood gradually increased, whereas that of the sand-heat-treated *C. fargesii* wood increased before 200 °C but slightly decreased at 215 °C. The change in moisture content causes changes in bond configuration of the noncrystalline regions of adjacent cellulose molecules and polyoses, resulting in swelling and shrinking. The increase in CrI indicates a decrease in the amorphous region, so the change in the CrI could explain that the shrinkage ratio of heat-treated *C. fargesii* wood decreased as temperature increased (Akgül *et al.* 2007).

There are two explanations for the increase in crystallinity. First, it could have been due to the degradation of amorphous regions. In addition, the increased crystallization in the wood likely contributed. As the non-crystalline region degraded thermally, the relative crystalline content in the wood increased. The increase in crystallinity could have been because of crystallization in the quasi-crystalline amorphous regions due to the rearrangement or reorientation of cellulose molecules inside them. Wood cellulose contains more quasi-crystalline regions than pure cellulose because crystals in hemicellulose, xylan, and mannan are capable of crystallizing during heat treatment

(Bhuiyan *et al.* 2000; Akgül *et al.* 2007; Yin *et al.* 2016). At the later stages of heat treatment, depolymerization occurs in both the crystalline and amorphous regions, the cellulose macromolecular chain breaks, the glucosidic linkage is cut, and decreases in crystallinity and polymerization appear (Bhuiyan *et al.* 2000).

Table 5. CrI of *C. fargesii* Wood Under Different Heat Treatment Temperatures and Media

| Factor | CrI (%) |
|----------------|--------------|
| Reference | 39.73 ± 0.78 |
| Sand, 170 °C | 42.15 ± 1.57 |
| Sand, 185 °C | 45.57 ± 1.07 |
| Sand, 200 °C | 49.37 ± 0.18 |
| Sand, 215 °C | 45.43 ± 0.90 |
| Vacuum, 170 °C | 40.28 ± 0.35 |
| Vacuum, 185 °C | 41.57 ± 1.42 |
| Vacuum, 200 °C | 42.87 ± 1.2 |
| Vacuum, 215 °C | 46.01 ± 0.80 |

TGA Analysis

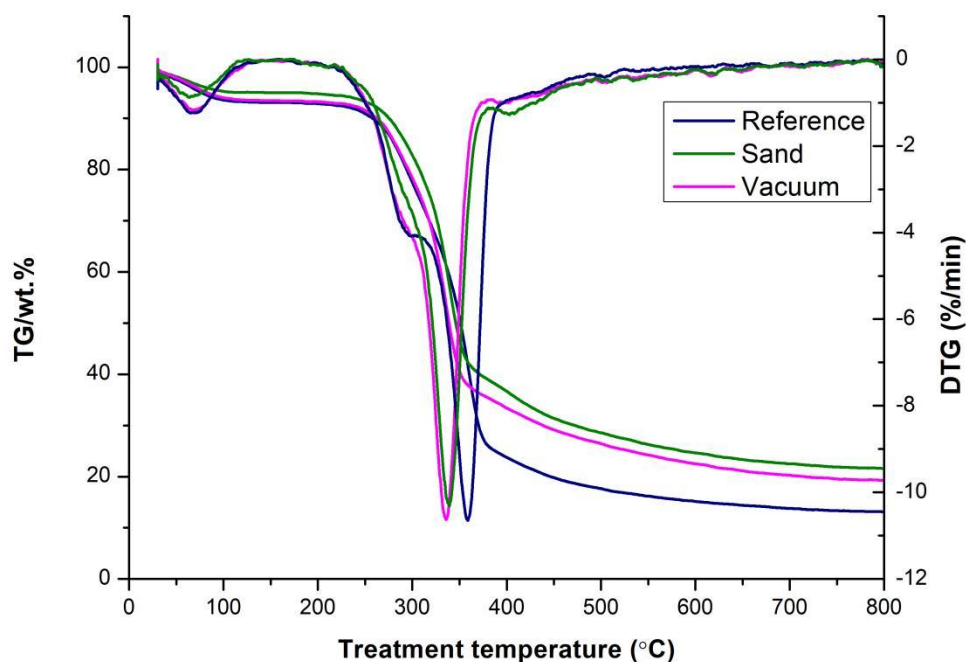


Fig. 5. TG and DTG curves of reference, sand and vacuum heat-treated *C. fargesii* wood

TG and DTG curves can be seen from Fig. 5. The final mass gradually increased, followed by reference (13.14%), vacuum heat treated (19.27%), and sand heat treated (21.61%). The pyrolysis process of wood is essentially the pyrolysis of the main chemical components in wood. Compared with cellulose and hemicellulose, the pyrolysis process of

lignin tends to form more coke, high carbon residue rate indicates high lignin content. Which confirmed that the degradation of wood that was heat-treated in the vacuum medium was less severe than the sand medium (Yuan *et al.* 2020).

CONCLUSIONS

1. When heated at same temperature and for the same duration, the dimensional stability of the heated *C. fargesii* wood in the sand medium was higher than that in the vacuum medium, and its color was darker.
2. A marked change in oven-dry density appeared after 200 °C for sand-heat treatment. The volume shrinkage of the heat-treated *C. fargesii* wood in the vacuum medium at 215 °C was quite similar to that in the sand medium at 185 °C.
3. The change pattern of color traits for the heat-treated *C. fargesii* wood varied across the different media, and two change patterns of chroma (a^* , b^*) were observed. The ΔE^* value of the heat-treated *C. fargesii* wood in the sand medium at 170 °C was quite similar to that in the vacuum medium at 215 °C.
4. The degree of change in chemical content for the heat-treated *C. fargesii* wood in the sand medium was much higher than that in the vacuum medium, which was also observed *via* FTIR and XRD.
5. The analysis of chemical contents showed that *C. fargesii* wood in the sand medium degraded heavier than that in the vacuum medium. The difference in thermal *C. fargesii* wood properties between samples treated in the sand and vacuum media were mainly caused by volatile content. During the process of wood heat treatment, the volatility remained in the heat environment in the sand medium, whereas it was released from the heat environment in the vacuum medium.

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