

CHANGES IN THE CHEMICAL STRUCTURE AND DECAY RESISTANCE OF HEAT-TREATED NARROW-LEAVED ASH WOOD

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ABSTRACT

We analyzed the effects of heat treatment on the chemical structure of wood from narrow-leaved Ash (*Fraxinus angustifolia*), a fast-growing and economically valuable species. We also analyzed the effects of heat treatment on the wood's resistance to four decay fungi. Narrow-leaved Ash wood samples were heated with saturated steam to 140, 180, 200, and 220°C for 2, 4, and 6 h. The relative contents of extractable components were analyzed, as well as the levels of holocellulose, cellulose, and lignin. In addition, the density, equilibrium moisture content, and pH of the samples were measured. To determine the effects of heat treatment on resistance to decay fungi, the samples were exposed to the white rot fungus *Trametes versicolor*, dry rot fungus *Serpula lacrymans*, and the brown rot fungi *Coniophora puteana* and *Gloeophyllum trabeum*. Changes in the chemical composition of the wood due to heat treatment were correlated with increased resistance to fungal decay. While the hemicellulose content was dramatically reduced with increasing temperature and treatment duration, the lignin content increased proportionately. Thus, heat treatment is an environmentally friendly method of preserving narrow-leaved Ash wood against various decay fungi.

Keywords: Chemical structure, decay resistance, *Fraxinus angustifolia*, thermal modification.

INTRODUCTION

A variety of mechanical, chemical, and biological factors can lessen the durability of wood products, leading to economic losses, and the cutting of trees to replace destroyed wooden materials adds to the threat of deforestation (Calonego *et al.* 2010).

Under suitable climatic conditions, wooden materials face biological degradation due to various organisms, which feed on the natural polymers (Paes *et al.* 2004). To extend the life of wood, a number of methods have been developed, including various modification processes and treatment with wood-protecting substances (Oliveria 1986). However, the use of wood preservatives is often limited or banned due to environmental pressures (Kartal *et al.* 2004). Therefore, environmentally friendly methods to preserve wood are needed (Hill 2006, Cao *et al.* 2011). Heat treatment is one such method that is effective against wood decay fungi (Esteves and Pereira 2009).

Heating has been shown to improve the dimensional stability (González-Peña *et al.* 2004, hygrosopicity (Hakkou *et al.* 2005), and decay resistance (Homan *et al.* 2000) of wood, but it weakens wood's mechanical properties (Viitaniemi *et al.* 2002). Hemicellulose, amorphous cellulose, and lignin are subject to degradation or modification, and the extractives evaporate or polymerize (Viitaniemi *et al.* 2002). Thermal modification alters the chemical properties of wood (Weiland and Guyonnet 2003), making heat-treated wood more resistant to decay (Lekounougou *et al.* 2009). The optimal temperature and time of such heat treatment varies among non-naturally resistant wood species (Kamdem *et al.* 2002, Calonego *et al.* 2010).

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Narrow-leafed Ash (NLA) is a fast-growing tree that is commonly cultivated on plantations (Cicek and Yilmaz 2002). Its wood is used in many products, including furniture, flooring, sports equipment, wainscoating, and cladding panels (Bozkurt and Erdin 1989). However, the wood's low natural resistance to decay organisms shortens its useful life. Therefore, we examined the effect of heat treatment on the service life of NLA wood and its resistance to decay fungi. This is the first such study to date.

MATERIALS AND METHODS

Wood samples

Three narrow-leafed Ash (*Fraxinus angustifolia* Vahl) trees, each approximately 22 years old, were randomly selected from Düzce Province, Turkey. Timber (1 m long) cut from 1.5 m heights of the trees were air-dried away from direct sunlight. All test samples were prepared from the sapwood, which comprises a large part of NLA (Bozkurt and Erdin 1989).

Heat treatment

The specimens were dried to approximately at 3% moisture content in a drying oven at 80°C for 24 h. Then, using saturated steam, the samples were heated to 140, 170, 200, and 220°C for 2, 4, and 6 h. After heat treatment, the oven temperature was reduced to 20°C, as recommended by Hakkou *et al.* (2006). The percent anhydrous mass loss due to heat treatment was calculated as

$$\text{Mass loss (\%)} = \frac{m_0 - m_1}{m_0} \quad (1)$$

where m_0 and m_1 are the masses (g) before and after heat treatment, respectively. The densities of the samples were calculated as

$$\text{Density} = \frac{m}{v} \quad (2)$$

where m is the mass (g) of the sample and V is the volume (cm^3) of the wood blocks. The pH (TAPPI T 509 om-83) and densities (TS 2472) of the heat-treated samples were compared with those of the air-dried and oven-dried untreated samples (control).

