Strength and Stiffness of Thermally Rectified Eucalyptus Wood Under Compression

Marcio Rogério da Silva^{a*}, Gilmara de Oliveira Machado^a, José Otávio Brito^b, Carlito Calil Junior^a

^aLaboratory of Wood and Timber Structures, Sao Paulo University – USP, Av. Trabalhador São-carlense, 400, CP 780, CEP 13566-590, São Carlos, SP, Brazil ^bLaboratory of Chemistry, Cellulose and Energy, Forest Sciences Department, Luiz de Queiroz" College of Agriculture – ESALQ, University of São Paulo – USP, Av. Pádua Dias, 11, CEP 13418-900, Piracicaba, SP, Brazil

Received: August 20, 2012; Revised: March 5, 2013

The aim of this work was the evaluation of the thermal-rectification process of reforestation wood *Corymbia citriodora* Hook by measuring of mechanical properties under compression parallel to the grain and also determining of chemical composition. The tested samples were thermally treated in a furnace with nitrogen-atmosphere at heating rate of 0.033 °C.min⁻¹, at temperatures of 160, 180, 200, 220 and 240 °C. The chemical components and mechanical properties were affected with the thermal rectification process. The contents ranged from 17.85 to 3.51% extractives, 30.44 to 53.86% lignin, 69.56 to 46.14% holocellulose and 0.31 to 0.47% ashes. The samples strength decreased from 20% to 50% and the elasticity modulus increased about 47%. The characteristic values of strength under compression were determined and these changes were about 23% lower than Brazilian standard. The best mechanical properties of *Corymbia citriodora* were obtained at 180 °C.

Keywords: thermally treated wood, hardwoods, mechanical properties, compression strength, chemical composition

1. Introduction

Wood thermal treatment is an alternative to chemical treatment in wood preservation and has been used to improve timber quality¹. Wood thermal rectification is defined as a result of controlled pyrolysis that finishes before the beginning of the exothermic reactions and carbonization process at about 280 °C². Thermally rectified wood is obtained by the principle of thermal degradation of its constituents, mainly extractives and hemicelluloses, in an inert atmosphere, or under controlled oxygen atmosphere.

The thermal treatment can be accomplished between 150 and 280 °C, and at temperatures higher than 220 °C, approximately, the changes in the wood are greater³.

Changes in wood properties during heat treatment depend on the method of thermal modifications, the wood species and its characteristic properties, the moisture content of the wood, the prevailing atmosphere, treatment duration and temperature. The temperature has more influence than time on many properties. Above 150 °C alterations on the physical and chemical properties of wood are permanent⁴⁻⁶. Besides, European heat treatment technologies of wood show that not only the different species of wood but also the same wood species of different geographical origin can behave differently when the same program of thermal treatment is used⁷

The thermal-rectification process causes changes in cell wall constituents and extractives and also of the physical and mechanical properties of wood. Polyoses are much more susceptible to thermal degradation than other polymeric wood constituents, due to their low molecular weight, branched, amorphous structure with different and substituted monomeric units. Polyoses degrade at lower temperature (160-220 °C)^{5,8}. The amount of cellulose cristallinity is increased due to degradation of amorphous cellulose, resulting in inaccessibility of hydroxyl groups to the water molecules contributing to a decrease of equilibrium moisture content in addition to the major effect caused by hemicellulose degradation. Cellulose degradation becomes important beyond 220 °C9. Lignin is classified as the most stable component during the wood thermal treatment, showing thermoplastic behaviour above 150 °C, and the temperature range in which lignin takes place is between 220 and 250 °C^{6,10}. Additionally, as the result of chemical modification, heat treatment induces darkness on original color of wood, reduces the moisture content, which explains the decrease in wood shrinkage and swelling. However, the strength properties start to weaken at the same time.

Thermal-rectification technique improves wood resistance against weathering, swelling properties, biological resistance to decay. Other improvements are: reduction in the moisture content of equilibrium, increase in the dimensional stability, attractive dark color and increase in wettability.^{1,2,5,11-13}.

The major disadvantage of thermal treatment is the changes in the wood mechanical properties. The strength of Spruce wood thermally treated under compression was studied by Yildiz; it was observed that at higher temperatures and longer periods of treatment, the strength to failure under compression was lower than untreated wood⁴. Similar

^{*}e-mail: marciomr@sc.usp.br

results about mechanical properties were found by other studies, in which reductions on the strength properties and elasticity modulus were obtained^{6,14-16}. The decrease in some mechanical properties of thermally rectified wood limits its use in structural applications. Thus, thermal treatment in wood has mainly been done in softwoods, and for non-structural purposes. However, there has been a recent interest in the use of modified wood for structural applications¹⁷.

