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RESEARCH ARTICLE

Thermal Degradation and Charring Rate of *Corymbia Citriodora* and *Eucalyptus Grandis* Wood Species

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Abstract: This research reports an investigation of the potential of *Eucalyptus grandis* and *Corymbia citriodora* for structural applications in civil construction with an emphasis on the wood-charring process in fire condition. Published data on wood carbonization to determine the charring rate for structural propose are sparse in Brazil as there have been only a few studies in this direction. The rate at which the wood converts in char is determinant to evaluate the fire endurance, because the failure of wooden structural elements and its composites exposed to fire occurs through reduction of cross section. The fire resistance depends on cross sections dimensions that are gradually reduced when exposed to fire. Several tests were performed to evaluate the variables that mostly affect the charring rate. The chemical composition, shrinkage, thermal gravimetric analysis (TGA) and measurements of calorific value were also performed. The TGA results indicated that both species were stable up to 250ºC. The average calorific value of *Corymbia citriodora* was slightly less than that of *Eucalyptus grandis*, whose value was 17849J/g. The chemical analysis revealed that *Corymbia citriodora* had approximately three times more ash and about 4% more content of extractives than *Eucalyptus grandis*. The latter had almost 6% more lignin and 2% more cellulose than *Corymbia citriodora*, but 8% less hemicelluloses. The charring tests showed that both woods had similar charring rates. In addition, statistical analyses showed that shrinkage and lignin content are the main factors affecting the charring process.

Keywords: Charring rate, Chemical characterization, Corymbia citriodora, Eucalyptus grandis, Thermal degradation, Wood.

INTRODUCTION

Wood constitutes the largest carbon reserve in nature. It is a renewable material whose replenishment can be planned by means of reforestation. Wood utilization consumes less energy than other materials used in civil construction, such as steel, cement and aluminum. Thus, the use of wood for construction is an environmental responsibility and a viable option [1, 2].

Eucalyptus species have a variety of properties that make them ideal sources of wood for construction: fast growth and maturation, adaptability to diverse ecosystems, inherent genetic variability and potential to be crossed with other species. In Brazil, most *Eucalyptus* plantations are located in the South and Southeastern regions, near to the cellulose and paper mills, as well as the steel foundries. *Corymbia citriodora* and *Eucalyptus grandis* show the greatest potential to be used as structural timber, due to their acceptable physical and mechanical properties [3, 4].

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On account of its potential adoption as a renewable raw material in structures, it is important to acquire a wide range of data on the chemical and physical properties of charred *Eucalyptus* wood [5]. Wood is a material constituted by low-molecular-weight organic compounds called extractives and macromolecules such as cellulose, hemicelluloses and lignin. These substances are all combustible and suffer thermal decomposition or carbonization on exposure to fire [6 - 8].

In the fire process, because of the dimension of structural elements and the consumption of oxygen by combustion reaction, the carbonization occurs on surface to inner part of the timber. Wood carbonization consists in a pyrolysis process, in the temperature at about 450ºC. A low supply of oxygen forces the wood to decompose into a variety of substances, forming charcoal, which is a black porous solid consisting mainly of elemental carbon. Whereas wood is a combustible material, the time taken for the wood to be turned into char is a measure of its fire resistance [9, 10].

When the behavior of wood is compared with that of other materials in structures exposed to severe fire conditions, it is found that structural wood performs well at high temperatures, despite its inflammability. During the charring process the wood forms a layer of carbon on its surface that acts as a thermal insulation barrier. Since wood is a bad conductor of heat, the internal temperature increases slowly, so that the inner layers of wood are relatively protected from fire. For this reason, wood pieces remain in service under conditions where steel fails, even though the latter is not at all inflammable. It is important to emphasize that wood does not distort when submitted to high temperatures as steel does, so the wood in a structure is preserved against collapse [1, 11].

Owing to this particular property of carbonization, wood is a proper choice to employ safely in structural elements. Some examples illustrate this, such as escape ladders and emergency doors that have wood in their composition. More detailed knowledge of the burning process of *Corymbia citriodora* and *Eucalyptus grandis* species can lead to their safe and rational use.