Decay test

Decay resistance tests were conducted according to the European standard (1996) EN 113. Control and heat-treated test specimens were dried at $80 \pm 2^\circ\text{C}$ for 24 h and then weighed to 0.01 g precision. The blocks were sterilized by autoclaving at $100 \pm 2^\circ\text{C}$ for 20 min. The samples were then exposed to the white rot fungus *Trametes versicolor* (L: Fr.) Pilat. (FFPRI 1030), the brown rot fungi *Coniophora puteana* (Schum.:Fr.) Karst. (Mad-515) and *Gloeophyllum trabeum* (Pers.) Murrill (Mad-617-R), and the dry rot fungus *Serpula lacrymans* (*Merilius lacrymans*) (Wulf. ex Fr.) (FPRL 12C). All fungal cultures were obtained from Forest Products Laboratory (Madison, WI, USA). *Trametes versicolor* and *G. trabeum* were grown on 3.9% potato dextrose agar medium, while *C. puteana* and *S. lacrymans* were grown on 3.7% malt extract agar medium. The Petri dishes (9 cm in diameter) were filled with 15 ml of the sterile culture medium ($121 \pm 1^\circ\text{C}$ for 30 min) and incubated with a piece of mycelium at 24°C and 75% relative humidity for one week. After inoculation, samples of the heat-treated and control wood (30 x 15 x 5 mm [longitudinal x radial x tangential directions]) were placed in the Petri dishes, with a feeder strip laid across the samples to foster growth of the mycelium on the samples. After 12 weeks, the samples were cleaned of the fungal mycelia and weighed to calculate the moisture content. The samples were then dried at $80 \pm 2^\circ\text{C}$ for 24 h and weighed to calculate the percentage of mass loss.

Determination of the chemical composition of the wood

Chemical analyses were conducted to compare the chemical composition of the heat-treated and control Ash wood samples. The wood samples were chipped and ground into powder using a laboratory-scale Wiley's mill (TAPPI T 257 cm-85), and the moisture content of the sawdust was determined (TAPPI T 264 om-88). The ground samples were then analyzed for extractable [hot water (TAPPI T 207 om-88), cold water (TAPPI T 207 om-88), 1% NaOH (TAPPI T 212 om-88), and alcohol-benzene (TAPPI T 204 om-88)] lignin (TAPPI T 222 om-88), holocellulose (Wise and Karl 1962), and cellulose (Kurschner-Hoffer method, Browning 1967). The hemicellulose content of the samples was determined by subtracting of cellulose content from holocellulose (Pettersen 1984). Each experiment was carried out in triplicate.

Statistical analyses

Statistical analyses were performed using SPSS 19 software. The effects of treatment temperature and time on mass loss, wood density, chemical changes, and decay resistance were evaluated using an ANOVA and Duncan's comparison test.

RESULTS AND DISCUSSION

Table 1 shows pH values, densities of air-dried and oven-dried, mass loss for treated and untreated NLA wood samples. The pH of the untreated wood was 5.7. The pH decreased with increasing temperature, with the maximum change (pH 3.9) occurring after treatment at 220°C for 6 h.

The mass loss of the heat-treated wood correlated roughly with the treatment temperature and duration. Little mass was lost until the temperature reached 200°C, at which point the mass loss increased rapidly. The duration of heat treatment had no significant effect on the mass lost up to 180°C. Mass losses at this temperature result from the degradation and evaporation of wood components during heat treatment (Viitaniemi and Jämsä 1996). At temperatures above 200°C, the cellulose and hemicellulose (the main components of the wood) are degraded, and lignin is condensed (Sundqvist *et al.* 2006, Tumen *et al.* 2010). Hence, an accelerated loss of mass was observed at treatment temperatures of 200°C and higher.