In this study the effects of the compression strength characteristic value for the eucalyptus wood was investigated. There are few publications about mechanical properties of thermally rectified hardwoods and the results can help in structural calculations of wood treated by heat.

2. Experimental

In this work, the studied species was Corymbia citriodora (Hook.) (C. citriodora), grown in Brazil, at eighteen years old. The wood moisture content was 12% (±2) with density of 1.000 kg.m⁻³. All the thermally rectified samples were analyzed and compared with untreated wood. The thermal treatment was performed in an electrical furnace, which had a metal box with lid inside. Seven wood pieces with dimensions of 56 cm length, 16 cm width and 6 cm thickness were analyzed. These wood pieces were placed inside the box and two steel bars with one centimeter of diameter between the pieces. It was necessary to promote gas circulation around the wood. Thermal degradation of wood heated in the presence of oxygen is faster than heated wood in an oxygen-free atmosphere4. Thus, nitrogen gas was injected inside the metal box with constant flux along all thermal treatment to avoid the wood oxidation.

The temperature control was monitored using seven thermocouples of type K. One was installed inside the furnace, another one in the metal box and five on the wood piece. Three thermocouples were put on the first wood piece and two on the sixth wood piece, which were placed in order to measure the temperature in its geometrical center and ends. This strategy was adopted to ensure the homogenization of the temperature of all the heated material.

The thermal-rectification process was started at 160 °C and carried out with difference of 20 °C between each treatment until the wood started the flashover. The thermal-rectification process was done with an increase in furnace temperature from room temperature until 100 °C; this phase had a short duration of 40 min. Afterwards, the wood heating rate was 0,033 °C.min⁻¹ until the thermal rectification temperature was achieved with a standard deviation of ±5 °C. In the last step, the temperature was decreased to room temperature only with air circulation system connected.

After heat treatment, the wood pieces were cut, tests of compression in the direction to the grain to determine the strength (f_{c0}) and elasticity modulus (E_{c0}) were carried out following the NBR 7190/97 Brazilian Standard¹⁸. They were determined from the maximum compression load ($F_{c0,max}$) applied in standard specimens with cross-sectional area of 5 × 15 cm. The slope of the secant line tension-deformation curve was defined by points ($\sigma_{10\%}$; $\varepsilon_{10\%}$) and ($\sigma_{50\%}$; $\varepsilon_{50\%}$), corresponding respectively, 10% and 50% of the compression strength parallel to the grain. All these

values were obtained for different levels of temperature according to Equations 1 and 2.

$$f_{c0} = F_{co,max}/A \tag{1}$$

$$E_{c0} = \left(\sigma_{50\%} - \sigma_{10\%}\right) / \left(\varepsilon_{50\%} - \varepsilon_{10\%}\right) \tag{2}$$

where $F_{\rm co,max}$ is the maximum compression load applied, in the samples during the test, in N; A is the cross-section area of samples, in ${\rm m^2}$; $\sigma_{10\%}$ and $\sigma_{50\%}$ are compression stress corresponding to 10% and 50% of strength (${\rm f_{c0}}$) and $\varepsilon_{10\%}$ and $\varepsilon_{50\%}$ are the specific strains measured of samples, corresponding to tensions of $\sigma_{10\%}$ and $\sigma_{50\%}$.

In addition, the characteristic values of strength by compression were also calculated, following the NBR 7190/97 Brazilian Standard¹⁸, according to Equation 3.

$$X_{w,k1} = \left(2 \cdot \frac{x_1 + x_2 + \dots + x_n}{\frac{n}{2} - 1} - x_n}{\frac{n}{2} - 1} \cdot 1, 1\right)$$
(3)

where n is the number of samples. The results should be in crescent order $x_1 \le x_2 \le ... x_n$, disregarding the highest value if the number of samples is odd and it can't be admitted for the $X_{n,k}$ values smaller than x_1 and the 0,7 of the mean value.

The calculation of the mean characteristic value of compression strength was obtained according to Equation 4, following the NBR 7190/97 Brazilian Standard^{18,19}.

$$X_{w,k2} = 0.7.X_m (4)$$

where X_m is mean value of strength.

To each temperature of thermal treatment there were three blocks, with names of BLI, BLII and BLIII and so six samples were obtained by block.

