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Application of thermogravimetric analysis as a pre-selection tool for *Eucalyptus* spp.

Lucas de Freitas Fialho[1], Angélica de Cássia Oliveira Carneiro[1], Clarissa Gusmão Figueiró[1], Antônio Policarpo Souza Carneiro[2], Paula Gabriella Surdi[1], Benedito Rocha Vital[1], Mateus Alves de Magalhães[1], Letícia Costa Peres[1]

[1] Universidade Federal de Viçosa, Departamento de Engenharia Florestal, Viçosa, MG, Brasil. E-mail: l.freitasfialho@gmail.com; cassiacarneiro1@gmail.com; clarissagfigueiro@gmail.com; paulasurdi@gmail.com; bvital@ufv.br; mateusmagalhaes91@gmail.com; leticiacostaperes@gmail.com
[2] Universidade Federal de Viçosa, Departamento de Estatística, Viçosa, MG, Brasil. E-mail: policarpo@ufv.br

ABSTRACT: The aim of the study was to evaluate the use of thermogravimetric analysis in the pre-selection of genetic materials. Twenty-five *Eucalyptus* spp. genetic materials were used. The analysis of the data consisted of three stages; first, was carried out an exploratory study of the wood and charcoal properties. Subsequently, a Pearson correlation analysis was performed between the parameters of thermogravimetric analysis (TGA) and the properties of wood and charcoal. Finally, once the presence of significant correlations between these properties was verified, pre-selection of genetic material was carried out. The loss of mass in the temperature range of 300-450ºC, from thermogravimetric analysis (TGA), showed the highest number of correlations between wood and charcoal properties, which allowed the use of this TGA variable in pre-selection of genetic materials. Genetic materials 9 (Hybrids of *E. urophylla* and *E. maidenii*), 10 (Hybrids of *E. urophylla* and *Eucalyptus* sp.), 19 (Hybrids of *E. urophylla*, *E. camaldulensis*, *E. grandis* and *Eucalyptus* sp.) And 21 (Hybrids of *E. urophylla*, *E. camaldulensis*, *E. grandis* and *Eucalyptus* sp.) presented potentials for charcoal production, through pre-selection.

Key words: carbonization; clones; gravimetric yield; steel industry

Aplicação da análise termogravimétrica como ferramenta de pré-seleção de *Eucalyptus* spp.

RESUMO: O objetivo do estudo foi avaliar a utilização da análise termogravimétrica na pré-seleção de materiais genéticos. Foram utilizados 25 materiais genéticos de *Eucalyptus* spp. A análise dos dados consistiu em três etapas, primeiramente, foi realizada um estudo exploratório das propriedades da madeira e do carvão vegetal. Posteriormente, foi realizada uma análise de correlação de Pearson, entre os parâmetros da análise termogravimétrica (TGA) e tais propriedades. Por fim, uma vez constatada a presença de correlações significativas entre a TGA e as propriedades da madeira e do carvão, foi realizada a pré-seleção de materiais genéticos. A perda de massa na faixa de temperatura de 300-450ºC, proveniente da análise termogravimétrica (TGA), apresentou o maior número de correlações entre as propriedades, o que propiciou o uso desta variável da TGA na pré-seleção de materiais genéticos. Desta forma, os matérias genéticos 9 (Híbrido de *E. urophylla* e *E. maidenii*), 10 (Híbrido de *E. urophylla* e *Eucalyptus* sp.), 19 (Híbrido de *E. urophylla*, *E. camaldulensis*, *E. grandis* e *Eucalyptus* sp.) e 21(Híbrido de *E. urophylla*, *E. camaldulensis*, *E. grandis* e *Eucalyptus* sp.) apresentaram potenciais para produção de carvão vegetal, por meio da pré-seleção.

Palavras-chave: carbonização; clones; rendimento gravimétrico; siderurgia

Introduction

The use of renewable sources of energy, such as forest biomass, is a practice that contributes to the sustainability of productive sectors. Factors such as the diversification of the energy matrix and the independence of fossil fuels are the main advantages of using such raw materials (Figueiró et al., 2019).

