EFFECT OF HEAT TREATMENT ON THE CHANGE IN COLOR AND DIMENSIONAL STABILITY OF ACACIA HYBRID WOOD

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Acacia hybrid (*Acacia mangium x auriculiformis*), a wood species of low dimensional stability which is used almost exclusively for pulp, paper, or as firewood, was heat treated in nitrogen at 210-230 ºC for 2 to 6 hours. The changes in color and anti-swelling efficiency (*ASE*) of wood after heat treatment were determined for the different heat treatment conditions. The results show that heat treatment mainly resulted in the darkening of wood tissues, and heat-treated wood had better dimensional stability than those of the control samples. Chemical modifications of wood components were determined by FT-IR analysis. Spectra indicated that the hydroxyl group content was reduced by increased treatment intensity. This result coincides with the increase in dimensional stability of heat-treated wood. Heat treatment of acacia hybrid wood shows an interesting potential to improve the quality and value for solid wood products from plantation-grown wood species.

Keywords: Acacia Hybrid; ASE; Color; FT-IR; Heat Treatment

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INTRODUCTION

Heat treatment of wood is an environmentally friendly wood protection method, which results in value added wood products. One of the properties improved most by this treatment is the dimensional stability (Esteves et al. 2007; Kocaefe et al. 2008). Also dark color acquired during this treatment is very attractive (Brischke et al. 2007; Esteves et al. 2008b). More recently, heat treatment of wood has become a well established procedure, and there are a growing number of industrial treatment centers in various countries in Europe and Canada. Plato Wood in the Netherlands, ThermoWood in Finland, Rectification in France, and Le Bois Perdure in Québec, are some of the centers specializing in heat treatment. Several wood species are heat-treated under different process conditions, depending on the species and the end-uses of the product. All of these processes use sawn wood and treatment temperatures between 160 ^{o}C and 260 ^{o}C, but they differ in terms of processing conditions, such as the presence of a protective gas (nitrogen), steam, dry processing, or use of oils (Esteves and Pereira 2009).

Fast-grown wood generally contains a high proportion of juvenile wood with poorly developed heartwood. A fast rate of growth results in wide growth rings and low density wood, which exhibits inferior dimensional stability and durability against biological deteriorations (Li 2002). Some species of fast-grown wood which are of particular interest to Vietnam are the naturally occurring acacia hybrids, which were first

discovered in 1991 at the Bavi research station in Hanoi, Vietnam. The parents of these natural hybrids are *A. mangium and A. auriculiformis* (Kha 2001). The growth rate of these acacia hybrids is almost double compared to that of their parents; wood production of normal acacia is 12 m^3/ha per year while hybrids produce 22 m^3/ha per year under similar growing conditions (Kim et al. 2008). Thus, the hybrids produce on average an additional 10 cubic meters of wood per hectare each year.

In recent years, large areas of acacia hybrid plantation have been established in Vietnam, but because of inferior qualities of fast-grown wood, such as poor dimensional stability and durability, the wood produced can only be sold at very low prices. At present, acacia hybrids are harvested at about 7 years of age and used mainly for pulp, paper, and fiberboard production. With the advent of the heat-treatment technology, the possibility arises of transforming this poor quality wood into a value-added product capable of competing with traditional tropical hardwoods for some applications.

In this paper we report the results on the dimensional stability improvement of acacia hybrid wood, and changes in color of treated wood by using a heat treatment in nitrogen in the range 210 to 230 °C. The objective is to increase the timber value of mature acacia hybrid trees and to decrease the usage of tropical woods.

EXPERIMENTAL

Materials

This study used six acacia hybrid trees at 8 years of age with breast height diameter (*DBH*) ranging from 23 to 25 cm that were collected from a trial plantation forest in Bavi, Hanoi, Vietnam. Approximately the same amount of heartwood was cut from each log to prepare wood samples 20x20x30 mm in size with clear radial, tangential, and transverse faces for dimensional stability and color measurements. Samples were divided into twelve treatment groups, and each treatment group had a total of 30 samples. All samples were conditioned for three weeks at 20 ^oC and 50% relative humidity prior to heat treatment.