For the chemical analysis, the pieces of wood were reduced in small particles to pass through a 42 mesh screen (0.355 mm pore size) and to be retained in a 60 mesh screen (0.250 mm). The moisture content of all samples was determined before each assay according to Tappi Standard, 1999²⁰. The chemistry analyses were done to a total extractive according to standard TAPPI 204 cm-9721 and TAPPI 207 cm-9922. These samples were extracted in a soxhlet with a mix hexane/etanol (1:1 v/v) for 8 hours and boiling water for 3 hours, in order to remove nonpolar and polar extractive fraction. The extractive content was determined by mass difference, before and after the extraction. The resulting extractive-free wood was used to determine the Klason lignin content by the sum of the insoluble and soluble lignin fractions according to the TAPPI T222 om-9823 and TAPPI T250 198524 standards. The percentage of ashes was determined according to a standard procedure TAPPI T211 om-93, 198525. The holocellulose content was determined by difference between lignin content and extractive-free wood mass²⁶. The samples were analyzed in duplicate to determine a standard deviation

Statistical analyses were conducted using the software Minitab 16. Strength and modulus of elasticity under compression parallel to the grain results were compared between the blocks for each temperature and also between the temperatures using variance analysis (ANOVA) and the Tukey test at 95% confidence interval.

3. Results and Discussion

The thermal treatment was done with 20 °C of difference between treatments. The thermally rectified wood treatment was carried out at 160, 180, 200, 220 and 240 °C. The value at 240 °C was the highest temperature that could be used in the wood for the thermal treatment. This fact was due to the flashover of Corymbia citriodora that started at about 253 °C. As a result, it was impossible to control the temperature that reached up to 330 °C, inside of the piece of wood. For this reason, the wood was carbonized. After each thermal treatment temperature range was achieved, the temperature was maintained for 150 min at 160 and 180 °C, and 120 min at 200, 220 and 240 °C. It was necessary to wait for the temperature gradient to be homogeneous in all piece of wood, with a standard deviation of ± 5 °C. At lower temperatures the wait time was greater due to the low energy available in the system. Figure 1 shows the curve of thermal treatment at 200 °C. The final temperature in this process was achieved in 51.17 h, with wait time of 150 min. Thus, the total time to finish the thermal rectification process was 53.17 h. After that, just the furnace air circulation system remained turned on.

An important factor that influenced heat-treated wood was the changes in its chemical composition. The wood of *C. citriodora* was subjected to a characterization of its main macromolecular components. The results are shown in Table 1. The chemical composition obtained for untreated *C. citriodora* are in accordance with results by Silva²⁷, in which the authors reported similar chemical composition to Klason lignin and holocellulose.

As showed in Table 1, the content of extractives decreased about 80% when the temperature increased from room temperature to 240 °C (17.85% to 3.51%). The ashes composition was similar for almost all treatments. Only at 240 °C there was a little increase. These changes of the extractives content were probably caused by the volatilization of different extractives from the wood due to heat, while others were degraded. Almost all of the original extractives disappeared, and new compounds were formed including monosaccharides and others^{11,28}. For the Eucalyptus globulus thermally treated at 190 and 200 °C, for different times, 2, 6 and 12 hours, the extractives content increased in the beginning of the treatment and decreased afterwards²⁹. The extractives content from temperatures of 120 to 180 °C decreased for Pinus caribea and increased for Eucalyptus saligna. The authors concluded that these different behaviors can be explained by differences in chemical constituents between softwoods and hardwoods³⁰. Thus, the extractives contents can be changed in function of

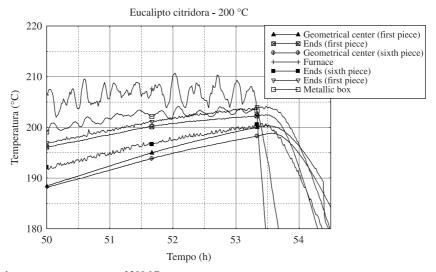


Figure 1. Thermal treatment at temperature of 200 °C.

Table 1. Chemical characterization of the thermally treated wood.

Temperature (°C)	Extractives	Ashes	Klason Lignin	Holocellulose
Untreated	17.85 ± 0.69 a	0.31 ± 0.02 a	30.44 ± 0.01 a	69.56 ± 0.02 a
160	$14.76 \pm 0.08 \text{ b}$	0.33 ± 0.01 a	$37.47 \pm 0.24 \text{ b}$	$62.53 \pm 0.38 \text{ b}$
180	10.22 ± 0.54 c	0.29 ± 0.01 a	33.49 ± 0.72 c	$66.51 \pm 1.08 \text{ c}$
200	$9.59 \pm 0.10 \text{ c}$	0.33 ± 0.02 a	$44.04 \pm 0.17 d$	$55.96 \pm 0.3 d$
220	$6.35 \pm 0.14 d$	0.30 ± 0.01 a	51.71 ± 0.14 e	48.29 ± 0.29 e
240	3.51 ± 0.24 e	$0.47 \pm 0.03 \text{ b}$	$53.86 \pm 0.4 \text{ f}$	$46.14 \pm 0.86 \text{ f}$

Values are mean \pm standard deviation (SD). Means followed by the same letter are not significant (Tukey = 5%).

the wood species and treatment program utilized, in which the lowest extractive content was at 240 °C, with 3.51%.