MATERIAL AND METHODS

Two species were selected for the present investigation: *Eucalyptus grandis* and *Corymbia citriodora*. Four different 27-year-old trees of each species were tested. To have representative samples, the wood was collected by cutting disks which were subsequently cut to obtain the specimens. The charring rate, chemical composition, calorific value, density, moisture content were evaluated, besides a thermogravimetric analysis being conducted.

Thermogravimetric Analysis (TGA) was performed in a NETZSCH TG 209 thermobalance in a dynamic nitrogen atmosphere at a flow rate of 20 mL min-1 and a heating rate of 10(C min-1 from room temperature to about 700°C.

For the chemical analysis, the pieces of wood were reduced to small particles enough to pass through a 42 mesh screen (0.355 mm pore size). The moisture content of all samples was determined before each assay. The samples were treated in a soxhlet extractor containing water and organic solvents (cyclohexane and ethanol, P.A. grade). Firstly, the sample was extracted with ethanol for 4 hours. Then, a 1:1 cyclohexane/ethanol extraction was performed over 8 hours. Finally, the samples were subjected to a 3-hour extraction in distilled water and the fibers dried at 60°C. The extractive content was determined by mass difference, before and after the extraction. The following analyses were performed on extractive-free samples. The ash content was measured as described in TAPPI T211 om-93 [12]. The lignin content was determined as the sum of the insoluble and soluble lignin, using standard methods given in TAPPI T250 [13]. High performance liquid chromatography (HPLC) was used to analyze the cellulose and hemicellulose contents, as specified in TAPPI T 249 cm-85 [14]. All tests were carried out in triplicate.

IKA C5000 Duo Control calorimeter was used to evaluate the calorific value of the sample in a decomposition vessel containing pure oxygen at a pressure of 30 bars. The moisture content was determined for each sample and was maintained at 12% in plastic bags. The equipment was calibrated at 24.15ºC. There were three replicates per treatment.

The shrinkage tests were measured in the axial, radial and tangential directions with respect to the wood fiber, following the Brazilian standard ABNT NBR 7190 [15]. The measurements were made on 12 blocks of wood (2.0x3.0x5.0cm) per species.

One-dimensional charring measurements were carried out on wood test-pieces (6.2×17.2×17.5cm) in a vertical furnace, in conformity with ASTM E119-95a [16]. There were 12 samples per test. Six thermocouples were inserted at three depths (5mm; 10mm; 15mm) for each piece of wood and 290°C was adopted as the basic temperature of the char layer.

RESULTS AND DISCUSSION

Fig. (**1**) and Table **1** present data on TG analysis. There is a pattern common to all the figures. Considering initially only the range from room temperature to 120°C, all the analyzed samples have an initial mass loss of about 10% due to the loss of residual moisture. It can also be seen in Fig. (**1**) that at higher temperatures, from 220°C to 320°C, the process of hemicelluloses-thermal degradation starts with a mass loss of 25%. Subsequently, cellulose and lignin decomposition occurs in the range from 325°C to 380°C (cellulose) and from 250°C to 500°C (lignin). Over this entire interval there is a great mass loss of about 70%. From a molecular point of view, random rupture of the chains occurs, resulting in the release of low-molecular-weight components and, consequently, a large mass loss is observed in the TG analysis.