Heat Treatment

Heat treatment was conducted in an oven filled with nitrogen, where samples were exposed to temperature at 210 ^oC, 215 ^oC, 220 ^oC, or 230 ^oC for 2, 4, or 6 hours. It took approximately one hour to heat the samples from room temperature to the treating temperature, after which the temperature was kept constant for the predetermined duration.

At the end of the treatment samples were cooled and stored in desiccators before weighing. The mass loss (*ML*) after heat treatment was estimated according to the following formula:

$$ML\ (\%) = (m_o - m_{ht})/m_o \times 100 \quad (1)$$

where m_o is the initial mass of the oven-dried sample, and m_{ht} is the mass of the same sample after the heat treatment.

Measurement of Dimensional Stability

The Anti-swelling Efficiency (*ASE*) was calculated based on dimensional change of samples immersed in distilled water for 30 days as follows (Rowell 2005):

$$ASE\ (\%) = [(S_o - S_{ht})/S_o] \times 100 \quad (2)$$

where S_o and S_{ht} are percent volumetric swelling of untreated wood and heat-treated wood, respectively.

$$S\ (\%) = [(V_w - V_d)/V_d] \times 100 \quad (3)$$

where V_w is volume of sample immediately after water immersion and V_d is the volume of immersed sample after over-dried at 103±2 ^{o}C.

Measurement of Color

The color of the wood surfaces was measured using a NF-333 Spectrophotometer before and after heat treatment. The CIELAB system is characterized by three parameters, L^*, a^*, and b^*. The L^* axis represents the lightness, $+a^*$ is the red, minus a^* for green, $+b^*$ for yellow, minus b^* for blue, and L^* varies from 100 (white) to zero (black). The L^*, a^*, and b^* color coordinates of each samples before and after heat treatment were used to calculate the total color change ΔE as a function of the mass loss according to the following formulas (Zhang et al. 2009):

$$\Delta L^* = L^*_{ht} - L^*_o \quad (4)$$

$$\Delta a^* = a^*_{ht} - a^*_o \quad (5)$$

$$\Delta b^* = b^*_{ht} - b^*_o \quad (6)$$

$$\Delta E = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \quad (7)$$

where ΔL^*, Δa^*, and Δb* are the changes between the untreated and the treated values. L^*, a^*, and b^* contribute to the total color change ΔE. A low ΔE corresponds to low color change.

Fourier Transform Infrared Spectroscopy (FT-IR)

Untreated and treated wood samples were taken from the same annual ring of the wood. FT-IR spectra of untreated and treated samples were measured by direct transmittance using the KBr pellet technique (1 mg/ 200 mg). Spectra were recorded using a Nicolet Magna-IR 560 E.S.P spectrometer. All of the spectra were measured at a resolution of 4cm^{-1}, and 40 scans were taken per sample. Peak heights of absorption bands were measured by OMNIC software (Version 8.0, Nicolet Instruments Corporation, USA) according to the previously established methods (Pandey and Pitman 2003; Wang and Ren 2008).

RESULTS AND DISCUSSION

Mass Loss by Heat Treatment

The change of mass loss as a function of temperature for different treatment times is shown graphically in Fig. 1. The results show that mass loss was directly related to treatment severity, which depends on the treatment time and the temperature. Temperature is the dominating factor over duration of heating in increasing mass loss, and the same mass loss can be obtained at shorter treatment time with higher temperature or by using longer treatment time with lower temperature (Esteves et al. 2008a). For example, mass loss of wood samples was about 8.1±0.5% when heated at 215 °C for six hours but only required two hours at 230 °C.