The wood density was inversely correlated with treatment temperature and duration. The lowest densities occurred in samples treated at 220°C for 4 and 6 h (Table 1). The difference between these samples and the control samples was statistically significant ($p < 0.05$). The equilibrium moisture content (EMC) of the wood samples decreased with heat treatment. The usual 11.8% moisture content of untreated wood was reduced to 5.7% in the samples treated at 220°C for 4 h.

Table 1. Effect of heat treatment on some physical properties of NLA wood.

Temperature (°C)	Time (h)	pH	EMC (%)	Mass loss (%)		Air-dry density (g/cm ³)	Oven-dry density (g/cm ³)	
Control		5.7	11.8	-		0.77 (0.01)	0.74 (0.01)	<i>cd</i> <i>cde</i>
140	2	5.5	11.5	0.52 (0.05)	<i>a*</i>	0.76 (0.01)	0.75 (0.02)	<i>cde</i> <i>de</i>
	4	5.3	11.4	0.68 (0.10)	<i>ab</i>	0.75 (0.02)	0.73 (0.02)	<i>de</i> <i>bcd</i>
	6	5.3	11.3	1.05 (0.10)	<i>abc</i>	0.77 (0.02)	0.75 (0.02)	<i>de</i> <i>de</i>
180	2	5	10.3	1.27 (0.05)	<i>bc</i>	0.79 (0.03)	0.77 (0.02)	<i>e</i> <i>e</i>
	4	4.7	9.9	1.45 (0.03)	<i>c</i>	0.77 (0.01)	0.75 (0.01)	<i>de</i> <i>de</i>
	6	4.4	8.8	8.54 (0.17)	<i>d</i>	0.74 (0.02)	0.71 (0.02)	<i>bcd</i> <i>bc</i>
200	2	4.7	8.4	12.71 (0.28)	<i>e</i>	0.76 (0.03)	0.74 (0.03)	<i>cde</i> <i>cde</i>
	4	4.2	8.3	14.08 (0.73)	<i>f</i>	0.75 (0)	0.73 (0)	<i>de</i> <i>bcd</i>
	6	4.3	7.1	17.15 (0.81)	<i>g</i>	0.75 (0.01)	0.73 (0.01)	<i>bcd</i> <i>bcd</i>
220	2	4.3	6	17.01 (0.75)	<i>g</i>	0.73 (0.02)	0.71 (0.02)	<i>bc</i> <i>bc</i>
	4	3.9	5.7	24.65 (0.83)	<i>h</i>	0.69 (0.07)	0.67 (0.07)	<i>a</i> <i>a</i>
	6	3.9	5.8	27.38 (0.48)	<i>i</i>	0.71 (0.03)	0.70 (0.02)	<i>ab</i> <i>ab</i>

* $p < 0.05$ (Duncan's test). Means within each column and factor followed by the same letter are not significantly different. Values in parenthesis are standard deviations. EMC: Equilibrium moisture content.

Chemical Content

The chemical compositions of the heat-treated and untreated samples are presented in table 2. The average holocellulose content in the untreated samples was 78.38%. The holocellulose content decreased with a treatment duration of 2 h or more, with the lowest content occurring in samples treated at 220°C for 4 (51.39%) and 6 h (50.59%). This decrease in holocellulose content was basically due to a loss of substantially hemicellulose. These results are in agreement with those of previous studies using other wood types (Fengel and Wegener 1989, Yildiz 2002, Hill 2006, Khalid *et al.* 2010).

Table 2. Chemical characterization of NLA wood.