Regarding the availability of forest biomass, Brazil stands out among the other countries. The edaphoclimatic conditions, improvement of silvicultural techniques and the development of efficient breeding programs guarantee the superiority of the country in the world scenario of forest production (Vital et al., 2013; IBÁ, 2017).

However, to maximize the utilization of this kind of biomass in Brazilian forest sectors, it is still necessary a greater adaptation of feedstock for particular uses, which frequently isn't considered for the different sectors of forest production (Pereira et al., 2016; Carneiro et al., 2017a). In the charcoal sector, for example, the selection of superior genetic materials is substantiated, mainly in variables as plants phytosanitary conditions, volumetric increase and wood basic density, once these proprieties are relatively easy to determine (Pereira et al., 2013a).

Though studies have evidenced the need of more complete analysis of the inherent characteristics of feedstock in the selection of superior genetic materials, contemplating variations existing in wood properties, in the anatomical, chemical and physical structure, besides the variables of the carbonization process (Pereira et al., 2013b; Santos et al., 2016; Ribeiro et al., 2017; Rocha et al., 2017).

Daily in a forest company, the complete characterization of wood and charcoal proprieties can be presented as an economically onerous routine, turning, in several cases, impracticable, mainly when working with high numbers of genetic materials.

In this context, the application of pre-selection of genetic materials for charcoal production can be an interesting alternative to reduce characterization costs of individuals. Once pre-selected, a completed characterization is made with a relatively smaller number of materials, which leads to cost reduction.

The pre-selection can be performed with proprieties usually determined in the routine of companies (plants phytosanitary conditions, volumetric increase and wood basic density), together with other proprieties that are viable economically and enable the acquisition of important information on the quality of the material.

The thermogravimetric analysis, for example, is an interesting way of characterizing biomass to charcoal production (Pereira et al., 2013b). This technique provides relevant data to the industrial production of charcoal in relatively short time and certain specificity when associated with other techniques, once it provides information about the thermic degradation of wood components in function of the temperature ranges (Shen et al., 2010).

Therefore, the result of the thermogravimetric analysis can be correlated with most of the properties of interest of wood and charcoal. In this sense, the objective of this study was to evaluate the use of thermogravimetric analysis in the pre-selection of genetic materials, by means of Pearson's correlation analysis between thermogravimetric analysis and the proprieties of wood and charcoal.

Material and Methods

There were 25 genetic materials of *Eucalyptus* spp. (Table 1), with 87 months of age, cultivated in 3 x 3 meters spacing, from a clonal test in plots, with six lines and four plants per line, belonging to a forest company in the municipality of Itamarandiba, Minas Gerais.

Three trees with medium dimeter were selected from each of the twenty-five clones, totalizing seventy-five trees. The trees that presented visual defects and/or were located at the border were excluded.

Table 1. Information about the *Eucalyptus* spp. genetic materials.

Identification	Genetic material
1	*Eucalyptus cloeziana*
2	Hybrid of *Eucalyptus urophylla* and *Eucalyptus* sp.
3	Hybrid of *Eucalyptus urophylla* and *Eucalyptus* sp.
4	Hybrid of *E. urophylla* and *Eucalyptus* sp.
5	Hybrid of *E. urophylla* and *Eucalyptus* sp.
6	Hybrid of *E. urophylla* and *Eucalyptus* sp.
7	Hybrid of *E. urophylla* and *Eucalyptus* sp.
8	Hybrid of *E. grandis* and *E. urophylla*
9	Hybrid of *E. urophylla* and *E. maidenii*
10	Hybrid of *E. urophylla* and *Eucalyptus* sp.
11	Hybrid of *E. urophylla, Eucalyptus* sp. and *E. globulus*
12	Hybrid of *E. urophylla, E. camaldulensis, E. grandis* and *E. maidenii*
13	Hybrid of *E. urophylla, E. camaldulensis, E. grandis* and *E. globulus*
14	Hybrid of *E. urophylla, E. camaldulensis, E. grandis* and *Eucalyptus* sp.
15	Hybrid of *E. camaldulensis, E. grandis, E. urophylla* and *Eucalyptus* sp.
16	Hybrid of *E. urophylla, E. camaldulensis, E. grandis* and *Eucalyptus* sp.
17	Hybrid of *E. urophylla, E. camaldulensis, E. grandis* and *Eucalyptus* sp.
18	Hybrid of *E. urophylla, E. camaldulensis, E. grandis* and *Eucalyptus* sp.
19	Hybrid of *E. urophylla, E. camaldulensis, E. grandis* and *Eucalyptus* sp.
20	Hybrid of *E. urophylla, E. camaldulensis, E. grandis* and *Eucalyptus* sp.
21	Hybrid of *E. urophylla, E. camaldulensis, E. grandis* and *Eucalyptus* sp.
22	Hybrid of *E. urophylla, E. camaldulensis, E. grandis* and *Eucalyptus* sp.
23	Hybrid of *E. urophylla, E. camaldulensis, E. grandis* and *Eucalyptus* sp.
24	Hybrid of *E. urophylla, E. pellita* and *Eucalyptus* sp.
25	Hybrid of *E. urophylla, E. pellita* and *Eucalyptus* sp.