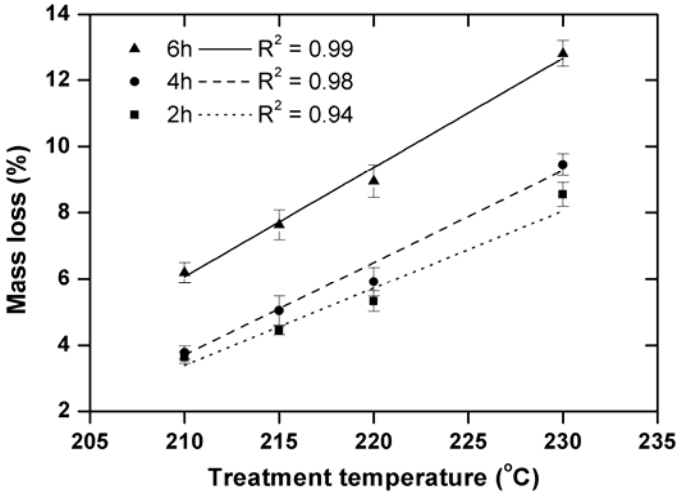

Fig. 1. Mass loss of wood with heat treatment

FT-IR Analysis

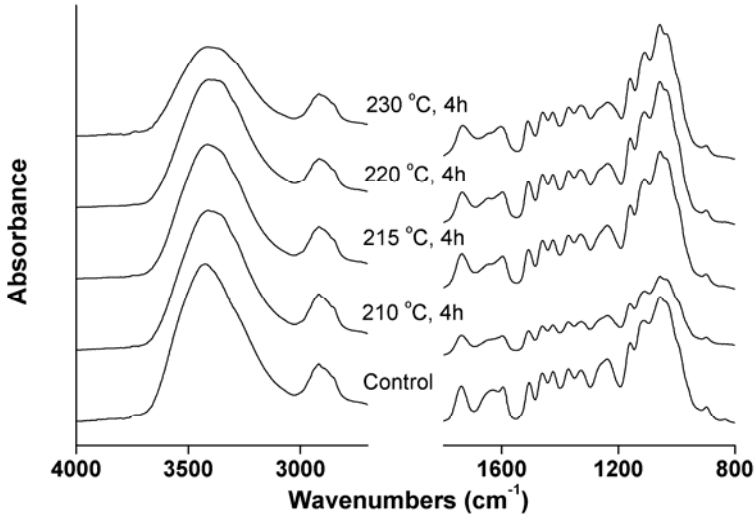

Fig. 2. FT-IR spectra of untreated and treated acacia hybrid wood samples

The FT-IR spectra of wood had changed considerably from that of untreated wood (Fig. 2). The C-H stretches around 2900 cm^{-1} were slightly decreased compared to the hydroxyl peak around 3400 cm^{-1} and the C-O stretch at 1060 cm^{-1} (Table 1). This may indicate that some hydrocarbon compounds had been lost during heat treatment (Liu et al. 1998).

Table 1. Changes in the C-H Peak of Wood Samples with Heat Treatment

Item	Treatment Temperature (°C)				
	Control	210	215	220	230
I_{2917}/I_{3423}	0.28	0.26	0.26	0.26	0.23
I_{2917}/I_{1060}	0.69	0.63	0.54	0.54	0.46

The decrease in the intensity of the O-H absorption band (around 3400 cm^{-1}) revealed that the hydroxyl group content was reduced by thermal treatment. The reduction of hydroxyl group content can explain the high dimensional stability of heat-treated wood. The reduction can be explained by the earlier found occurrence of cross-linking reactions (Tjeerdsma et al. 1998).

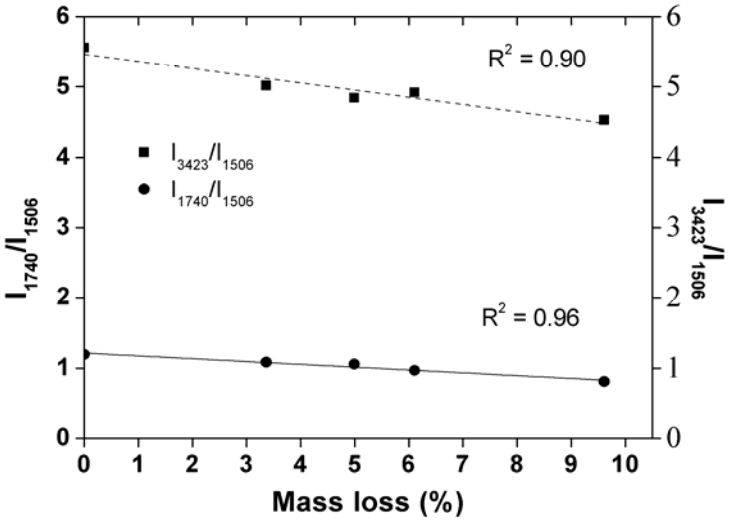

Fig. 3. Relationship between the mass loss by heat treatment and the changes in hydroxyl and carbonyl peaks