Temp. (°C)	Time (h)	Holocellulose (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)	Solubility (%)				
							Hot water	Cold water	Alcohol benzene	1% NaOH	
Control		78.38 (0.30)	<i>f*</i> 53.45 (0.21)	<i>g</i> 24.93	21.40 (0.09)	<i>cd</i> 0.83 (0.02)	<i>cd</i> 5.14 (0.75)	<i>bc</i> 6.33 (0.69)	<i>fg</i> 4.18 (1.17)	<i>abc</i> 13.49 (0.19)	<i>a</i>
	2	74.30 (0.72)	<i>e</i> 52.51 (1.42)	<i>fg</i> 21.79	21.76 (0.07)	<i>cd</i> 1.10 (0.44)	<i>e</i> 6.29 (0.42)	<i>de</i> 6.82 (0.11)	<i>g</i> 5.43 (0.09)	<i>de</i> 14.84 (0.08)	<i>b</i>
	4	75.56 (0.25)	<i>e</i> 50.59 (0.12)	<i>cde</i> 24.97	22.34 (0.01)	<i>de</i> 0.97 (0.09)	<i>de</i> 5.34 (0.22)	<i>bc</i> 6.08 (0.22)	<i>efg</i> 4.03 (0.03)	<i>ab</i> 15.46 (0.10)	<i>c</i>
	6	75.93 (0.27)	<i>e</i> 52.65 (0.58)	<i>fg</i> 23.28	19.89 (0.34)	<i>ab</i> 1.34 (0.11)	<i>f</i> 4.82 (0.12)	<i>ab</i> 5.51 (0.27)	<i>def</i> 5.02 (0.10)	<i>bcde</i> 17.95 (0.16)	<i>d</i>
	2	74.37 (0.19)	<i>e</i> 51.45 (0.16)	<i>def</i> 22.92	19.52 (0.51)	<i>a</i> 1.04 (0.17)	<i>de</i> 5.34 (0.12)	<i>bc</i> 4.79 (0.05)	<i>bcd</i> 3.80 (0.09)	<i>a</i> 15.41 (0.09)	<i>c</i>
	4	74.01 (1.12)	<i>e</i> 50.21 (1.44)	<i>cd</i> 23.8	21.82 (0.72)	<i>cde</i> 0.60 (0.13)	<i>abc</i> 5.13 (0.06)	<i>ab</i> 4.02 (0.11)	<i>ab</i> 3.94 (0.14)	<i>ab</i> 17.72 (0.46)	<i>d</i>
	6	66.37 (0.33)	<i>d</i> 49.66 (1.30)	<i>c</i> 16.71	20.95 (0.32)	<i>bc</i> 0.47 (0.11)	<i>ab</i> 5.28 (0.07)	<i>bc</i> 4.91 (0.05)	<i>cd</i> 4.24 (0.08)	<i>abc</i> 23.76 (0.48)	<i>f</i>
	2	66.21 (0.18)	<i>d</i> 50.61 (0.35)	<i>cde</i> 15.6	20.56 (0.73)	<i>abc</i> 0.55 (0.17)	<i>ab</i> 5.77 (0.16)	<i>cd</i> 5.90 (0.61)	<i>ef</i> 4.09 (0.12)	<i>ab</i> 21.70 (0.26)	<i>e</i>
	4	56.36 (3.99)	<i>c</i> 53.39 (0.38)	<i>g</i> 2.97	23.04 (2.23)	<i>e</i> 0.54 (0.02)	<i>ab</i> 6.56 (0.04)	<i>e</i> 5.33 (0.06)	<i>de</i> 5.44 (0.10)	<i>de</i> 27.89 (0.53)	<i>g</i>
	6	53.99 (0.30)	<i>b</i> 50.02 (0.86)	<i>cd</i> 3.97	30.79 (0.29)	<i>f</i> 0.70 (0.03)	<i>bc</i> 7.70 (0.37)	<i>f</i> 4.14 (0.12)	<i>abc</i> 6.15 (0.07)	<i>ef</i> 34.93 (0.56)	<i>t</i>
	2	54.78 (0.16)	<i>bc</i> 51.36 (0.67)	<i>def</i> 3.42	34.40 (0.62)	<i>g</i> 0.44 (0.03)	<i>ab</i> 5.04 (0.14)	<i>bc</i> 4.13 (0.11)	<i>abc</i> 4.33 (0.13)	<i>abc</i> 28.15 (0.37)	<i>g</i>
	4	51.39 (2.22)	<i>a</i> 47.61 (2.07)	<i>ab</i> 3.78	37.47 (0.15)	<i>h</i> 0.43 (0.02)	<i>a</i> 4.20 (0.11)	<i>a</i> 4.06 (0.86)	<i>ab</i> 5.27 (0.16)	<i>cde</i> 34.24 (0.26)	<i>h</i>
	6	50.59 (0.21)	<i>a</i> 48.15 (1.50)	<i>b</i> 2.44	41.15 (0.91)	<i>i</i> 0.42 (0.04)	<i>a</i> 4.81 (0.33)	<i>ab</i> 3.67 (0.13)	<i>a</i> 7.14 (0.60)	<i>f</i> 36.37 (0.36)	<i>j</i>

* $p < 0.05$ (Duncan's test). Means within each column and factor followed by the same letter are not significantly different. Values in parenthesis are standard deviations.

