Scientific Article

WOOD AND CHARCOAL QUALITY IN THE SELECTION OF *Eucalyptus* SPP. CLONES AND *Corymbia torelliana* X *Corymbia citriodora* FOR STEEL INDUSTRY

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ABSTRACT – Wood from planted forests is the main input in the charcoal production chain. However, the heterogeneity of charcoal, in terms of its physical, chemical and mechanical properties, and the low yield in production processes is among the main problems faced by industries. To select the best clones for the production of charcoal for steelmaking, the objective of this work was to evaluate the properties of wood, in addition to the yield and quality of charcoal from different genotypes of *Eucalyptus* and *Corymbia*. Five clones of *Eucalyptus* spp., 8 years old and one of *Corymbia torelliana* x *Corymbia citriodora*, 4 years old were studied. In the wood were determined the basic density, structural chemical composition, thermogravimetric analysis (TG/DTG), crystallinity index and higher heating value. Carbonizations were carried out in a muffle oven, with a total time of 270 minutes, starting at 150°C and ending at 450°C. The gravimetric yield, apparent density, higher heating value and proximate analysis of charcoal were determined. The wood basic density varied between 477 and 652 kg/m^3, with the highest value observed for the *Eucalyptus cloeziana* clone. This clone also had the highest total lignin content (32.6%), the highest charcoal yield (36.3%) and charcoal with the highest apparent density (466 kg/m^3). The two clones of *Eucalyptus urophylla* had the highest heating value for charcoal, whose mean was 7545 kcal/kg. The clone of *Corymbia torelliana* x *Corymbia citriodora*, having an apparent density greater than 500 kg/m^3 at 4 years of age, stood out in terms of productivity. All evaluated clones have potential for charcoal production, however, the *Eucalyptus cloezian*a clone stood out positively, being the most suitable for charcoal production.

Keywords: Lignin; Density; Higher heating value.

QUALIDADE DA MADEIRA E DO CARVÃO VEGETAL NA SELEÇÃO DE CLONES DE Eucalyptus *SPP. E* Corymbia torelliana *X* Corymbia citriodora *PARA SIDERURGIA*

RESUMO – A madeira oriunda de florestas plantadas é o insumo principal na cadeia produtiva do carvão vegetal. No entanto, a heterogeneidade do carvão vegetal, em termos de suas propriedades físicas, químicas e mecânicas e o baixo rendimento nos processos de produção, está entre os principais problemas enfrentados pelas indústrias. Visando selecionar os melhores clones para a produção de carvão vegetal para uso siderúrgico, o objetivo desse trabalho foi avaliar as propriedades da madeira, além do rendimento e qualidade do carvão vegetal provenientes de diferentes genótipos de ***Eucalyptus*** *e* ***Corymbia****. Foram estudados cinco clones de Eucalyptus spp., com idade de 8 anos e um de* ***Corymbia torelliana*** *x* ***Corymbia citriodora****, com idade de 4 anos. Na madeira, determinou-se a densidade básica, composição química estrutural, análise termogravimética (TG/DTG), índice de cristalinidade e poder calorífico superior. Foram realizadas carbonizações em forno mufla,* *com tempo total de 270 minutos, iniciando em 150°C e finalizando em 450°C. Determinou-se o rendimento gravimétrico, a densidade aparente, o poder calorífico superior e a composição química imediata do carvão vegetal. A densidade básica da madeira variou entre 477 e 652 kg/m³, sendo que o maior valor foi observado para o clone de* ***Eucalyptus cloeziana****. Este clone também apresentou o maior teor de lignina total (32,6%), maior rendimento em carvão vegetal (36,3%) e carvão vegetal com maior densidade aparente (466 kg/m³). Os dois clones de* ***Eucalyptus urophylla*** *apresentaram maior poder calorífico superior para o carvão vegetal, cuja média foi 7545 kcal/kg. O clone de* ***Corymbia torelliana*** *x* ***Corymbia citriodora****, por ter densidade aparente superior a 500 kg/m³, aos 4 anos de idade, foi o destaque em termos de produtividade. Todos os clones avaliados possuem potencial para a produção de carvão vegetal, porém o clone* ***Eucalyptus cloeziana*** *se destacou positivamente, sendo o mais indicado para a produção de carvão vegetal.*

Palavras-Chave: Lignina; Densidade; Poder calorífico superior.

1. INTRODUCTION

Of the total energy consumed, considering primary uses, the use of non-renewable fuels represents 85%. The world demand for energy is constantly expanding and could increase 46% by 2050 (EIA, 2021). In countries with newly industrialized economies and in transition such as the BRICs (Brazil, Russia, India and China), the opening of trade leads to an increase in demand for energy. However, biomass energy is the best choice for these countries, as this energy source is more available in these areas, in addition to mitigating environmental pollution (Danish and Wang, 2019).

