

CHEMICAL CHARACTERIZATION AND FTIR SPECTROSCOPY OF THERMALLY COMPRESSED EUCALYPTUS WOOD PANELS

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In memoriam of Dr. Thomas C. MANNES

ABSTRACT

In this study, the change in the chemical properties of the thermally modified eucalyptus (*Eucalyptus camaldulensis*) wood boards were examined by wet chemical analysis and FTIR spectroscopy. The eucalyptus wood boards were modified with a laboratory type hot-press for four different groups at press pressures of 2 or 4 MPa and temperatures of 150°C or 180°C and compared to untreated control. After this, hot water, 1% NaOH, ethanol-cyclohexane, ethanol, and methanol-water solubility values were determined for the treated samples. In addition, the content of klason lignin, acid soluble lignin, holocellulose, and α -cellulose were investigated. The solubility values (except for the ethanol solubility) increased in the modified wood when compared to the untreated control. A decrease in the content of acid soluble lignin, holocellulose and α -cellulose was observed while the content of klason lignin in the modified wood was increased. According to the FTIR analysis results, significant changes were observed in the spectra of the modified samples. These findings were in agreement with the results of wet chemical analysis.

Keywords: Cell wall components, chemical composition, *Eucalyptus camaldulensis*, thermal modification, wood composites, wood solubility.

INTRODUCTION

Wood is a renewable, recyclable, non-toxic biomaterial and for this reason it has been used in numerous applications by humankind. Wood materials obtained from plantations have gained importance in recent years because of their fast and economic production concept. The *Eucalyptus camaldulensis* Dehn. (Turkish river red gum) grown in a plantation in Mersin, Turkey, has some advantageous properties such as high growth rate, and low price. Thermal modification methods have been used to improve dimensional stability properties such as thickness swelling, water absorption, and durability of wood materials (Burmester 1973, Giebeler 1983), and various thermal modification methods such as Plato Process, Retification Process, Boise Perdure, Oil-Heat Treatment Process, and ThermoWood Process have been developed (Militz 2002).

Thermal compression technique performed with hot press is used to increase physical and mechanical performance properties of wood-based materials. Thermally compressed wood is called as staypak (Seborg *et al.* 1945), Stamm (1964) while compressed wood pretreated with phenol formaldehyde is called compreg (Stamm 1964, Stamm and Harris 1953). In addition, the surface densification of wood

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has been studied by Tarkow and Seborg (1968).

There are many scientific studies which investigate various thermal modification processes of wood materials. Wang and Cooper (2004) worked on the vertical density profile (VDP) of thermally compressed balsam fir wood. Wang and Cooper (2005) investigated the influences of grain orientation and surface wetting on the VDP of thermally compressed fir and spruce wood materials. They revealed that the thermally compressing process affected VDP characteristics of the wood materials. The VDP, drying properties, and hardness of pine solid wood panels were determined by Unsal and Candan (2007) and Unsal and Candan (2008). Biological properties such as decay and termite resistance of the hot-press modified pine wood materials were searched by Unsal *et al.* (2008) and Unsal *et al.* (2009). Candan *et al.* (2010) determined surface characteristics of the Douglas fir wood veneers modified with a hot-pressing process. A research done by Dogu *et al.* (2010) revealed that thermally compressing process significantly affected anatomical structure of the pine solid wood materials. Thermal modification by a hot-press also affects surface wettability and roughness characteristics of the wood materials (Unsal *et al.* 2011). Candan *et al.* (2012) modified plywood panels thermally and stated that contact angle and surface roughness values were significantly changed by the modification parameters. Color properties have an importance by costumers. Thermally compressing process significantly influenced the color parameters of pine wood materials (Atik *et al.* 2013). Thermal modification method affects performance properties of the paulownia (Candan *et al.* 2013a) and poplar (Candan *et al.* 2013b) wood materials. Changes in microscopic characteristics because of thermally compressing procedure were examined by Dogu *et al.* (2016) and Dogu *et al.* (2017).

Properties of chemically treated wood-based materials depend on process temperature and pressure. Deformations in chemical structure of wood materials by heat application appear at approximately 150°C. However, temperature alone is not causing changes in wood components. There are also some other factors that influence the thermal degradation process, such as time of the treatment, atmosphere, pressure and water content (Fengel and Wegener 1984, Hill 2006).