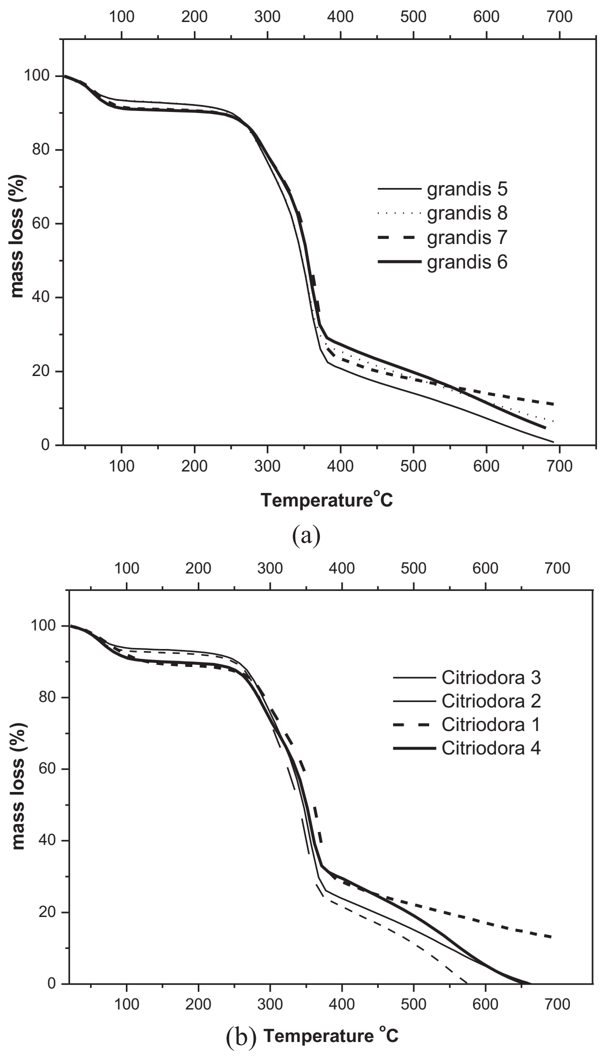

Fig. (1). Thermogravimetric curves for *Eucalyptus grandis* (**a**) and *Corymbia citriodora* (**b**) wood species.

Above 500°C, complete thermal decomposition takes place, leaving a residue of about 18% for *Eucalyptus grandis* and 22% for *Corymbia citriodora*. This residue consists mainly of inorganic salts (from the sap) and probably organic substances not totally decomposed, forming charcoal.

It was observed that *Eucalyptus grandis* has a higher thermal stability than *Corymbia citriodora*, although *Corymbia citriodora* shows a richer content of residues which contributes to forming charcoal.

The calorific value of a piece of wood is a measure of the amount of heat released per gram by total combustion. The standard deviation follows each result (three samples being used), see Table **1**.

Table 1. Results of the measurement of calorific value of *E. citriodora* and *E. grandis* woods.

Properties	*Corymbia citriodora*
Initial mass (g)	0.54 ± 0.04
Calorific value (J/g)	17358.67 ± 614.59
Properties	***Eucalyptus grandis***
Initial mass (g)	0.51 ± 0.01
Calorific value (J/g)	17848.67 ± 47.92

The mean value is 17848 J/g for *Eucalyptus grandis* and 17359 J/g for *Corymbia citriodora*. The Analyses of Variance (ANOVA), with 5% of significance, revealed the calorific values for *Corymbia citriodora* and *Eucalyptus grandis* do not differ significantly, showing P-value superior to 0.05. As for the calorific value, to other properties investigated, the normality data and equivalence between variances were verified, using the Anderson-Darling and Levine's tests respectively, both at the 5% of significance level, with consideration of normality data and equivalence between variances as the null hypothesis for the tests.

An important factor that influences wood charring is its chemical composition. The extractives of wood and water are the less stable wood components and begin to decompose at low temperature and the major components, cellulose, hemicelluloses and lignin, decompose at higher temperatures. The cellulose fraction contributes most to flaming combustion, while the lignin fraction supports most of the subsequent glowing combustion.

The woods were subjected to a detailed characterization of their main macromolecular components. The results of the wood chemical analysis are shown in Table **2**. According to Barrichelo e Brito [3], *Eucalyptus grandis* has an ash content from 0.1% to 0.2% approximately, extractives content from 4% to 8 %, lignin content from 26% to 30%, cellulose about 54% and hemicellulose about 20%.

Table **2** shows *Corymbia citriodora* achieved an average ash content about three times that of *Eucalyptus grandis*. The ash content in wood is normally low; rarely it is lower than 0.2% or greater than 1% in dry wood. Specifically for *Eucalyptus* wood, the ash content rarely reaches 1% of its dry mass.

Table 2. Chemical composition (%) of wood from *Corymbia citriodora* and *Eucalyptus grandis*.