Energy from trees planted in Brazil reached 90.91 million GJ in 2021, which corresponds to an increase of 27.5% compared to 2017 (IBÁ, 2022). In addition, carbon sequestration during tree growth favors the reduction of CO2 emissions into the atmosphere, thus mitigating global greenhouse gas emissions (Zhang et al., 2012; Shahbaz et al., 2017). In this context, forest biomass stands out as a primary source of renewable energy, in the form of wood, charcoal, waste from the forest-based industry, among other materials of plant origin (Brand, 2010).

Among the various species for planting, aiming at wood production, those of the genus *Eucalyptus* and *Corymbia* stand out due to their fast growth, resistance to adverse conditions and the possibility of denser plantings (Lopes et al., 2017). Of the areas destined to cultivate forests for commercial purposes in Brazil, *Eucalyptus* plantations correspond to 76% of the total coverage, equivalent to 7.53 million hectares (IBA, 2022). In 2018, 12% of the total area of planted trees was destined to the production of charcoal for the steel industry (IBÁ, 2019).

Brazil is the largest producer of charcoal for industrial purposes, accounting for 12% of world production (IBÁ, 2022). The total amount of pig iron produced in Brazil in 2021 was 33.8 million tons, with 77% having coal as raw material and 23% charcoal. Wood from planted forests is the main input in the charcoal production chain. The main producing state was Minas Gerais, responsible for 40% of the total production (SINDIFER, 2022).

The heterogeneity of charcoal, in terms of its physical, chemical and mechanical properties and the low yield in production processes, is among the main problems faced by industries (Vieira et al., 2013; Pereira et al., 2021). In addition to clonal variability, the interaction between clones and planting site can influence the properties of wood and charcoal (Neves et al., 2011). In this context, increasing the charcoal yield and its quality is essential to increase the competitiveness of this input in the steel industry. In general, there are many *Eucalyptus* and, more recently, *Corymbia* genotypes that have been developed or are in the development phase for charcoal production. However, only growth variables, commonly used as genotype selection criteria, are not enough to produce charcoal with satisfactory yield and quality. Therefore, physical and chemical properties of wood and charcoal, in addition to the gravimetric yield estimated in laboratory furnaces, need to be considered in the selection criteria, in order to obtain answers regarding the yields and quality expected by the steel sector.

Therefore, the objective of this work was to determine the quality indices of wood (basic density, crystallinity index, structural chemical composition, higher heating value) and charcoal (gravimetric yield, apparent density, proximate analysis, higher heating value) of *Eucalyptus* and *Corymbia* clones and their correlations and indicate the best clones to serve the charcoal industry.

2. MATERIALS AND METHODS

2.1. Materials

Woods of six genotypes were evaluated (Table 1), originating from a clonal test, located in the municipality of Paraopeba, Minas Gerais, cultivated in spacing of 3x2 meters. Five trees were selected for each of the six clones, totaling 30 trees (experimental units).

From each tree, six discs of 5 cm thickness were removed, corresponding to breast height and 0, 25, 50, 75 and 100% of the commercial height of the tree, with a diameter of 6 cm. From the disks, two opposing wedges were obtained, passing through the pith, used to determine the basic density of the wood. The remainder of each disc was sectioned and a composite sample was formed, being destined for carbonization and chemical and thermogravimetric analyses.

2.2. Wood properties

The basic density of the wood was determined by the method of immersion in water, in accordance with the ABNT NBR 11941 (ABNT, 2003) standard. The mean basic density values of each tree were calculated by weighting the densities of the wedges taken along the trunk, using the volume of the logs between two consecutive disks as a weighting factor, as described by Vital (1984).

For the chemical characterization, higher heating value and thermogravimetric analysis, the wood samples were transformed into sawdust, using a Wiley-type mill, in accordance with the TAPPI 257 standard (TAPPI, 2021). The fraction classified between 40 and 60 mesh was used.

Table 1 – Clones evaluated and their respective cut ages.
***Tabela 1** – Clones avaliados e suas respectivas idades de corte.*

Clone	Genetic material	Age (years)
1	*Eucalyptus spp.*	8
2	*Eucalyptus spp.*	8
3	*Eucalyptus urophylla*	8
4	*Eucalyptus urophylla*	8
5	*Eucalyptus cloeziana*	8
6	*Corymbia torelliana x Corymbia citriodora*	4

The higher heating value of wood was determined according to the methodology described by DIN EN 14918 (DIN, 2010) standard, using an adiabatic bomb calorimeter model IKA200, in dynamic mode.

The determination of moisture content in oven-dry wood was carried out according to the TAPPI 264 standard (TAPPI, 2022). The levels of wood extractives were determined in duplicates, according to TAPPI standard 204 cm-17 (TAPPI, 2017), using the total extractives determination method, substituting ethanol/benzene for ethanol/toluene. The insoluble lignin contents were determined in duplicate by the Klason method, modified according to the procedure proposed by Gomide and Demuner (1986). The soluble lignin was determined by spectrometry, according to Goldschimid (1971), from the dilution of the filtrate resulting from the procedure for obtaining the insoluble lignin. The total lignin content was obtained by adding the soluble and insoluble lignin values. The percentage of holocellulose was calculated by difference, subtracting the sum of total lignin, extractives and ash from 100. The percentage of ash in the wood was determined according to the ASTM D1102-84 (ASTM, 2021) standard, using a porcelain crucible.