Main chemical components of thermally modified wood materials are very stable up to 100°C temperature. However, the degradation of polysaccharides takes place rapidly at higher temperatures. Of the polysaccharides, cellulose is more stable under heat treatment when compared to hemicelluloses. However, also cellulose chain length decreases under high temperature treatments (Hill 2006). Lignin is the most stable chemical component of wood materials against thermal degradation (Fengel and Wegener 1984). When the wood material is exposed to heat treatment below 140°C, condensable fractions (carbon oxides and, trace organic degradation products) occurs with loss of water and volatile extractives. As the temperature is further increased, acetic acid, formic acid, and methanol as well as CO₂ gas are formed especially from the hemicelluloses (Hill 2006).

The specific aim of this research was to determine the influences of the press temperature and the press pressure parameters on the chemical components of the eucalyptus wood materials. For this objective, the cellulose, lignin, hemicelluloses, and extractives were studied with traditional wet chemical techniques. Infrared (IR) spectroscopy procedure was also carried out.

MATERIALS AND METHODS

Materials

Turkish River Gum (*Eucalyptus camuldensis* Dehn.) wood was used in this study. The logs were obtained from Mersin, Turkey and cut into boards measuring 150 mm by 500 mm by 18 mm. Two experimental wood panels were obtained from per log. All of the experimental boards were placed in a climate chamber adjusted 20±2°C and 65%±5 relative humidity (RH).

Methods

Thermal modification

Thermal modification of the eucalyptus wood boards was performed using a laboratory type hot-press located in the Wood Composites Manufacturing Laboratory at the Department of Forest Products Engineering, Istanbul University. Experimental design of the thermal treatments conducted with wood boards is shown in Table 1. Prior to the heat treatments, the modified and control samples were conditioned at 20 ± 2 °C and $65\pm 5\%$ RH in a climate chamber for three weeks.

Table 1. Experimental design of the thermally modified wood boards.

Groups	Press Pressure (MPa)	Temperature (°C)	Press Duration (min)
Control	-	-	-
S1	4	150	45
S2	2	150	45
S3	4	180	45
S4	2	180	45

Chemical analyses

The chipped eucalyptus wood boards were grinded in a Wiley mill. Prior to the chemical analysis, the samples were screened to particle size range ranging from 40 to 100 mesh T-257 cm-85 method (TAPPI 1992a). After this, hot water, 1% NaOH, ethanol-cyclohexane, and, ethanol solubilities were determined according to TAPPI Test Methods T-204 om-88 (TAPPI 1992b), T-207 om-88 (TAPPI 1992c), T-212 om-88 (TAPPI 1992d). The amount of klason lignin was estimated using 72% sulfuric acid and 40% hydrobromic acid by Runkel and Wilke (1951). Acid soluble lignin was determined by using a UV/Vis-spectrophotometer according to TAPPI UM 250 (TAPPI 1985). Holocellulose was prepared using sodium chlorite solution and acetic acid at 75°C according to procedure used by Jayme (1942) and Wise *et al.* (1946). Amount of α -cellulose was determined according to T-203 cm-99 method (TAPPI 1983). Methanol:water extraction of the samples was performed as described previously (Balaban and Ucar 2001).

FT-IR spectroscopy

For FTIR analysis, the finely ground wood samples were dried in a hot oven at 50°C for 24 hours. The changes in the chemical structure of the ground samples were investigated by using an attenuated total reflectance with fourier transform infrared spectroscopy (ATR-FTIR, Bruker, Tensor 37). The spectra were recorded in the wavenumber range from 400-4000 cm^{-1} and 32 scans per sample with a resolution of 4 cm^{-1} were used. The evaluation of the spectra were carried out using the Bruker OPUS software.