The lignin content was not significantly changed until the treatment temperature reached 200°C for at least 2 h. This result is in agreement with that of a previous study (Yildiz 2002). The relative lignin content of the untreated samples was 21.4%, whereas it was significantly greater in the samples treated at 200°C. The highest lignin content (41.15%) was observed in samples treated at 220°C for 6 h an increase of ~92% compared with the untreated. Of the main components of wood, lignin is the most resistant to thermal degradation (Fengel and Wegener 1989). The relative increase in lignin content with heat treatment is associated with structural changes (cross-linking) in lignin composition (Esteves *et al.* 2008, Boonstra and Tjeerdsma 2006). Lignin also undergoes polycondensation reactions with other cell wall components (Esteves *et al.* 2008). Thus, the lignin content increases proportionally with a decreasing polysaccharide (cellulose and especially hemicelluloses) content (Kotilainen 2000).

The mean relative hemicellulose content of the samples heated to 140 or 180°C for 2 and 4 h was similar to that of the control samples. However, the mean hemicellulose content decreased significantly with a treatment temperature of 200°C for 4 h. The loss of hemicellulose was 84-90% greater in the heat-treated samples than in the controls. The lowest hemicellulose content (2.4%) was observed in samples treated at 220°C for 6 h. In contrast to these results, Sivonen *et al.* (2002) showed that hemicelluloses are affected by heat treatment even at relatively low temperatures; however, similar to our results, the hemicellulose content decreased with increasing treatment temperature and time compared to the controls.

The mean cellulose content of untreated NLA control samples was 53.45%. Although the cellulose content decreased slightly at treatment temperatures below 220°C, the decline was not linearly correlated with the treatment temperature and duration. The decrease in cellulose content following treatment at 220°C for 6 h was only ~11% compared to the controls. Cellulose undergoes limited deformation with heat treatment due to its high molecular weight crystalline structure. Especially, the amorphous structure of cellulose is probably deformed at temperature above 200°C (Bhuiyan and Hirai 2005). As a result, the slight decrease in cellulose content at temperatures above 200°C (Sundqvist 2004). The amount of components soluble in 1% NaOH increased linearly during heat treatment (Table 2). The relative content of 1% NaOH-soluble components was 13.49% in the control samples and 28% in the samples heated to 200°C for 4 h. Even at the lowest treatment temperature of 140°C for 2 h, the content of 1% NaOH-soluble components increased 10% relative to the controls. This increase probably resulted from the dissolution of carbohydrate, the lightest 1% NaOH-soluble component in wood considering its molecular mass (Tümen *et al.* 2010). The relative content of hot water-soluble components increased slightly with increasing heat treatment up to 220°C and then decreased by ~18% after 4 h at 220°C compared to the controls. A previous study (Yildiz 2002) found that the relative content of hot water-soluble components decreased with temperatures ranging from 180 to 200°C. The relative content of alcohol-benzene (2:1) extractable components was 4.18% in the controls. This content increased with increasing treatment temperature and duration. The greatest content of alcohol-benzene-extractable components was observed in the samples heated to 220°C for 6 h (7.14%), which is a 71% increase over controls.

In summary, the data in table 3 show that treatment temperature and duration significantly ($p < 0.05$) affected the holocellulose, cellulose, hemicellulose, lignin, hot water-extractable, alcohol-benzene-extractable and 1% NaOH-extractable components of NLA wood.

Table 3. ANOVA of the chemical content of heat-treated NLA wood with different treatment parameters.

Dependent Variable	Source of variance	Sum of Squares	df	F	Sig. *
Holocellulose	Temperature	2348.8	3	534	0.000
	Time	1931	3	439	0.000
Cellulose	Temperature	81.4	3	30.4	0.000
	Time	118.6	3	44.2	0.000
Hemicellulose	Temperature	1261.4	3	858.3	0.000
	Time	304.5	3	207.2	0.000
Lignin	Temperature	1261.4	3	858.3	0.000
	Time	304.5	3	207.2	0.000
Hot water	Temperature	14.3	3	27	0.000
	Time	2.2	3	4.1	0.014
Alcohol-benzene	Temperature	9.4	3	8.4	0.000
	Time	14.7	3	13.2	0.000
1% NaOH	Temperature	1249.2	3	4088.4	0.000
	Time	1407.6	3	4606.9	0.000

* $p < 0.05$ (Duncan's test).