To determine the crystallinity index, composite samples classified between sieves of 200 and 270 mesh were used. About 0.1g of sample was fixed on a quartz slide, using enough PVA glue to form a thin compact layer on the slide. The technique used to calculate the crystallinity index was X-ray diffraction. This technique uses the scattering of X radiation by organized structures (crystals), which allows morphological studies to be carried out on materials, determining their structure and crystalline fraction (Baumhardt Neto, 2003). X-ray diffraction analyzes were carried out at room temperature in a D8-Discover diffraction system (Bruker) equipped with a Cu tube (L=1.5418 angstroms, 40kV and 40 mA) and a Goebel mirror. A θ - 2θ scan from 10 to 40 degrees was used, with a step of 0.05 degrees per second. Using the OriginLab 2019 software, the cellulose crystallinity index was calculated using the method by Segal et al. (1959).

Thermogravimetric analysis (TG) was performed to evaluate the mass loss as a function of temperature and the curve of the first derivative of mass loss

(DTG). For the analysis, the DTG-60H device, Shimadzu, was used. The analyzes were carried out under a nitrogen gas atmosphere, at a constant flow of 50 $ml.min^{-1}$, using approximately 2 mg of sawdust selected in overlapping sieves of 200 and 270 mesh, the fraction used was that retained in the latter, in open alumina capsule. The thermogravimetric curves were obtained from 50°C up to a maximum temperature of 600°C, with a heating rate of $10°C.min^{-1}$. From the TG curves, mass loss calculations were made in the following temperature ranges: room temperature up to 100°C, 100-200°C, 200-250°C, 250-300°C, 300-350°C, 350-400°C and 400-450°C. The residual mass at a temperature of 450°C was also calculated, taking into account the dry mass, at a temperature of 100 °C.

2.3. Properties of charcoal

For wood carbonization, approximately 400 g of wood, composed of all heights, with dimensions of 1x1x5 cm, oven-dry, were inserted into a cylindrical metallic reactor. The reactor was placed inside a muffle oven, model GP2000G. The process was conducted with respective initial and final temperatures of 150 and 450°C, with an increase of 50°C every 30 minutes, remaining for 60 minutes at temperatures of 400 and 450°C, in a total time of 4.5h. After each carbonization, the gravimetric yields of charcoal were determined, according to (Equation 1).

$$Gravimetric\ yield = \frac{charcoal\ mass}{wood\ dry\ mass} \quad \text{Eq.1}$$

The apparent relative density of the charcoal was determined by the hydrostatic method, through immersion in mercury, as described by Vital (1984). Six sample density determinations were carried out by carbonization and the apparent density was obtained by the arithmetic mean. The higher heating value of charcoal was determined according to the methodology described by DIN EN 14918 (DIN, 2010) standard, using an adiabatic bomb calorimeter model IKA200, in dynamic mode.

The proximate analysis of charcoal, which corresponds to the contents of volatile matter, ash and fixed carbon, was determined according to ASTM D1762 − 84 (ASTM, 2021) standard, replacing the platinum crucible with a porcelain crucible and the temperature for determination of ash content from 750°C to 600°C.

2.4. Statistical analysis

The experiment consisted of 6 treatments (clones) and 5 repetitions (trees). Data were submitted to the Lilliefors test, to test normality, and the Cochran test, to test the homogeneity of variances. Then the data were submitted to analysis of variance (ANOVA), and when differences were established between them, the Tukey test was applied at a 95% significance level. To determine the existing correlations between the properties of wood and charcoal, Pearson's correlation coefficient at 5% significance was used. Statistical analyzes were performed using the sofware Statsoft Statistica 7.0 (Statsoft, 2004).

3. RESULTS

In (Table 2) are presented the mean values of basic density, structural chemical composition, crystallinity index and higher heating value of the different clones.

The highest basic density value, with a significant difference, was observed for the clone *Eucalyptus*

Table 2 – Physical, chemical and energetic properties of wood from the evaluated clones.
Tabela 2 – *Propriedades físicas, químicas e energéticas da madeira dos clones avaliados.*