RESULTS AND DISCUSSION

Chemical analyses

The solubility values of the thermally modified wood boards are shown in Table 2. The hot water solubility values of the wood boards were decreased with the thermal compression. The solubility of 1% NaOH of the samples increases with rising hot-press pressure and temperature. It could be due by

the increase in low molecular weight carbohydrates, hemicellulose and, cellulose degradation products in the samples. With thermal effect, solubility of lignin contributes to this increase too (Korotkova *et al.* 2015). With thermal effect, lignin starts to degrade but at a lower rate than other component of the wood. Besides that, there was no significant difference between S3 and S4 sample, which showed that increase in the press pressure has limited effect on the carbohydrate degradation. These results were in agreement with Ates *et al.* (2009), Batista *et al.* (2016b) and Neiva *et al.* (2015).

Amount of non-polar extractives in samples were determined with successive ethanol-cyclohexane and ethanol extractions. Ethanol-cyclohexane and ethanol solubility values were 2,6% and 4,1% respectively (Table 2.) The table shows an increase in ethanol-cyclohexane solubility values of the samples with rising treatment pressure and hot-press temperature in comparison with control sample. Brito *et al.* (2008) observed a similar result. However, in contrast to Brito *et al.* (2008), ethanol solubility values of the samples have a significant decrease in comparison with control sample. The reason for this difference can be the method of thermal modification.

Methanol-water solubility values (5,1%) in the control samples are given in Table 2. Wanxi *et al.* (2015) determined the methanol solubility as 5,8% for the untreated sample of same species. Significant reduction was observed in the methanol-water solubility of the modified wood samples with increasing thermal modification temperature. This decline may be due to the auto-condensation reactions of phenolic compounds of the wood by the thermal effect (Rakić *et al.* 2004, Pizzi 1994). It has also been shown that the increase in pressure applied to the modification has a limited effect on the methanol-water solubility.

Table 2. Solubility values of the thermal modified wood boards.

Groups	Hot Water (%)*	1% NaOH (%)*	EtOH-Cyclohexane (%)*	EtOH (%)*	Methanol-Water (%)*
Control	7,4 (0,1)	24,0 (0,2)	2,6 (0,1)	4,1 (0,1)	5,1 (0,0)
S1	5,9 (0,2)	26,0 (0,2)	2,9 (0,1)	1,5 (0,2)	4,9 (0,1)
S2	6,0 (0,2)	24,4 (0,3)	2,8 (0,2)	2,2 (0,2)	3,1 (0,1)
S3	5,7 (0,2)	27,5 (0,4)	4,5 (0,3)	0,4 (0,1)	4,3 (0,1)
S4	6,1 (0,1)	27,1 (0,2)	3,9 (0,2)	0,9 (0,1)	3,1 (0,0)
*based on oven-dry wood, mean of three replicates, values in parentheses are standard deviations.					

The results of lignin content of unmodified- and thermally modified wood boards are shown in Table 3. Amount of residual lignin shown in second column of the table is higher than expected values for eucalyptus wood. The reason for this is that presence high amount of the phenolic compounds in the wood (Cadahía *et al.* 1997). The phenolic compounds could be condensed and remain as the klason lignin in acidic conditions, it is believable that the klason lignin content is somewhat overestimated, if the wood material was prepared without an additional 1% sodium hydroxide extraction (Gonultas and Ucar 2013, Hafizoglu *et al.* 1997). The lignin contents determined after successive ethanol/cyclohexane, ethanol and 1% sodium hydroxide extractions would be considered as true lignin values. Table 3 shows amount of residual lignin value after 1% NaOH extraction in third column. In addition, acid soluble lignin and total lignin contents of samples are given in Table 3. The klason lignin value was increased significantly with increasing temperature and pressure effect. The relative increase of the klason lignin content in the samples was due to decreased amount of cellulose and hemicellulose caused by thermal degradation and being condensed the degradation product of carbohydrates such as aldehydes with lignin and other phenolic compounds (Tjeerdsma *et al.* 1998, Esteves *et al.* 2013). These results were in agreement with Alén *et al.* (2002), Ates *et al.* (2009), Boonstra and Tjeerdsma (2006), Brito *et al.* (2008) Fengel and Wegener (1984). The content of acid soluble lignin remained relatively constant in all samples besides the sample S3.

Table 3. Lignin content of the thermally modified wood boards.