In relation to lignin content there was an increase up to 76% with thermal treatment (30.44 to 53.86%). The amount of Klason's lignin increases with increasing temperature during thermal treatment^{4,5,9,26,31}. It is mainly caused by degradation of the hemicelluloses (during hydrothermolysis) and cellulose (during curing). Condensation reactions of lignin, most probably also contribute to this high lignin content. Especially when the hydrothermolysis temperature is raised to 185 °C, more hemicelluloses cleavage products (depolymerisation) are available, which can contribute to polymerization reactions of lignin (e.g. condensation) during curing^{9,32}. The results in the literature are in accordance with the results showed in this paper, in which the lignin content increased with increasing temperature and the highest content was at 240 °C with 53.86%. Exceptionally at 180 °C, the lignin content was 10% lower than at 160 °C. The average mass density with humidity 0% (+ 2%) was calculated for untreated wood and at temperature of 160, 180, 200, 220 and 240 °C and the results obtained in this case were 0,97; 0,92; 0,86; 0,89; 0,81 and 0,82 g/cm³, respectively. The wood that was thermally treated at temperature of 180 °C had lower density than 160 °C due a natural variability of pieces in study. The change of density can be great because it is related to with juvenile and mature wood, difference between heartwood and sapwood and place of origin³³. Thus, the exothermic reactions started between 180 and 200 °C due to the presence of secondary reactions favored by the slow increase of temperature and by confinement of the pyrolysis gases. This reaction is stronger in thicker pieces of wood and due to the difficulty of gases in leaving the porous matrix³⁴. So, the lower density of wood treated at 180 °C favored a decreased in occurrence of secondary reactions, and as a consequence, there was an increase in the holocellulose content while the lignin content decreased at temperature of 180 °C, in relation at temperature of 160 °C.

It was also possible to observe that there was an inverse correlation between lignin (30.44 to 53.86%) and holocellulose content (69.56 to 46.14%) for all temperatures. Thus, the holocellulose content was opposite to lignin content, in which there was a decrease along the treatment and the highest reduction was 46.14% at 240 °C. The holocellulose content decreases during the treatment caused by depolymerization of the hemicelluloses during the hydrothermolysis and some degradation of the cellulose during curing⁹. Very little cellulose is degraded at temperatures below 200 °C, in which degradation becomes important beyond 220 °C9. The cellulose has a highly ordered crystalline structure and the crystallinity of cellulose increases due to degradation of the amorphous cellulose, which provides a great stability to the cellulose chains and protects them against acid attack during hydrolysis. The accessibility of the glucosidic bonds is very limited when compared to those of hemicellulose. The low thermal stability of hemicelluloses compared to cellulose is usually explained by the lack of crystallinity, in which chemical modification starts by deacetylation followed by depolymerization catalyzed by the released acetic acid. On

the other hand, the dehydratation induces formation of the furfural and hydroxymethylfurfural^{4,28,29}. The reduction in the holocellulose content was high with the increase in temperature of thermal treatment, in which the hemicellulose was the first component to be affected, followed by cellulose, causing changes in the properties of *C. citriodora*.

The statistical analyses ANOVA and Tukey test, to the extractives, Klason lignin and holocellulose content showed significant differences at 5% significance level. Only thermal treatment at 180 and 200 °C were statistically similar in relation to extractive contents. In relation to ashes, only results of the thermal treatment at 240 °C were statistically different. It was probably due the degradation of polysaccharides and volatile compounds which reduced the organic component of wood. No group thermally treated was statistically similar the untreated wood for the Klason lignin and holocellulose content.

With the changes in the chemical composition, the mechanical properties were affected. Table 2 shows mean results of six samples to each block (f_{c0}, E_{c0}) and mean results of eighteen samples to each temperature $(f_{c0}, E_{c0})^{**}$ by compressive strength parallel to the grain for untreated and thermally rectified wood. According to the results obtained on the compression strength to thermally treated wood, it was possible to calculate the characteristic values of compression strength (f_{c0k}) according to NBR 7190/97 Brazilian Standard^{18,19}. To each temperature, there were six samples by block. Therefore, the calculations on the characteristic values were made with eighteen samples because the treatments were made with three blocks and the results are shown in Table 2. The moisture content of the wood affects their mechanical properties. For the values of moisture content below the fiber saturation point (FSP), about 25% the mechanical properties of wood increase with the reduction of moisture content¹⁹. Thus, it was necessary to control the moisture content of untreated wood in 0% (+2) to ensure that the mechanical properties were similar to thermally rectified wood, which after the treatment were without moisture content (dry wood).