Clone	Basic density (kg/m^3)	Total extractives (%)	Total lignin (%)	Holocellulose (%)	Ash (%)	Crystallinity index (%)	*Higher heating value (cal/g)
E. spp. 1	574 (9) b	5.3 (0.4) d	26.6 (1.6) b	67.9 (1.5) a	0.13 (0.04) b	72.66 (2.26) a	4674 (41)
E. spp. 2	582 (18) b	6.1 (0.3) cd	27.7 (0.8) b	66.2 (0.9) ab	0.12 (0.03) b	73.28 (1.65) a	4694 (36)
E. urophylla 1	477 (14) d	7.0 (0.6) bc	27.5 (1.3) b	65.2 (1.8) ab	0.22 (0.06) b	74.28 (1.72) a	4703 (28)
E. urophylla 2	520 (10) c	8.1 (1.1) ab	27.8 (2.0) b	63.9 (1.5) b	0.18 (0.08) b	72.74 (0.45) a	4678 (25)
E. cloeziana	652 (30) a	9.4 (1.1) a	32.6 (1.3) a	57.8 (1.6) c	0.14 (0.03) b	74.42 (1.15) a	4689 (114)
C. torelliana x *C. citriodora*	575 (20) b	6.6 (1.1) bcd	27.9 (0.2) b	64.6 (1.0) ab	0.91 (0.15) a	69.04 (2.74) b	4643 (12)

*No significant differences were observed in the Analysis of Variance for this property. Means (standard deviation) followed by the same letter do not differ from each other in the column by the Tukey Test at 5% probability.
**Não foram observadas diferenças significativas na Análise de Variância para esta propriedade. Médias (desvio-padrão) seguidas de mesma letra não diferem entre si na coluna pelo Teste de Médias Tukey a 5% de probabilidade.*

cloeziana (652 kg/m³) while the lowest value, with a significant difference, was observed for the wood of the clone *E. urophylla* 1 (477 kg/m³). *Eucalyptus* spp. 1, *Eucalyptus* spp. 2 and *C. torelliana* x *C. citriodora* presented basic density of 574, 582 and 575 kg/m³, respectively, with no significant difference between them.

The clone *E. cloeziana* had the highest value of total extractives (9.4%), but it did not differ significantly from the clone *E. urophylla* 2 (8.1%). The lowest values were observed for the clones *E.* spp. 1, *E.* spp. 2 and *C. torelliana* x *C. citriodora*, ranging from 5.3 to 6.6%.

Regarding the lignin content, only the *Eucalyptus cloeziana* clone differed significantly from the others, obtaining 32.6% of total lignin, while the others had contents in the range between 26.6 and 27.9%.