Proprieties of wood and charcoal

For the volume calculation, measurements were made every meter of the stem, from the cutting base of each tree to the minimum diameter of 7 cm. The volume of each section was calculated according to the formula proposed by Smalian, obtaining the total volume of each tree by adding the values of each section (Ribeiro et al., 2017).

The basic density of wood was determined according to the method of water immersion, described by the norm NBR 11941 (ABNT, 2003). The morphological analysis of the fibers was performed according to the methodology used by Pereira et al. (2013a).

To determine the contents of carbon, oxygen, hydrogen and nitrogen, a thermal conductivity detector was used, where each element has a specific peak and interaction. The analysis was made in an Elemental Vario Micro Cube model CHNS-O.

The total extractives content was determined according to TAPPI 204 om-88 (TAPPI, 2001). The soluble and insoluble lignin were determined according to Gomide & Demuner (1986) and Goldschmidt (1971), respectively. The total lignin content was obtained by adding the insoluble and soluble lignin contents. The ash content was determined according to the norm NBR 8112 (ABNT, 1986). The holocellulose content was calculated by subtracting from 100 the contents of lignin, extractives and ash.

The higher heating value of wood was determined, in duplicates, using an IKA300 adiabatic calorimeter, according to the methodology described by NBR 8633 (ABNT, 1984).

The carbonization of the wood was carried out in a muffle-type electric oven using approximately 300 grams of dry wood in a drying oven, in 103 ± 2°C, to constant mass. A metal container of approximately 0,003 m^3 was used for performing the carbonization inside the muffle.

The heating control was performed manually at increments of 50°C every 30 minutes, corresponding to a heating rate of 1,67°C min^{-1}, until the final temperature of 450°C, remaining stabilized in the latter by 60 minutes. At the end of the process, the charcoal yield was determined by gravimetry.

The contents of volatile matter and ash of the charcoal were determined according to NBR 8112 (ABNT, 1986). The fixed carbon content was calculated by subtracting from 100 the contents of volatile matter and ashes. The higher heating value was determined using a IKA300 adiabatic calorimeter, according to the methodology described by NBR 8633 (ABNT, 1984).

The thermogravimetric analysis of the wood was performed with previously selected samples that passed through the sieve with a mesh of 40 mesh and were retained in the 60 mesh sieve. The analyzes were carried out in the equipment DTG-60H, Shimadzu, under nitrogen gas atmosphere, with a constant flow of 120 ml min^{-1}. The thermogravimetric curves were obtained using approximately 2 mg of sawdust, from 100°C to maximum temperature of 600°C, with a heating rate of 10°C min^{-1}.

From the thermogravimetric curves, mass loss calculations were carried out in the following temperature ranges: 100-200°C, 200-300°C, 300-450°C. The residual mass was also calculated at 450°C.

Data analysis

The experiment was set up in a completely randomized design with twenty-five treatments (genetic materials), with three replicates (trees), totaling seventy-five sample units.