The strength and stiffness properties were influenced by the increase of temperature. In the first temperature of treatment, changes were found, in which the average loss was about 40% for the strength properties (f_{c0}). At high temperatures the changes were a little higher and the lowest results were obtained for the treatment at 220 °C, with average loss of 51%. The best temperature observed for the treatment of wood was at 180 °C, in which the average loss was only 25%. One of causes of high loss of the compression strength in the first temperature (160 °C) was the presence of sapwood in the samples, in which Silva³⁵ reported that compression strength (f_{c0}) in the sapwood is about 10% less than heartwood.

A study of compression parallel to grain in spruce wood (*P. orientalis*) was performed⁴. The samples were heated to 130, 150, 180 and 200 °C and the results found for the compression strength generally deteriorated with increase in temperature. The reductions in the strength properties were related to the rate of thermal degradation and to the losses of substance after heat treatments. The decrease in strength of wood is mainly due to depolymerization reactions of

Table 2. Strength and stiffness properties, and characteristic values of the compression.

Temperature (°C)	Treatments	$f_{c0}(MPa)$	f _{c0} (MPa)**	E_{c0} (GPa)	E _{c0} (GPa)**	$f_{c0k}(MPa)$
Untreated 0%	BLI	79 ± 7 A	84 ± 6 a	17 ± 2 A	19 ± 3 a	77
	BLII	$85 \pm 6 \text{ A}$		$20 \pm 3 \text{ AB}$		
	BLIII	$86 \pm 6 \text{A}$		$21 \pm 2 A$		
160	BLI	$33 \pm 6 \text{ A}$	$48 \pm 13 \text{ bd}$	$12 \pm 2 A$	20 ± 6 ab	33
	BLII	$57 \pm 12 \text{A}$		24 ± 4 B		
	BLIII	$53 \pm 7 \text{ B}$		$25 \pm 3 \text{ B}$		
180	BLI	$69 \pm 7 \text{A}$	$63 \pm 12 c$	$27 \pm 2 A$	$25 \pm 3 c$	43
	BLII	$71 \pm 7 A$		$24 \pm 2 \text{ AB}$		
	BLIII	$50 \pm 11 \; \text{B}$		$23 \pm 3 \text{ B}$		
200	BLI	$59 \pm 12 \text{A}$	53 ± 11 bc	$23 \pm 5 \text{A}$	24 ± 4 bc	38
	BLII	$51 \pm 11 A$		$25 \pm 4 \text{A}$		
	BLIII	$51 \pm 11 A$		$24 \pm 5 \text{ A}$		
220	BLI	$44 \pm 7 \text{ A}$	$41 \pm 6 d$	$19 \pm 3 A$	$17 \pm 2 a$	33
	BLII	$35 \pm 3 \text{ B}$		$16 \pm 2 \text{ AB}$		
	BLIII	$44 \pm 9 \text{A}$		$15 \pm 1 \text{ B}$		
240	BLI	$38 \pm 6 \mathrm{A}$	$47 \pm 9 \text{ bd}$	$17 \pm 3 \text{ A}$	$19 \pm 3 \text{ a}$	35
	BLII	$46 \pm 8 \text{A}$		$18 \pm 3 \text{ AB}$		
	BLIII	56 ± 6 B		$22 \pm 4 \text{ B}$		

Values are mean \pm standard deviation (SD). Statistical results are shown to capital letters by blocks (BLI, BLII and BLIII) and small letters by different temperatures. Means followed by the same letter are not significant (Tukey = 5%). ** mean results.

wood polymers. The first reason for the strength loss is the degradation of hemicelluloses, which are less stable to the heat than cellulose and lignin. Changes or losses of hemicellulose play key roles for the strength properties of wood heated in high temperatures. The hemicelluloses degrades first, mainly regarding the arabinose and xylose²⁹. The degradation of cellulose becomes important around 220 °C. Thus, the changes of content holocellulose were due mainly to hemicellulose degradation in low temperature. As a result, the increase of the holocellulose content at 180 °C was probably by the increase of hemicellulose content and for this reason the results of strength compression were higher than strength at 160 °C.