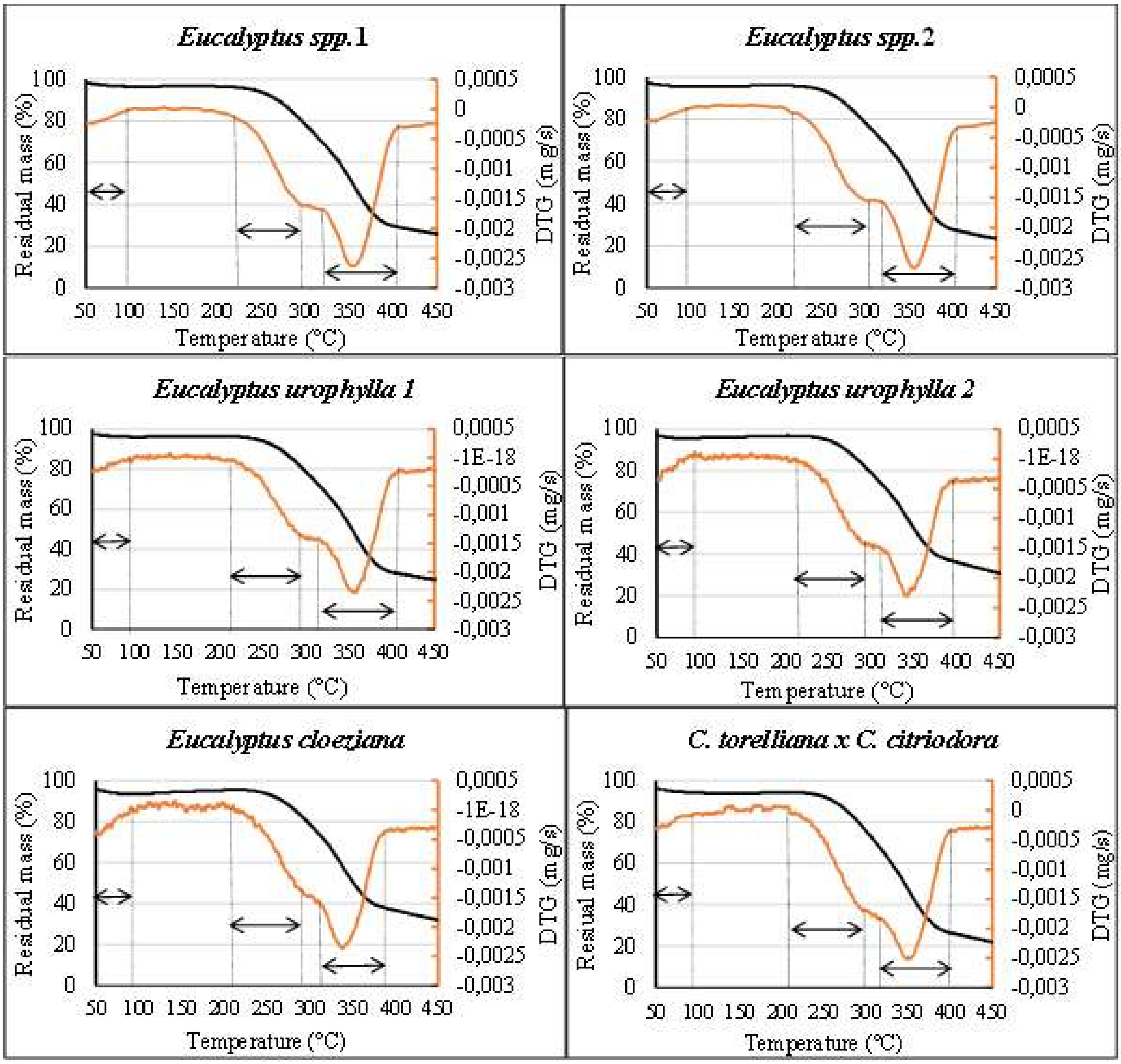

Figure 1 – Mass loss curves as a function of temperature (TG) and its derivatives (DTG) of the woods of the evaluated clones, with the designation of the ranges with the greatest mass loss.
Figura 1 – *Curvas de perda de massa em função da temperatura (TG) e suas derivadas (DTG) das madeiras dos clones avaliados, com designação das faixas de maior perda de massa.*

Table 3 – Mass loss by temperature range in thermogravimetric analysis.
Tabela 3 *– Perda de massa por faixa de temperatura na análise termogravimétrica.*

Clone	Temperature Ranges (°C)							Residual mass*
	Until 100	100-200	200-250	250-300	300-350	350-400	400-450	
E. spp. 1	3.6	0.0	2.7	15.4	25.8	22.6	4.1	26.8
E. spp. 2	4.3	0.0	2.4	15.2	25.7	24.8	4.8	24.4
E. urophylla 1	4.2	0.0	2.1	15.3	27.5	23.8	3.7	26.0
E. urophylla 2	4.5	0.0	2.0	15.5	26.5	16.5	5.0	32.5
E. cloeziana	6.4	0.0	2.0	14.8	28.1	14.3	4.4	34.2
C. torelliana x *C. citriodora*	5.7	0.0	2.4	16.6	28.4	20.4	4.3	23.6

* Residual mass, considering dry wood mass.
**Massa residual, considerando-se a massa de madeira absolutamente seca.*

The holocellulose content was higher in the E. spp. 1, which did not differ significantly from *E*. spp. 2, *E. urophylla* 2 and *C. torelliana* x *C. citriodora*, varying between 64.6 and 67.9%. In turn, the Eucalyptus cloeziana clone obtained 57.8% of holocellulose, which is the lowest value observed. The ash content varied little between the genetic materials, with only the clone *C. torelliana* x *C. citriodora* differing significantly from the others, presenting a value of 0.91%, while the others obtained values ranging between 0.13 and 0.22 %.

The *Eucalyptus cloeziana* clone had the highest crystallinity index, 74.42%, and the *Corymbia torelliana* x *Corymbia citriodora* clone had the lowest crystallinity index, 69.04%. The other clones obtained intermediate values.

By analysis of variance, there was no effect of the clone on the calorific value of the wood. The highest value was 4703 kcal/kg, obtained for the clone *E. urophylla* 1, while the lowest value was 4643 kcal/kg, obtained for the *C. torelliana* x *C. citriodora* clone.

The thermogravimetric curves (TG/DTG) of the studied clones are shown in (Figure 1), with the temperature varying from 50 to 450ºC.

The percentage of mass loss in each temperature range and the residual mass are shown in (Table 3).

The mean values of the gravimetric yield and charcoal properties of the evaluated clones are presented in (Table 4).

The *Eucalyptus cloeziana* clone had the highest charcoal yield (36.3%). The lignin content and the extractive content correlated positively with charcoal yield, both obtaining correlations of 0.8. Holocellulose content and charcoal yield were negatively correlated (-0.9).

The charcoal produced with the wood of *E. urophylla* 1 had the lowest apparent density (316 kg/m^3), while the charcoal produced with the wood of the clone *Eucalyptus cloeziana* had the highest apparent density (466 kg/m^3). The clones *E. urophylla* 1 and *E. urophylla* 2 did not differ significantly from each other in terms of higher heating value, with values of 7564 and 7526 kcal/kg, respectively. The other clones had a lower value of higher heating value, ranging between 7175 and 7291 kcal/kg.