As can be seen from Fig. 3, the ratios of relative intensity of hydroxyl peak with carbohydrate band (1506 cm^{-1}) decreased with increasing intensity of treatment. In addition, the carbonyl peak at around 1740 cm^{-1} was reduced in comparison to the aromatics stretch at 1506 cm^{-1}, indicating a loss of this component from the surface. Detailed peak positions and assignments (Li 2003; Pandey 1999) of untreated and treated wood samples are listed in Table 2.

Table 2. Assignment of Absorption IR Spectral Peaks in Heat-Treated Acacia Hybrid Wood

Wavenumber (cm^{-1})					Band assignment [a]
Control	210 °C	215 °C	220 °C	230 °C	
3423	3418	3414	3412	3410	O-H stretching in hydroxyl groups
2918	2917	2917	2917	2915	C-H stretching in methyl and methylene groups
1739	1738	1737	1735	1734	C=O stretching in unconjugated ketone
1596	1597	1597	1597	1603	C=C stretching of the aromatic ring (S)
1506	1508	1508	1508	1510	C=C stretching of the aromatic ring (G)
1461	1460	1460	1460	1459	CH2 deformation stretching in lignin and xylan
1424	1424	1424	1424	1425	Aromatic skeletal combined with C-H in-plane deformation and stretching
1371	1371	1371	1371	1370	Aliphatic C-H stretching in methyl and phenol OH
1328	1327	1329	1329	1327	C1-O vibrations in S derivatives, CH in-plane bending in cellulose I and cellulose II
1238	1238	1238	1236	1237	Syringyl ring breathing and C-O stretching in lignin and xylan
1159	1160	1159	1159	1159	C-O-C asymmetric stretching in cellulose I and cellulose II
1112	1110	1109	1110	1109	Ring asymmetric stretching
1056	1057	1057	1057	1058	C-O valence vibration

[a] S: syringyl; G: guaiacyl

The degree of crystallinity is an important parameter, and it directly affects the properties of polymers (Mo et al. 1994). Table 3 presents the changes of crystallinity of heat-treated acacia hybrid wood samples determined by means of the FT-IR spectroscopic method (Akgül et al. 2007; Ates et al. 2009).

Table 3. Changes in Crystallinity of Acacia Hybrid Wood Samples with Heat Treatment

Treatment Temperature (°C)	I_{1421}/I_{896}	I_{1371}/I_{667}	I_{1371}/I_{2917}
Control	2.10	1.79	0.41
210	2.17	1.96	0.39
215	2.33	2.12	0.41
220	2.28	2.07	0.38
230	2.09	2.04	0.43

The ratio of peak intensity at 1421 and 896 cm^{-1} (I_{1421}/I_{896}), at 1,371 and 667 cm^{-1} (I_{1371}/I_{667}), and at 1371 and 2917 cm^{-1} (I_{1731}/I_{2917}) in FT-IR spectra of wood samples was used as an approach for the determination of crystallinity of celluloses in wood samples (Åkerholm et al. 2004; Ates et al. 2009; Hassan et al. 2000). The results show that all of the relative crystallinity index values of heat-treated acacia hybrid wood slightly increased compared to that of the control sample (Table 3). The increase in crystallinity may be explained as crystallization in quasi-crystalline amorphous regions due to rearrangement or reorientation of cellulose molecules inside these regions; the higher

crystallization in wood cellulose may be due to the decrease in amorphous regions by thermal decomposition (Akgül et al. 2007; Bhuiyan et al. 2000).