Species	Specimens	Ashes	Extractives
Corymbia citriodora	1	0.45 ± 0	11.83 ± 1.35
	2	0.52 ± 0	14.39 ± 1.45
	3	0.33 ± 0	15.58 ± 0.37
	4	0.26 ± 0	18.34 ± 0.65
Eucalyptus grandis	5	0.11 ± 0	9.45 ± 0.49
	6	0.10 ± 0	12.74 ± 0.73
	7	0.17 ± 0	10.12 ± 0.59
	8	0.17 ± 0	11.01 ± 1.42
Species	**Specimens**	**Lignin**	**Cellulose**
Corymbia citriodora	1	26.00 ± 0.27	47.61 ± 0.81
	2	25.67 ± 0.11	46.71 ± 0.26
	3	24.77 ± 0.04	46.10 ± 0.48
	4	24.65 ± 0.20	48.25 ± 2.02
Eucalyptus grandis	5	28.93 ± 0.18	52.67 ± 0.53
	6	31.26 ± 0.09	50.18 ± 0.36
	7	31.08 ± 0.36	50.89 ± 0.26
	8	32.53 ± 0.57	46.77 ± 0.55
Species	**Specimens**	**Hemicelluloses**	
Corymbia citriodora	1	20.27 ± 0.10	
	2	19.64 ± 0.33	
	3	20.86 ± 0.61	
	4	22.01 ± 0.61	

(Table 2) contd.....

Species	Specimens	Ashes	Extractives
Eucalyptus grandis	5	12.22 ± 0.31	
	6	13.25 ± 0.05	
	7	12.15 ± 0.19	
	8	13.08 ± 0.04	

Table **2** also shows that the extractive content is rather variable among the samples of each wood species, being somewhat higher in *Corymbia citriodora* than in *Eucalyptus grandis*. Extractives may reach 20% of the wood grown in tropical conditions, whereas they constitute up to 8% of the wood dry mass in temperate climate species.

Regarding lignin content, *Eucalyptus grandis* shows values slightly higher than *Corymbia citriodora*, considered significant by the ANOVA. The first also has higher cellulose content than *Corymbia citriodora*, with a difference of around 4%. The opposite is found in relation to the hemicellulose content, which differs by around 10%.

During carbonization of wood, shrinkage and deformation occur due to the loss of water impregnating the cell walls, resulting in fissures. Shrinkage of wood occurs commonly due to the loss of moisture, however, few information has been reported about the shrinkage during carbonization. During the combustion, steam is formed and migrates from the inside to the outside of the specimen. The movement and loss of this water vapor promote external fissures in the wood samples during shrinkage.

Table **3** shows that the shrinkage differs in the axial, tangential and radial directions of the wood. The densities of species are quite similar and do not seem to have a great influence on the shrinkage results by the analyses of variance.

Table 3. Shrinkage results for *Corymbia citriodora* and *Eucalyptus grandis*.

Species	Sp.	Axial (%)	Radial (%)
Corymbia citriodora	1	0.14 ± 0.07	6.08 ± 0.29
	2	0.90 ± 0.27	8.29 ± 0.62
	3	0.29 ± 0.15	8.20 ± 0.48
	4	0.27 ± 0.02	7.33 ± 0.48
Eucalyptus grandis	1	0.02 ± 0.05	7.90 ± 0.68
	2	0.10 ± 0.11	8.89 ± 0.23
	3	0.55 ± 0.35	6.70 ± 0.13
	4	0.24 ± 0.05	5.93 ± 0.13
Species	**Sp.**	**Tangential (%)**	**Volumetric (%)**
Corymbia citriodora	1	7.97 ± 0.15	15.87 ± 0.40
	2	8.78 ± 0.18	20.01 ± 0.18
	3	8.49 ± 0.59	19.73 ± 0.16
	4	9.25 ± 0.13	19.22 ± 0.79
Eucalyptus grandis	1	6.97 ± 0.35	17.30 ± 1.78
	2	7.88 ± 0.06	19.40 ± 0.02
	3	6.37 ± 0.85	15.10 ± 0.69
	4	9.28 ± 0.39	17.47 ± 0.66
Species	**Sp.**	**Density (g/cm^3)**	
Corymbia citriodora	1	1.09 ± 0.04	
	2	1.06 ± 0.5	
	3	1.08 ± 0.03	
	4	1.04 ± 0.02	
Eucalyptus grandis	1	0.93 ± 0.01	
	2	0.95 ± 0.02	
	3	0.62 ± 0.04	
	4	0.93 ± 0.01	

The radial and tangential shrinkage are about 8%, while the axial shrinkage is very little. The results of the ANOVA show that the shrinkage in *Corymbia citriodora* is slightly higher than that in *Eucalyptus grandis*. Thus, *Corymbia citriodora* has a lower dimensional stability than *Eucalyptus grandis*.