No significant differences were observed for volatile matter and fixed carbon contents. Charcoal

Table 4 – Physical and chemical properties of charcoal from the evaluated clones.
Tabela 4 *– Propriedades físicas e químicas do carvão vegetal dos clones avaliados.*

Clone	Gravimetric yield (%)	Apparent density (kg/m³)	Higher heating value (kcal/kg)	Volatile matter (%) *	Ash (%)	Fixed carbon (%)*
E. spp. 1	32.4 (0.4) c	363 (15) bc	7287 (87) b	25.5 (0.2)	0.40 (0.10) c	74.1 (0.3)
E. spp. 2	33.5 (0.4) b	383 (22) b	7291 (79) b	25.3 (0.7)	0.32 (0.11) c	74.4 (0.7)
E. urophylla 1	33.8 (0.2) b	316 (15) c	7564 (159) a	25.5 (1.0)	0.72 (0.06) b	73.8 (1.0)
E. urophylla 2	33.6 (0.6) b	353 (43) bc	7526 (119) a	25.2 (0.9)	0.52 (0.08) bc	74.3 (0.8)
E. cloeziana	36.3 (0.6) a	466 (64) a	7175 (32) b	26.5 (1.5)	0.38 (0.09) c	73.2 (1.5)
C. torelliana x *C. citriodora*	32.2 (0.5) c	385 (9.0) b	7178 (132) b	25.0 (0.4)	2.32 (0.27) a	72.7 (0.3)

*No significant differences were observed in the Analysis of Variance for this property. Means (standard deviation) followed by the same letter do not differ from each other in the column by the Tukey Test at 5% probability.
**Não foram observadas diferenças significativas na Análise de Variância para esta propriedade. Médias (desvio-padrão) seguidas de mesma letra não diferem entre si na coluna pelo Teste de Médias Tukey a 5% de probabilidade.*

produced from wood of *C. torelliana* x *C. citriodora* clone had the highest ash content (2.32%).

4. DISCUSSIONS

4.1. Physical and chemical properties of wood

The wood of the genus *Corymbia* stands out for its density greater than 550 kg/m^3, already at 45 months of age (Loureiro et al., 2019; Medeiros et al., 2016). In fact, for wood clones of *C. torelliana* x *C. citriodora*, a density of 575 kg/m^3 was observed. Wood density is directly influenced by anatomical properties. Fibers with a larger wall fraction, pores with smaller diameters and higher frequency contribute to the increase in woody matter, increasing the density (Pereira et al., 2016). The cutting age for most eucalypts plantations varies between 6 and 8 years (Gonçalves et al., 2017). The *Eucalyptus* clones evaluated in this study were cut at 8 years old and presented similar or lower density to the *C. torelliana* x *C. citriodora* clone, harvested at 4 years old.

For the production of charcoal, it is desirable that the basic density of the wood is greater than 500 kg/m^3, as denser woods generate denser charcoal (Santos et al., 2011). Within this context, among the 6 clones evaluated, only the clone of *Eucalyptus urophylla* 1 does not have a satisfactory density for carbonization, since its density was 477 kg/m^3. In turn, the 8-year-old *Eucalyptus cloeziana* clone stood out with a density of 640 kg/m^3, a value equal to that obtained by Magalhães et al. (2017) who described a mean value of 640 kg/m^3 for *Eucalyptus cloeziana*, at 7 years of age. The density of the *C. torelliana* x *C. citriodora* clone, with a value of 575 kg/m^3, is comparable to the density values obtained in the study by Loureiro et al. (2019), whose mean values were equal to 549 and 579 kg/m^3 for wood from clones of *C. citriodora* x *C. torelliana* and *C. torelliana* x *C. citriodora*, respectively, both aged 45 months. Pereira et al. (2016) found, for different clones of *E. urophylla*, mean density values ranging between 545 and 585 kg/m^3, higher values than the two clones of *Eucalyptus urophylla* in the present study that presented density of 520 and 477 kg/m^3.

Evaluating *Eucalyptus urophylla* clones at 7 years of age, Almeida et al. (2015) found extractive contents ranging from 8.52%. Loureiro et al. (2019), evaluating hybrid clones of *C. citriodora* and *C. torelliana*, found a mean content of extractives of 8.79%, which is higher than that found in the present study for the hybrid of these species.

Lignin has high resistance to thermal degradation due to having condensed structures in its composition, since C-C bonds are less reactive than C-O bonds (ether) (Heitner et al., 2010). In addition, the intermediate products formed in the pyrolysis process can condense, increasing the molar mass of the reaction product (Brebu and Vasille, 2010). These characteristics positively influence the yield and quality of charcoal. The clone of *Eucalyptus cloeziana*, due to its higher lignin content, has greater resistance to thermal degradation, being the most suitable for the production of charcoal.

Almeida et al. (2015) studying *Eucalyptus urophylla* wood at 7 years of age, found mean total lignin contents of 26%, a value similar to that found for clones of *Eucalyptus urophylla* 1 and 2 in the present study, which presented 27.5 and 27.8 % of lignin, respectively. Loureiro et al. (2019) found 26.3% of total lignin for hybrid clones of *C. citriodora* and *C. torelliana*, a value similar to that found in the present work (27.9%) for the clone *C. torelliana* x *C. citriodora*.