Groups	Klason Lignin % ⁺	Klason Lignin after 1% NaOH Extraction % [‡] (I)	Acid-Soluble Lignin % ⁺ (II)	Total Lignin % ⁺ (I+II)
Control	33,3 (0,7)	27,1 (0,4)	2,5 (0,1)	29,6 (0,5)
S1	34,0 (0,6)	28,8 (0,5)	2,3 (0,1)	31,1 (0,6)
S2	33,3 (0,7)	27,2 (0,5)	2,5 (0,2)	29,7 (0,7)
S3	40,0 (0,5)	37,4 (0,6)	1,3 (0,2)	38,7 (0,8)
S4	34,3 (0,7)	30,5 (0,3)	2,5 (0,1)	33,0 (0,4)

⁺based on oven-dry, extracted wood, [‡] 1 % NaOH extraction conducted after successive Et-OH/cyclohexane and Et-OH extractions, mean of three replicates, values in parentheses are standard deviations.

Total lignin percentages, yields of holocellulose and amount of α -cellulose in the samples were compiled in Table 4. The yields of holocellulose in the control sample was determined as 71,5 while this value was 69,4 for *Eucalyptus grandis* wood (Batista *et al.* 2016a). The holocellulose content of S3 sample was decreased significantly because due to their amorphous and branched polymeric structure especially hemicelluloses are less stable against the effect of the thermal degradation when compared to the other polymeric wood constituents (i.e., lignin and cellulose) (Fengel and Wegener 1984). The cleavage of glycosidic bonds of hemicelluloses is facilitated by deacetylation reactions causing the formation of acetic acid (Windeisen *et al.* 2007). After thermal treatment, most of the xylan is degraded (Fengel and Wegener 1984). The lower content of hemicelluloses might play a role on the better natural durability of the wood (Windeisen *et al.* 2007). On the other hand, the crystal structures of cellulose molecules are more resistant to thermal effects (Fengel and Wegener 1984). The thermal resistency of cellulose can be seen in Table 4.; only a relatively small decrease in the yields of α -cellulose was observed when compared to the decrease in holocellulose yields. The findings obtained from this study are supported by a study of Batista *et al.* (2016a).

Table 4. Cell wall components of the thermal modified wood boards.

Groups	Total Lignin (%) [*]	Holocellulose (%) [*]	α -cellulose (%) [*]
Control	29,6	71,5 (1,2)	42,7 (0,4)
S1	31,1	69,1 (1,5)	41,8 (0,3)
S2	29,8	70,0 (1,4)	42,2 (0,3)
S3	38,7	55,9 (1,8)	36,6 (0,6)
S4	32,9	66,9 (1,3)	39,8 (0,4)

^{*}based on oven-dry extracted wood, mean of three replicates, values in parentheses are standard deviations.

FT-IR spectroscopy evaluation

The IR spectra of the thermally modified or unmodified eucalyptus wood panels are shown in Figure 1.