Biological Performance

The mass losses in the control samples exposed to various decay fungi were 41.3% with *T. versicolor*, 23.3% with *S. lacrymans*, 36.2% with *C. puteana*, and 31.7% with *G. trabeum* (Table 4).

Table 4. Percent mass loss in heat-treated samples of NLA wood after exposure to various decay fungi.

Temperature (°C)	Time (h)	Mass loss (%)							
		<i>T. versicolor</i>		<i>S. lacrymans</i>		<i>C. puteana</i>		<i>G. trabeum</i>	
Control		41.3 (2.1)	<i>i</i> *	23.3 (3.7)	<i>e</i>	36.2 (2.8)	<i>h</i>	31.7 (3.3)	<i>e</i>
140	2	37.0 (3.5)	<i>h</i>	23.6 (2.5)	<i>e</i>	32.3 (2.2)	<i>fg</i>	31.1 (2.3)	<i>e</i>
	4	38.0 (1.8)	<i>hi</i>	17.7 (5.1)	<i>d</i>	34.2 (1)	<i>gh</i>	33.5 (2.9)	<i>e</i>
	6	31.1 (2.8)	<i>g</i>	15.5 (4)	<i>d</i>	33.4 (0.5)	<i>fg</i>	31.8 (3.6)	<i>e</i>
180	2	32.3 (1.1)	<i>g</i>	15.1 (4.9)	<i>d</i>	31.1 (5.1)	<i>f</i>	33.5 (2.8)	<i>e</i>
	4	35.7 (3.7)	<i>h</i>	7.3 (0.7)	<i>bc</i>	21.7 (0.1)	<i>e</i>	26.8 (3)	<i>d</i>
	6	27.1 (3)	<i>ef</i>	7.3 (0.5)	<i>bc</i>	21.4 (0.2)	<i>e</i>	24.8 (1.6)	<i>d</i>
200	2	30 (4.2)	<i>fg</i>	8.8 (0.9)	<i>c</i>	14.9 (0.7)	<i>d</i>	16.7 (1.2)	<i>c</i>
	4	26.3 (3.3)	<i>de</i>	4.7 (0.8)	<i>ab</i>	9.3 (0.2)	<i>c</i>	16.5 (4)	<i>c</i>
	6	20.1 (3.8)	<i>bc</i>	2.6 (1.7)	<i>a</i>	7.9 (2.2)	<i>bc</i>	10.1 (0.4)	<i>b</i>
220	2	23.2 (3.7)	<i>cd</i>	1.2 (0.3)	<i>a</i>	5.5 (0.5)	<i>b</i>	9.7 (0.1)	<i>b</i>
	4	17.4 (1.7)	<i>b</i>	1.2 (0.3)	<i>a</i>	2.5 (1.6)	<i>a</i>	5.3 (0.5)	<i>a</i>
	6	14.1 (2)	<i>a</i>	1 (0.5)	<i>a</i>	0.2 (0.2)	<i>a</i>	2.9 (0.2)	<i>a</i>

* $p < 0.05$ (Duncan's test). Means within each column and factor followed by the same letter are not significantly different. Values in parenthesis are standard deviations.

In the heat-treated samples exposed to *T. versicolor* (white decay fungus), the lowest mass losses occurred in the samples treated at 220°C for 4 and 6 h (17.4 and 14.1%, respectively). No significant change in mass loss was observed in samples treated at 140 and 180°C, regardless of the duration.

In samples exposed to *S. lacrymans* (dry decay fungus), the mass loss was significantly reduced in samples treated at 180°C for 4 h. At lower temperatures, the results were mixed. The lowest mass losses (<1.2%) were observed in samples treated at 220°C for 4 and 6 h. *S. lacrymans* is selectively depolymerises the cellulose and hemicellulose components of wood due to its actually a brown rot fungi (Hibbett and Donoghue 2001). In the samples exposed to *C. puteana* or *G. trabeum* (brown decay fungi), no significant change in mass loss occurred unless the treatment temperature was at least 180°C for 4 h. At 200°C for 4 h, the average mass loss was reduced to 9.3% with *C. puteana* and 16.5% with *G. trabeum*. For both species, the lowest mass losses were observed in samples treated at 220°C for 4 and 6 h (Table 4).