Pereira et al. (2013a), evaluating clones of *E. urophylla* at 7.5 years of age, found a mean value of 70.1% for the holocellulose content, a higher value than clones of *Eucalyptus urophylla* 1 and 2 in the present study, which had a content of holocellulose of 65.2 and 63.9%, respectively. Loureiro et al. (2019) found 64.2% for the mean holocellulose content in hybrid clones of *C. citriodora* and *C. torelliana*, a value similar to that found in the present work (64.6%) for the clone *C. torelliana* x *C. citriodora*. During the carbonization process, much of the initial mass is lost as a result of the degradation of holocellulose, the less stable components of wood (Vital et al., 2013). It is desirable that wood intended for charcoal production have a lower holocellulose content. The *Eucalyptus cloeziana* clone had the lowest holocellulose content (57.8%), so the wood from this clone tends to be more recalcitrant to mass loss in the carbonization process.

Pereira et al. (2013a), evaluating clones of *Eucalyptus* spp. at 7.5 years old, found a mean value of 0.14% for the ash content. Loureiro et al. (2019) found 0.67% ash when evaluating hybrid clones of

C. citriodora and *C. torelliana*. High ash content in wood is inconvenient, as it generates charcoal with a high inorganic content, which can cause deterioration in the blast furnace and compromise the quality of steel and metal alloys (Vital et al., 2013).

The observed crystallinity indices were similar to those found by Pereira et al. (2013a), who reported rates ranging from 67.0 to 70.6%. The authors found a correlation of 0.5 between crystallinity index and gravimetric yield in charcoal. Intermolecular hydrogen bonds, present in the crystalline region of cellulose, can contribute to the thermal stability of the wood and, consequently, to the charcoal yield (Pereira et al., 2013a).

The values found for the Higher Heating Value (HHV) are similar to those found by Carneiro et al. (2014), when evaluating *Eucalyptus grandis* and *Eucalyptus urophylla* wood (4600 kcal/kg), at 7 years of age. Loureiro et al. (2019) found a mean HHV of 4611 kcal/Kg for clones of *Corymbia citriodora* x *Corymbia torelliana*, at 45 months of age.

4.2. Thermal properties of wood

A similarity was observed between the thermal degradation profiles of the wood of the different clones, with small variations occurring in the temperatures corresponding to the maximum degradation peaks, observed between 250 and 400°C, related to the degradation of hemicelluloses and cellulose (Rambo et al., 2015). The TG/DTG curves in (Figure 1) show three ranges of thermal degradation. It was observed that in the range of 100 to 200°C there was no mass loss for the different studied clones. This range is known as the wood thermal stability zone (Fialho et al., 2019).

Yang et al. (2007) studying the thermal degradation of wood constituents, observed hemicellulose weight loss occurring mainly at 220 – 315°C and cellulose at 315 – 400°C, similar to what was found in this study. The greatest mass loss, and mean of 65% in the present study, is mostly related to holocellulose degradation and was observed between 250 and 400°C, with a more intense and accentuated peak close to 350°C. In fact, the mean value observed in the present study for the holocellulose content was 65.6%. Fialho et al. (2019), in turn, found more intense degradation between 300 and 450°C. The less accentuated peak corresponds to the higher degradation rate of hemicelluloses, whose mean degradation range was from 222 to 297°C and is related to an average mass loss of 18% between 200 and 300°C. The most intense peak corresponds to the range of maximum cellulose degradation, varying the degradation temperature from 317 to 401°C (Pereira et al., 2013b). In fact, a mean mass loss of 47% was observed between 300 and 400°C.

In turn, no peak degradation of lignin was observed, as this component degrades over a wide temperature range, with only a small fraction degrading at temperatures below 450°C (Vital et al., 2013). This structural component is the main constituent of charcoal. In the range from 250 to 400°C, it is observed that the *Eucalyptus cloeziana* clone had the lowest mass loss among the evaluated clones. This is due to the lower holocellulose content and higher lignin content present in its wood, as observed in (Table 2).

The highest residual mass values above 450°C were observed for *E. urophylla* 2 and *E. cloeziana* clones. Therefore, such clones have the necessary structure to withstand mass loss in industrial carbonization processes, whose final temperatures reported in the literature are between 350°C and 400°C (Donato et al., 2020; Figueiró et al., 2019; Ramos et al., 2023), providing higher charcoal yields. However, the residual mass observed for the wood of the other clones was greater than that found for the wood of the clones evaluated in the literature (Pereira et al., 2013b; Santos et al., 2012) whose charcoal produced had a satisfactory gravimetric yield. Therefore, such clones show great potential for charcoal production.

4.3. Gravimetric yield and charcoal quality

The clone of *Eucalyptus cloeziana*, which had the lowest content of holocellulose (58.0%) and the highest content of extractives (9.4%) and total lignin (32.6%), also had the highest gravimetric yield in charcoal (36.3%). The highest yield is associated with the highest lignin content, which due to the aromatic compounds in its composition that are resistant to mass loss in the pyrolysis process, contribute more to the charcoal yield (Vital et al., 2013).