Dimensional Stability

The dimensional stability of heat-treated wood was evaluated by the water-soaking method, and the relationship between the anti-swelling efficiency (*ASE*) of samples and the mass loss are shown in Fig. 4. The *ASE* of heat-treated wood was improved considerably compared to the control samples. A mass loss between 8.5-12% was enough to get the maximum reduction in swelling, and longer treatment times or higher temperatures did not benefit the swelling of wood (Fig. 4).

The improvement in dimensional stability of heat-treated wood is due to the reduction in relative proportion of hemicellulose when the wood is exposed to a high temperature (Hillis and Rozsa 1985; Tjeerdsma et al. 1998). Treatment at high temperature modifies and diminishes hemicellulose in wood. Since hemicellulose is highly hygroscopic, reduction in hemicellulose content brings better dimensional stability to the treated wood. The dimensional stability of wood was greatly improved by the thermal modification.

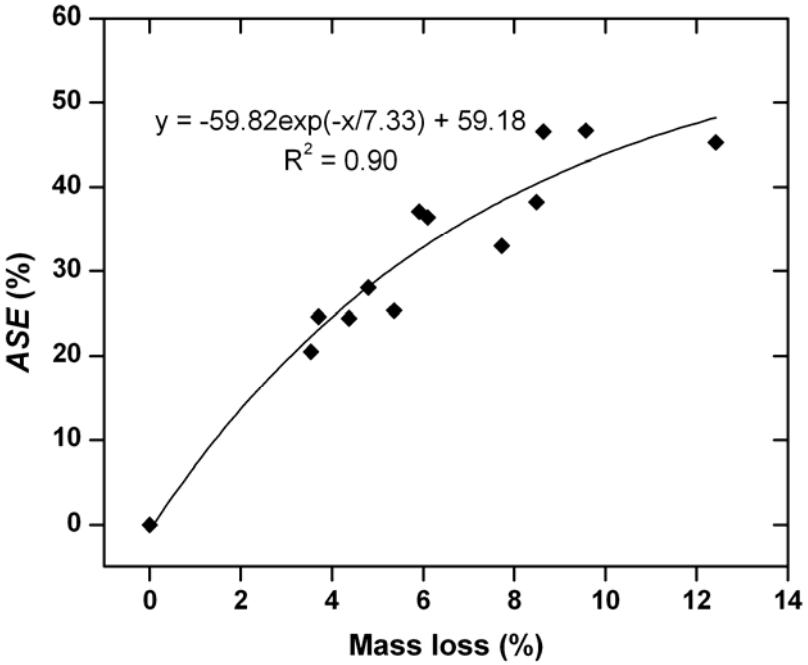

Fig. 4. Relationship between the *ASE* of heat-treated wood and the mass loss by heat treatment

Changes in Color

Figure 5 shows color changes on heat-treated samples with heat treatment. The color became significantly darker with increasing of treatment intensity, compared with control samples. The results can be explained with the changes taking place in extractives, lignin, and hemicelluloses during the heat treatment.