Table 5 shows the results of a multiple variance analysis of the effects of treatment temperature and duration on mass loss. Both temperature and duration significantly affected the mass losses of the samples.

Table 5. ANOVA of the effect of treatment temperature and duration on mass loss in NLA wood after exposure to various decay fungi.

Dependent Variable	Source of variance	Sum of Squares	df	F	Sig.*
<i>T. versicolor</i>	Temperature	2025.0	3	32.9	0.000
	Time	4140.5	3	67.4	0.000
<i>S. lacrymans</i>	Temperature	2357.5	3	95.9	0.000
	Time	4183.6	3	170.2	0.000
<i>C. puteana</i>	Temperature	7503.5	3	67.3	0.000
	Time	6252.7	3	56.1	0.000
<i>G. trabeum</i>	Temperature	5997.5	3	64.2	0.000
	Time	2714.5	3	29.1	0.000

* $p < 0.05$ (Duncan's test).

These differences in mass loss are directly correlated with the changes in chemical composition of the wood with heat treatment. During heat treatment, significant degradation of amorphous polysaccharides occurs at the cell membrane, and the hygroscopicity of the wood decreases (Esteves and Pereira 2009). Furthermore, with a reduction in the relative content of nutrients for decay fungi, resistance against the fungi increases (Esteves and Pereira 2009). We observed a reduction of as much as 90% in the hemicellulose content, depending on the treatment temperature and duration (Table 2). However, the relative lignin content increased proportionally to 48%. Hemicelluloses are highly sensitive to heat treatment, and in many studies losses occurred from the start of heat treatment (Weiland and Guyonnet 2003, Hakkou *et al.* 2006). Accordingly, lignin cross-linking and the lignin content both increase with heat treatment (Hakkou *et al.* 2006, Khalid *et al.* 2010). As known, while brown rot fungi are characterized by the removal of the polysaccharide components, white rot fungi degrade lignin and polysaccharides simultaneously (Hill 2006). Therefore, the decay resistant of NLA wood was increased not only brown rot, but also white rot fungi by heat treatment.

Additionally, The reduction in equilibrium moisture content decreases the wettability of wood and affects the enzymatic activities of fungi (Viitaniemi and Jämsä 1996, Kamdem *et al.* 2002, Almeida *et al.* 2009). Therefore, this factor should also increase the resistance of the wood to decay fungi. Another factor affecting the fungal resistance of the wood is pH. The natural pH of 5.7 was reduced to 3.9 in the heat-treated wood. The optimum pH for fungal growth is 5-6 (Bozkurt *et al.* 1993). Thus, heat treatment made the pH less favorable for fungal growth.

Finally, fungicidal extractives are produced during heat treatment (Kamdem *et al.* 2000). Although we observed no linear increase in certain extractable components (hot water, cold water, and alcohol-benzene) of the wood samples with heat treatment, we did observe a linear increase in 1% NaOH-soluble components with increasing treatment temperature and duration.

CONCLUSIONS

Heat treatment also causes a loss of mass in NLA wood. At temperatures of 180°C (6 h) and above these mass losses increased with increasing temperature and duration. The equilibrium moisture content of the wood also decreased with increasing treatment temperature and duration.

Heat treatment causes various changes in the chemical composition of NLA wood depending on the treatment temperature and duration. While the holocellulose content decreases at temperatures of 200°C and above, the lignin content increases proportionally. The hemicellulose content begins to decrease at relatively low temperatures and undergoes an extensive decline following treatment at 220°C for 4 h.

In these experiments, the heat-treated NLA wood became more resistant to four different species of decay fungi. While no significant change was observed in the mass losses caused by fungi up to a treatment temperature of 180°C, a significant decrease was observed at higher temperatures. This increase in resistance also increased with an increasing duration of heat treatment at the higher temperatures. This reduction in mass loss was correlated with the decrease in equilibrium moisture content of the wood and with the changes in the wood's chemical composition.

NLA is a fast-growing species with high economic value, but its wood has a low degree of natural durability. We conclude, however, that the durability of NLA wood against fungi can be increased through heat treatment, an environmentally friendly method of preservation, thereby increasing the wood's utility for various applications such as garden furniture, pool areas, flooring, siding, decks etc.

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