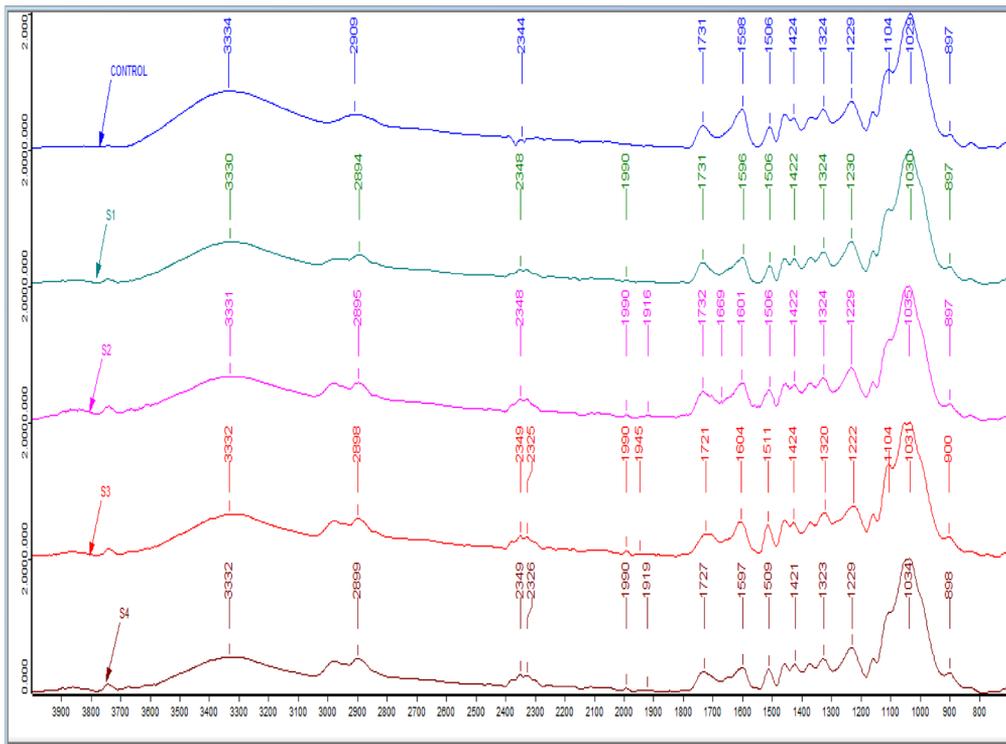


Figure 1. FTIR spectra of untreated and thermal modified wood boards.

The observed bands of the thermally modified or unmodified eucalyptus wood panels are presented in Table 5

Table 5. Main bands of infrared spectrum of the modified samples.

Wavenumber (cm ⁻¹)	Band Origin
3400-3330	OH stretching of alcohols, phenols, and acids ^{3,5,6,7,9}
2970-2820	C-H stretching in methyl and methylene groups ^{3,5,7}
1750-1720	C=O stretching in unconjugated ketons, carbonyls, aldehydes and ester groups ^{2,3,4,5,6,7,9,10}
1605-1598	Aromatic ring stretching in lignin ^{3,7}
1515-1506	Aromatic ring stretching in lignin; C=C stretching of the aromatic ring in lignin ^{1,2,3,4,6,9}
1470-1460	C-H deformation (asymmetric) ^{3,5,6,7,8}
1430-1420	Aromatic skeletal vibration with C-H deformation ^{2,3,5,7,10}
1370-1365	CH ₂ bending in cellulose and hemicellulose ^{4,5,7,8}
1330-1320	Syringyl ring breathing ⁷
1240-1229	Syringyl ring and C-O stretch in lignin and xylan ^{3,4,5,6,7}
1157-1156	C-O-C vibration in cellulose and hemicellulose ^{1,5,6,7,8}
1035-1029	C-H and C-O deformations ^{3,7,8}
897	C-H deformation of cellulose and hemicellulose ^{3,5,7}

¹Akgul *et al.* (2007), ²Ates *et al.* (2009), ³Esteves *et al.* (2013), ⁴Kocafe *et al.* (2008), ⁵Mattos *et al.* (2015), ⁶Missio *et al.* (2015), ⁷Müller *et al.* (2009), ⁸Peng *et al.* (2015), ⁹Tjeerdsma and Militz (2005), ¹⁰Yildiz and Gümüşkaya *et al.* (2007)