On the other hand, almost all results of the elasticity modulus (E_{c0}) of thermally rectified wood showed improvement indicating that the stiffness after treatment was increased. Only in the treatment at 220 °C the stiffness was less in only 2% when compared to untreated wood and the greatest increase was to the treatment at 180 °C. At high temperatures, 220 and 240 °C, the stiffness decreased in relation to treatments at 160, 180 and 200 °C. Nevertheless, the elasticity modulus to the high temperatures was similar to the untreated wood. Modulus of elasticity in bending for thermally treated wood was reported in fir (Abies spp.), aspen (Populus spp.), and birch (Betula spp.) and the results showed an increase of 25, 15 and 30%, respectively, compared with their untreated control³⁶. Similar results were found in other papers to aspen by Kocaefe and the increase in this case was approximately 40%16. Eucalyptus globulus was evaluated and the modulus of elasticity in bending of heat treated samples was higher than those of natural wood, despite a reduction in transverse tensile strength of the samples³⁷. Modulus of elasticity in bending was less affected, presenting lower degradation of cellulose and lignin compared to the hemicellulose²⁹. The degradation of amorphous cellulose was due to their less ordered molecules and increase in relative crystallinity of cellulose, improving the dimensional stability and stiffness in the same degree^{4,6,16}. This could explain the change in modulus of elasticity, in which for lower temperatures the increase of crystallinity of cellulose and lignin content provided an increase in the modulus of elasticity. With the increase of temperature, the holocellulose degradation was due mainly to decrease of cellulose content and as consequence the modulus of elasticity at high temperature decreased.

The relative changes of the mechanical properties in compression and the holocellulose content in function of the temperature are shown in Figure 2. The room temperature was defined at 30 °C and the average of the results in percentage to the three blocks thermally treated at each temperature showed an increase until the temperature of 180 °C followed by reduction in elasticity modulus. Similar behavior was found for holocellulose content. In general, the results on the compression strength decreased.

However, the temperature that provided the best result for the strength and stiffness properties to thermally rectified *C. citriodora* was at 180 °C with 63 MPa and 25 GPa.

Statistical analyses were done between the blocks I, II and III to each temperature, and the results showed that blocks with statistically similar strength properties were found for the untreated wood and for the treatment at 200 °C. For the modulus of elasticity the statistically similar result was to the treatment at 200 °C. The statistical difference between the blocks in a same temperature can't be assigned only by heat. The changes of the density can be great in trees the same lot because it is related with juvenile and mature wood, difference between heartwood and sapwood and place of origin. Thus, this variability can cause changes in mechanical properties of wood as compression, bending, tension and shear³³.

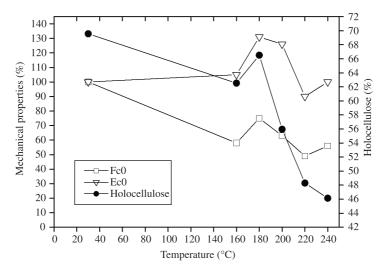


Figure 2. Mechanical properties and holocellulose content in function of temperature.

In relation to different temperature, there were changes along the temperature and there weren't statistically similar blocks for the untreated wood on strength properties. Thermally treated wood at the temperature at 160, 200 and 240 °C; 180 and 200 °C; and 160, 220 and 240 °C were statically similar. Untreated wood with treated wood at 160, 220 and 240 °C; and 160 and 200 °C and finally 180 and 200 °C presented statistically similar modulus of elasticity.

As a result, the thermal rectification process of wood caused alterations in the mechanical properties by changing chemical composition, with loss of the compression strength and gain of stiffness properties. For this reason, it was necessary to calculate the characteristic values of compression strength of the wood used in structural calculations.

The results obtained for characteristic values of compression strength of thermally treated wood were smaller than untreated wood. Regarding to strength properties, the best characteristic value was found the treatment at 180 °C with 43 MPa. The mean value of compression strength reported by NBR 7190/97 Brazilian Standard¹⁸ standard is 62 MPa. With this result it was possible to determine mean characteristic values of compression strength, in which the mean result obtained was 43 MPa. The characteristic value of compression strength in the thermal treatment at 180 °C in relation to mean characteristic value of compression strength reported by NBR 7190/97 Brazilian Standard¹⁸ was practically stable and in the other thermal treatments the maximum loss of strength was 23%. Thus, it is recommended the use of thermal treatment of wood eucalyptus C. citriodora at 180 °C.

A third order polynomial model can help to assess the behavior of the wood structural of element during a thermal treatment of wood process was used according to Equation 5.

$$f_{c0,k(T)} = -1.7593T^3 + 21.508T^2 - 83.161T + 137.33$$
 (5)

with a R^2 of 83.4%.

Where, T is the temperature value of thermal treatment of wood; $f_{c0,k(T)}$ is the characteristic value in the compression strength as a function of the temperature of thermal treatment of wood.