The clones that had the highest residual mass value in the thermogravimetric analysis were also the clones that had the lowest percentages of holocellulose, which are the least thermally stable wood components (Vital et al., 2013). The *Eucalyptus cloeziana* clone showed higher residual mass in thermogravimetric analysis and provided higher gravimetric yield in charcoal. In turn, the clone *C. torelliana* x *C. citriodora* was the clone that obtained the lowest residual mass and lowest gravimetric yield in charcoal. This correlation highlights the potential of the TGA technique in predicting the thermal resistance of genotypes for charcoal production.

Evaluating the apparent density of charcoal from different *Eucalyptus* species, Castro et al. (2013) found densities ranging from 260 to 420 kg/m^3, with a mean value of 340 kg/m^3. In turn, the apparent density of charcoal in the present work ranged from 316 to 466 kg/m^3, with a mean value of 378 kg/m3. The density of the charcoal is dependent on the density of the wood, since a greater mass per unit of volume is required to resist degradation reactions in the carbonization process, generating a greater mass of charcoal per volumetric unit (Santos et al., 2011). Evaluating the quality of charcoal from different genetic materials, Trugilho et al. (2015) found a mean apparent density of 440 kg/m3 for charcoal from *E. cloeziana*, when carbonizing wood at 7 years of age, similar to the density found in the present study for charcoal from the clone of *E. cloeziana* (466 kg/m^3).

Trugilho et al. (2015) found a higher heating value of 7450 kcal/kg when evaluating *Eucalyptus urophylla* charcoal, a value similar to that found in the present study for *Eucalyptus urophylla* clones. When evaluating the 7 year old *Eucalyptus cloeziana* charcoal, the authors found 7300 kcal/kg for the higher heating value, a higher value than that found in the present study for this clone (7175 kcal/kg). This difference may be associated with the higher fixed carbon content of the clones evaluated in the study by Trugilho et al. (2015) (approximately 80%) in relation to that found in the present study, that varied from 72 to 74%. The higher heating value is related to the fixed carbon content (Neves et al., 2011).

Volatile matter may mean less efficiency of charcoal as an iron ore reducer (Fialho et al., 2019). No significant difference was observed between the clones for this property, whose mean was 25.5%. Fixed carbon is the best parameter related to the volumetric use of the blast furnace and the reducing efficiency of charcoal (Carneiro et al., 2013). The mean fixed carbon content for the evaluated clones was 73.8%, with no significant difference between the results. Due to its higher lignin content, it was to be expected that the *Eucalyptus cloeziana* clone would generate charcoal with a higher fixed carbon content. However, this relationship, found in the work of Pereira et al., (2013a), was not observed in this study.

The high ash content can reduce the calorific value of charcoal, in addition to increasing blast furnace wear (Fialho et al., 2019). Clone *C. torelliana* x *C. citriodora* showed higher ash content (2.32%). In turn, the clones *Eucalyptus* spp 1, *Eucalyptus* spp 2 and *Eucalyptus cloeziana* showed lower ash contents, not differing significantly from each other, with a mean value of 0.37%. Higher ash contents in charcoal are related to higher ash contents in wood, since in the pyrolysis process there is no degradation of inorganic constituents (Pereira et al., 2013a).

Neves et al. (2011) found mean values of 19.0; 0.7 and 80.0% for the percentages of volatile matter, ash and fixed carbon, respectively, when evaluating charcoal from different *Eucalyptus* clones. Ramos et al. (2019) evaluating charcoal from clones of *E. urophylla* x *E. grandis*, found mean contents of 28.6% of volatile matter; 0.6% ash and 70.9% fixed carbon. The variations observed between the works cited and this study may be associated with the difference in the chemical and anatomical composition of the source materials, in addition to the differences in the carbonization parameters.

5. CONCLUSIONS

All clones showed potential for charcoal production. However, the *Eucalyptus cloeziana* clone was the most suitable for charcoal production. This clone showed the highest gravimetric yield in charcoal and the highest apparent density of the charcoal produced.

The clone of *Corymbia torelliana* x *Corymbia citriodora*, for having a density of 575 kg/m^3, at 4 years old, stands out among the others, with the potential to produce a greater amount of charcoal per unit volume, since the other clones were cut at 8 years old, with similar or lower density.

The gravimetric yield in charcoal was favored by the lignin content and extractives. In turn, the holocellulose content contributed negatively to the gravimetric yield.

AUTHOR CONTRIBUTIONS

Conceptualization: Oliveira LP, Carneiro ACO, Demuner IF; Experimental tests: Oliveira LP, Jorge FJ, Ferreira SO; Analysis of results: Oliveira LP, Carneiro ACO; Writing - original draft: Oliveira LP, Carneiro ACO; Writing - review and editing: Oliveira LP, Carneiro ACO, Peres LC, Demuner IF, Fernandes SA; Supervision and coordination of research: Carneiro ACO.

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