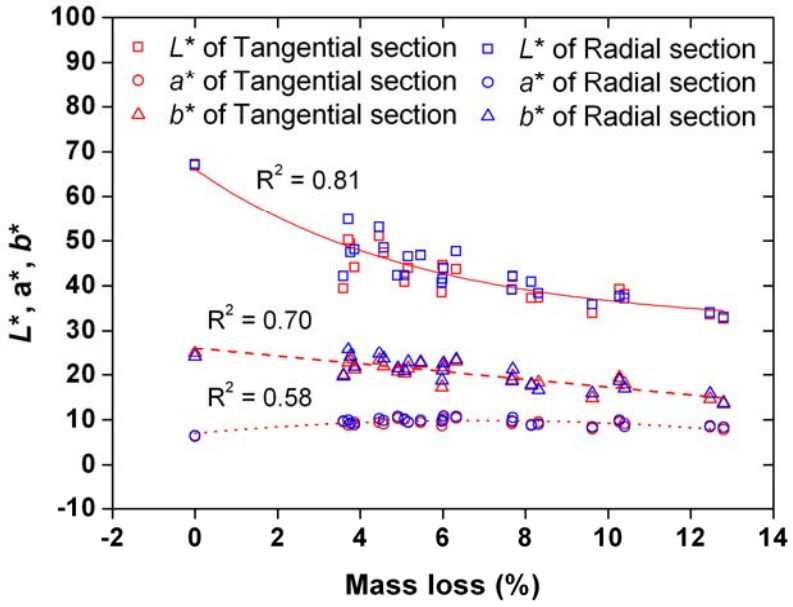

Fig. 5. Changes of *L**, *a**, *b** as function of mass loss

Colored byproducts formed during the degradation of hemicellulose might have a contribution to this change in appearance. Thermal treatment always results in darkening of the wood (Brischke et al. 2007; Esteves et al. 2008b). Heat-treated wood acquire a darker color similar to most tropical woods, which is an aesthetical advantage for some applications.

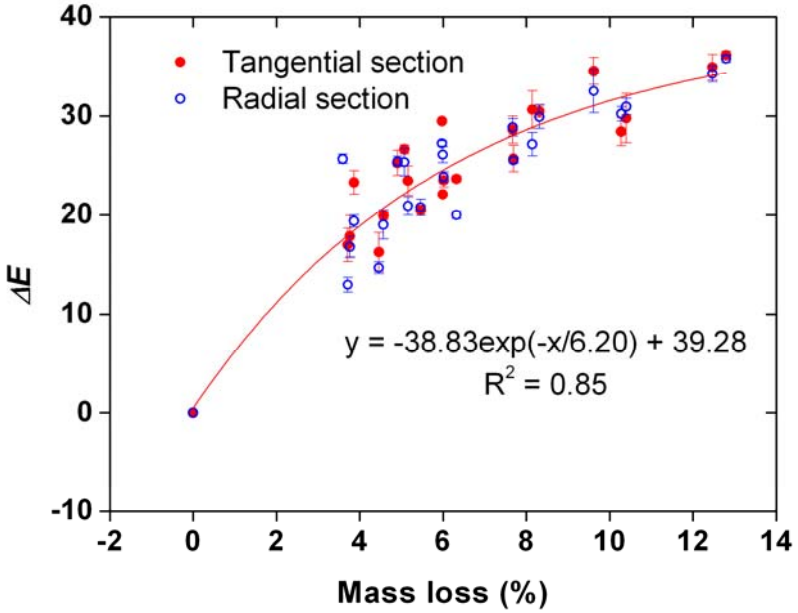

Fig. 6. Relationship between the color change (*ΔE*) of heat-treated wood and the mass loss by heat treatment

An excellent but non-linear relationship (R^2 = 0.81) was observed between the lightness (L^*) measured on wood samples surface and the mass loss (Fig. 5). Decreases by up to 51% and 43% of L^* and b^* with increasing intensity of the heat treatment, respectively, were observed, whereas a^* showed only a slight increase, with a maximum at approximately 6% mass loss, before slightly decreasing again. The total color change (ΔE) of treated samples is presented in Fig. 6. The results show that there was a significant correlation (R^2 = 0.85) between color change and treatment intensity. With the mass loss increasing from 4 to 13%, the color change increased from 0 to 37.

CONCLUSIONS

1. High temperature has a significant influence not only on the discoloration, but also on dimensional stability of acacia hybrid wood. The increasing *ASE* values of the samples with increasing of mass loss during heat treatment indicate that the dimensional stability of acacia hybrid wood is improved during heat treatment. The color change is advantageous for species with unappealing wood color, such as acacia hybrid.
2. The concentration of hydroxyl groups was found to be reduced after treatment. This result coincides with the increase in dimensional stability of heat-treated wood.
3. Heat treatment showed an interesting potential to improve the wood quality as regards color and its value for solid timber products from acacia hybrid. This technology provides an environmentally safe method of sequestering carbon and protecting sustainable common woods to give a new generation of value-added biomaterials with increased stability and durability without the use of toxic chemicals.

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