4. Conclusions

Thermo-rectification process for the C. citriodora in different temperatures had a significant influence on chemical composition and mechanical properties. The total extractives content suffers high reduction with increase of treatment temperature. The ashes content was practically the same and the lignin content increased with temperature. The mechanical properties were affected by the heat from the thermal treatment and with the increase of the temperature, the changes will be larger. The decrease of compression strength was due to the holocellulose content degradation, in which the first constituent affected was probably the hemicelulose. The elasticity modulus increased along the thermal treatment up to 180 °C most probably due the increase of the crystallinity of the cellulose and lignin content. At high temperatures holocellulose degradation was caused mainly by the decrease of the cellulose content and consequently the elasticity modulus decreased.

The characteristic values of compression strength also decreased for high temperatures and the results obtained for the treatment at 180 °C were in accordance with mean characteristic value of compression strength reported to ABNT NBR standard. As a result, the best temperatures for thermally treated wood of *C. citriodora* were at 180 and 200 °C to structural calculations, with characteristic values of compression strength of 43 and 38 MPa.

The mathematic model can be used to estimate the compression strength characteristic values as a function of wood thermal temperature considering specimens with standard dimensions according to NBR 7190/97 Brazilian Standard¹⁸.

Acknowledgements

The authors would like to acknowledge FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo) for the financial support given to this research. Also LaMEM (Laboratório de Madeiras e Estrutura de Madeiras), LQCE (Laboratório de Química, Energia e Celulose) and IQSC (Instituto de Química de São Carlos) for providing laboratory support.

References

- Awoyemi L and Jones IP. Anatomical explanations for the changes in properties of western red cedar (*Thuja plicata*) wood during heat. Wood Science and Technology. 2011; 45(2):261-267. http://dx.doi.org/10.1007/s00226-010-0315-9
- Borges LM and Quirino WF. higroscopicidade da Madeira de Pinus caribea var.hondurensis tratada térmicamente. Revista Biomassa & Energia. 2004; 1(2):173-182.
- Modes KS. Efeito da retificação térmica nas propriedades físico-mecânicas e biológica das madeiras de Pinus taeda e Eucalyptus grandis. [Dissertação]. Santa Maria: Universidade de Santa Maria; 2010. 100 p.
- Yildiz S, Gezer ED and Yildiz EC. Mechanical and chemical behavior of spruce wood modified by heat. *Building and Environment*. 2006; 41:1762-1766. http://dx.doi.org/10.1016/j. buildenv.2005.07.017
- Windeisen E, Strobel C and Wegener G. Chemical changes during the production of thermo-treated beech wood. Wood Science and Technology. 2007; 41:523-536. http://dx.doi. org/10.1007/s00226-007-0146-5
- Manríquez MJ and Moraes PD. Influence of the temperature on the compression strength parallel to grain of paricá. Construction and Building Materials. 2010; 24:99-104. http:// dx.doi.org/10.1016/j.conbuildmat.2009.08.003
- Poncsak S, Kocaefe D and Younsi R. Improvement of the heat treatment of Jack pine (Pinus banksiana) using ThermoWood technology. European Journal of Wood and Wood Products. 2011; 69:281-286. http://dx.doi.org/10.1007/ s00107-010-0426-x
- Poncsák S, Kocaefe D, Bouazara M and Pichette A. Effect of high temperature treatment on the mechanical properties of birch (*Betula papyrifera*). Wood Science and Technology. 2006; 40:647-663. http://dx.doi.org/10.1007/ s00226-006-0082-9
- Boonstra MJ and Tjeerdsma B. Chemical analysis of heat treated softwoods. *Holzforschung*. 2006; 64:204-211.
- Windeisen E and Wegener G. Behaviour of lignin during thermal treatmensts of wood. *Industrial Crops and Products*. 2008; 27:157-162. http://dx.doi.org/10.1016/j.indcrop.2007.07.015
- Poncsak S, Kocaefe S, Simard F and Pichette A. Evolution of extractive composition during thermal treatment of Jack Pine. *Journal of Wood Chemistry and Technology*. 2009; 29:251-264. http://dx.doi.org/10.1080/02773810902928582
- Hakkou M, Petrissans M, Zoulalian A and Gerardin P. Investigation of wood wettability changes during heat treatment on the basis of chemical analysis. *Polymer Degradation Stability*. 2005; 89:1-5. http://dx.doi.org/10.1016/j. polymdegradstab.2004.10.017
- 13. Moura LF and Brito JO. Efeito do termorretificação sobre as propriedades colorimétricas das madeiras de *Eucalyptus grandis e Pinus caribea var. hondurensis. Scientia Forestalis.* 2011; 39(89):69-76.
- Korkut S and Hiziroglu S. Effect of heat treatment on mechanical properties of Hazelnut wood (*Corylus colurna L.*). *Materials and Design.* 2009; 30:1853-1858. http://dx.doi. org/10.1016/j.matdes.2008.07.009
- Windeisen E, Helmut Bachle H, Zimmer B and Wegener G. Relations between chemical changes and mechanical properties of thermally treated wood. *Holzforschung*. 2009; 63:773-778.
- Kocaefe D, Poncsak S and Boluk Yaman. Effect of thermal treatment on the mechanical composition and mechanical properties of Birch and Aspen. *BioResources Technology*. 2008; 3(2):517-537.
- Majano AM, Hughes M and Cabo JLF. The fracture toughness and properties of thermally modified beech and ash at different moisture contents. Wood Science and Technology. 2012; 46:5-21. http://dx.doi.org/10.1007/s00226-010-0389-4