The OH tension which was determined at 3334 cm^{-1} . This peak corresponds to hydrogen bonded OH group that water and all main wood components contain (Kocaefe *et al.* 2008). In the thermally modified samples, some of the OH groups are replaced and this peak is reduced (Esteves *et al.* 2013, Mattos *et al.* 2015, Missio *et al.* 2015, Tjeerdsma and Militz 2005). The C-H stretching peak at 2909 cm^{-1} was increased and shifted to 2894 cm^{-1} with thermal modification process. This broadening may be due to oxidation and hydrolysis of acetyl groups from hemicelluloses (Esteves *et al.* 2013). The C=O stretching vibration was determined at 1731 cm^{-1} . This peak indicates carbonyl groups in the xylan. When this peak was examined further, the peak shrank and shifted to small wavenumbers with increasing temperature and pressure of the thermal modification process. Especially, this peak was shifted to a lower frequency (1721 cm^{-1}) compared to that of control sample, while at the same time the lowest holocellulose value (55,9%) in the S3 sample was determined. For FTIR analysis, similar results were described by Boonstra and Tjeerdsma (2006), Esteves *et al.* (2013), Kocaefe *et al.* (2008), Mattos *et al.* (2015), Missio *et al.* (2015), Tjeerdsma and Militz(2005), Peng *et al.* (2015), Yildiz *et al.* (2007). In the samples, the characteristic aromatic ring stretching vibration is observed at 1506 cm^{-1} . Cleavage of the aliphatic side chains in lignin and the formation of new cross-links in lignin with condensation reactions reduces the water absorption properties of the samples (Boonstra and Tjeerdsma 2006, Kocaefe *et al.* 2008). That peak increased and shifted to a large wavenumbers with rising the temperature and pressure of the thermal process (Esteves *et al.* 2013, Kocaefe *et al.* 2008, Missio *et al.* 2015, Müller *et al.* 2009, Tjeerdsma and Militz2005). The peak of aromatic ring stretching was shifted to 1511 cm^{-1} and 1509 cm^{-1} for S3 and S4 sample, respectively. For the S1 and S2 samples, the peak wavelength did not change. Similarly, results of total lignin values in the S3 (38,7%) and S4 samples (32,9%) was significantly increased compared to the control sample (29,6%) while the S1 (31,1%) and S2 (29,8%) samples had slight increase. The peak at 1424 cm^{-1} was C-H deformation in the lignin and cellulose. This peak was shifted to 1421 cm^{-1} and decreased with maximum pressure of the thermal process. This decrease was also obtained by Akgul *et al.* (2007), Ates *et al.* (2009), Esteves *et al.* (2013), Mattos *et al.* (2015), Müller *et al.* (2009), and Yildiz and Gümüşkaya(2007). The C-O vibration of the syringyl ring units was determined at 1324 cm^{-1} (Esteves *et al.* 2013, Kocaefe *et al.* 2008, Müller *et al.* 2009). With condensation reactions in the lignin units, this peak increased and shifted to small wavenumbers. While the lowest total lignin value was determined in the S3 sample, the peak wavelength shifted to 1320 cm^{-1} too. In the infrared spectrum of samples, the C-O carbonyl band in lignin and xylan units was observed at 1229 cm^{-1} . This peak appeared to decrease and broadened to small wavenumbers for thermally modified wood samples (Esteves *et al.* 2013, Kocaefe *et al.* 2008, Mattos *et al.* 2015, Missio *et al.* 2015, Müller *et al.* 2009, Peng *et al.* 2015). After thermal modification, an increase defined in the peak at 1104 cm^{-1} due to OH association of cellulose units. Especially, the increase in S1 and S3 samples may be due to formation of new alcohol and ester groups after the modification (Ates *et al.* 2009, Kocaefe *et al.* 2008, Mattos *et al.* 2015, Missio *et al.* 2015). The absorption peak at 897 cm^{-1} indicated the asymmetric deformation of cellulose and hemicellulose units (Esteves *et al.* 2013, Kocaefe *et al.* 2008, Müller *et al.* 2009). There was a decrease in this peak accompanied with increasing pressure and temperature of process, especially due to depolymerization of the hemicellulose units.

CONCLUSIONS

Thermal modification process by hot press proved to be a simple way to modify chemical properties of the wood to increase the possibility of end-use from wood of the fast growing species. It is demonstrated that the thermal modification process modified the chemical structure of eucalyptus wood boards, especially the holocellulose and extractives content.

Increasing press pressure and temperature of the modification resulted in a rise of hot water, 1% NaOH, EtOH-cyclohexane and, methanol-water solubility because of the new substances that are mainly produced from degradation of the hemicellulose and lignin. The klason lignin content less

increased in treatments at 150°C (2-4 MPa pressure) and significantly increased at the 180°C treatment. Lignin presents a higher resistance to thermal modification at moderate temperatures than other wood components. The results of wet chemical analysis of the modified wood showed that there are significant decrease holocellulose content of the S3 sample while the decrease for α -cellulose is relatively less for the sample because of highly thermal resistant of the cellulose.

FTIR spectroscopy in combination with wet chemical analysis is a practical method that can be used in the characterization of the modified wood. FTIR analyses also reveal significant differences in the chemistry of the modified wood. FTIR spectrometry analysis of the modified wood revealed the substitution of OH groups by the thermal compression. New cross-linking and auto-condensation reactions in lignin could be observed in the FTIR spectrum at 1507 cm^{-1} .

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