The charring rate of wood (Table **4**) generally refers to the one-dimensional rate (*e.g.* in millimeters per minute) at which wood changes to char. It is important to emphasize that the pieces suffered shrinkage and cracks during the heating process. This effect contributed to their thermal degradation, since cracking promotes the escape of gases and supply of oxygen for combustion.

Table 4. Charring rates for *Corymbia citriodora* and *Eucalyptus grandis*.

Corymbia citriodora	*M* ($\bar{y}$)
1	0.28 ± 0.01
2	0.25 ± 0.006
3	0.25 ± 0.006
4	0.28 ± 0.017
Eucalyptus grandis	*m* ($\bar{y}$)
5	0.26 ± 0.02
6	0.26 ± 0.01
7	0.268 ± 0.015
8	0.26 ± 0.01

Several characteristics of wood affect the charring rate, such as, permeability, anatomy, density, moisture content, and chemical composition. Density is recognized as the main factor determining the charring rate; generally, denser woods have a slower charring rate. The density of the two wood species is considered equivalent by the ANOVA.

An empirical linear model was used, including the properties of the wood such as chemical composition, calorific value, density, moisture content, and thermogravimetric analysis, but only radial shrinkage and lignin content were significant variables. Thus, regression analysis was used to develop the model, where the charring rate (m) is mainly a function of radial shrinkage and lignin content (Equation 1). The variables were transformed so as to obtain the model best fitted to the results and the coefficient of determination (R2) was 0.996. The value of the coefficient of determination always lies in the range zero to one. Usually, the higher the value of R2, the better the model.

$$m = 2.52978 \cdot RS + 0.93720 \cdot L \quad \textbf{(1)}$$

RS is the radial shrinkage and L is lignin content. This model indicates that the lignin is the component whose thermal degradation is a controlling factor in the wood-charring process. Table **5** shows the results from ANOVA for the linear regression (Equation 1). F-value obtained involves accepting the validity of fitted model obtained.

Table 5. Analysis of variance.

Source	DF	SQ	MS	F-value
Model	7	76934	10991	652.15
Error	17	286.49481	16.85264	
Total	24	77220		

CONCLUSION

An important factor that significantly affects wood charring is the thermal stability. The TGA results indicate that both species are stable in the range up to 250°C. At higher temperatures, from 250°C to 400°C, thermal degradation of the macromolecules starts, with great loss of mass - about 70%. The wood species has a high calorific value, 17846J/g for *Eucalyptus grandis* and 17359 J/g for *Corymbia citriodora*.

The chemical composition significantly affects wood charring. Chemical analysis reveals that *Corymbia citriodora* has about three times more ash content and about 4% more extractives than *Eucalyptus grandis*. The latter has almost 6% more lignin and 2% more cellulose than *Corymbia citriodora*, but 8% less hemicelluloses.

The radial and tangential shrinkage are about 8%, while the axial shrinkage is very little. The results show that the shrinkage in *Corymbia citriodora* is slightly higher than that in *Eucalyptus grandis*. Thus, *Corymbia citriodora* has a lower dimensional stability than *Eucalyptus grandis*.

The statistical results show that radial shrinkage and lignin content influence the charring velocity of the two species. The lignin content is an important factor that gives to the *Eucalyptus grandis* a higher thermal stability and contributes to the charcoal formation. The charred surface is important as it isolates the wood from high external temperatures. *Eucalyptus grandis* wood has better dimensional stability and the results indicate higher shrinkage and more cracks in *Corymbia citriodora* wood. External fissures were noted in the latter by the movement of water and steam.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

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