- Associação Brasileira de Normas Técnicas. NBR 7190: projeto de estruturas de madeira. Rio de Janeiro: ABNT; 1997.
- Calil CJ, Rocco FA and Dias AA. Dimensionamento de elementos estruturais de madeira. São Carlos: ed Manole; 2003. p. 152.
- Tappi Standard Methods. T 264 cm-97: Preparation of wood for chemical analysis. Atlanta: Tappi Press; 1999.
- Tappi Standard Methods. Solvents extractives of wood and pulp: T 204 cm-97. Atlanta: Tappi Press; 1997.
- Tappi Standard Methods. Water solubility of wood and pulp: T 207 cm-99. Atlanta: Tappi Press; 1999.
- Tappi Standard Methods. Acid-insoluble lignin in wood and pulp: T 222 om-98. Atlanta: Tappi Press; 1999.
- Tappi Standard Methods. T 250: Acid-soluble lignin in wood and pulp. Atlanta: Tappi Press; 1985.
- Tappi Standard Methods. T 211: Om-93. Ash in wood. Atlanta: Tappi Press; 1985.
- 26. Santos ID. Influência dos teores de lignina, holocelulose e extrativos na densidade básica e contração da madeira e nos rendimentos e densidade do carvão vegetal de cinco espécies lenhosas do cerrado. [Dissertação]. Brasília: Universidade de Brasília; 2008. 57 p.
- Silva MR, Machado GO, Deiner J and Calil C. Permeability measuremens of brazilian eucalyptus. *Material Research*. 2010; 13(3):281-286.
- Esteves B, Videira R and Pereira H. Chemistry and ecotoxicity of heat-treated pine wood extractives. Wood Science and Technology. 2011; 45:661-676. http://dx.doi.org/10.1007/ s00226-010-0356-0
- Esteves B, Graça J and Pereira H. Extractive composition and summative chemical analysis of thermally treated eucalypt wood. *Holzforschung*. 2008; 62:344-351. http://dx.doi. org/10.1515/HF.2008.057
- Brito JO, Silva FG, Leão MM and Almeida G. Chemical composition changes in eucalyptus and pinus woods submitted to heat treatment. *Bioresource Technology*. 2008; 99:8545-8548. PMid:18586488. http://dx.doi.org/10.1016/j. biortech.2008.03.069
- Repellin V and Guyonnet R. Evaluation of heat-treated wood swelling by differential scanning calorimetry in relation to chemical composition. *Holzforschung*. 2005; 59:28-34. http:// dx.doi.org/10.1515/HF.2005.005
- Brosse N, Hage RE, Chaouch M, Pétrissans M, Dumarçay S and Gérardin P. Investigation of the chemical modifications of beech Wood lignin during heat treatment. *Polymer Degradation* and Stability. 2010; 95:1721-1726. http://dx.doi.org/10.1016/j. polymdegradstab.2010.05.018
- 33. Benjamim CA. Comparação entre três critérios de amostragem para a avaliação da densidade básica da madeira de florestas implantadas de eucaliptos. [Dissertação]. Botucatu: Faculdade de Ciências Agronômicas, Universidade Estadual Paulista; 2002.
- 34. Rousset P. Choix et validation experimentale d'un modele de pyrolyse pour le bois traite par haute temperature: de la micro-particule au bois massif. [Tese]. École Nationale du Génie Rural des Eaux et des Forêts; 2004. 203 p.
- Silva MR. Determinação da permeabilidade em madeiras brasileiras de florestas plantadas. [Dissertação]. São Carlos: Universidade de São Paulo; 2007. 135 p.
- Shi JL, Kocaefe D and Zhang J. Mechanical behaviour of Québec wood species heat-treated using Thermo Wood process. *Holz Roh-Werkstoff*. 2007; 65:255-259. http://dx.doi. org/10.1007/s00107-007-0173-9
- Santos J. Mechanical behaviour of eucalyptus wood modified by heat. Wood Science and Technology. 2000; 34:39-43. http:// dx.doi.org/10.1007/s002260050006