Data analysis consisted of three steps. First, an exploratory study of wood and charcoal properties was carried out using software R version 3.4.3 (R Core Team, 2017). The position measurements (mean, minimum, maximum and amplitude) were determined, being presented in the graphical form of boxplot.

Subsequently, a Pearson correlation analysis was performed between the parameters of thermogravimetric analysis (TGA) and the properties of wood and charcoal. Finally, once the presence of significant correlations between these properties was verified, the next step consisted of the pre-selection of genetic materials.

For the pre-selection, the median for each variable to be used was calculated, so that genetic material that presented values above the median (for the variables where the highest value is desirable) and below the median (for the variables where the lower value is desirable) were pre-selected (Muttlak, 1998).

Results and Discussion

Exploratory Analysis

Figure 1 shows that the annual mean increment (AMI) ranged from 25.05 to 67.07 m^3 ha^{-1} $year^{-1}$, with a mean of 46.66 m^3 ha^{-1} $year^{-1}$.

In a forest enterprise with charcoal production, an increase in AMI means a higher volume of wood per hectare over a given period of time, which may favor the project economically. Regarding the average AMI of eucalyptus plantations in Brazil, the value found in 2016 was 35.7 m^3 ha^{-1} $year^{-1}$ (Ibá, 2017). Among the genetic material evaluated, 84% had higher AMI values than the Brazilian average.

The basic density of wood varied between 0.51 and 0.62 g cm^{-3} (Figure 1). It is recommended that the wood density is higher than 0.55 g cm^{-3} when it is intended to produce charcoal for the steel sector (Carneiro et al., 2017a). According

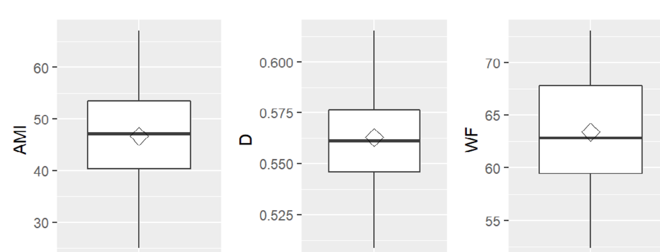

Figure 1. Variation of annual mean increment, basic density and wall fraction of the genetic materials. AMI = annual mean increment (m^3 ha^{-1} $year^{-1}$); D = basic density (g cm^{-3}); WF = wall fraction of fibers (%).

to this recommendation, approximately 80% of the analyzed genetic materials obtained average values equal to or higher than desired for this productive sector.

The density of wood is an important criteria for the evaluation of species for the production of charcoal, and is currently the property most used by companies in the sector (Pereira et al., 2013a). In the search for superior genetic materials of the genus Eucalyptus, it is desirable to have high basic density, since they result in a greater mass of wood in the kiln, and, consequently, an increase in the production of charcoal for the same volume of wood.

According to Paes et al. (2015), the higher densities are associated, among other factors, with higher wall fraction and smaller pore diameter. Therefore, the low variation observed for this property can be a consequence of the low variation rates also observed for the wall fraction and the pore diameter of the wood.

The average wall fraction of the fibers of the genetic materials was 63.38% and coefficient of variation of 7.62% (Figure 1). The genetic material with values above 60% of wall fraction (Siebeneichler et al., 2017) are considered potential for charcoal production. Among the analyzed materials, 40% did not fit this recommendation.

During the carbonization of the wood, a larger wall fraction can mean a larger amount of mass available, for a same volume unit, and, consequently, greater availability of energy for thermal degradation to occur (Pereira et al., 2016). Therefore, a high wall fraction can contribute to a higher density of wood, consequently, there will be a greater mass of wood in the kiln, as well as a reduction of transportation costs, which may increase the economic viability of the process.

The average carbon, hydrogen and oxygen contents of the wood were 48.50; 6.78 and 44.60% respectively (Figure 2). It is observed that the coefficient of variation obtained by these three elementary components of the wood was considered low, with values lower than 5%.

According to Qian et al. (2011) the elemental chemical composition of the wood is similar for the species of the genus Eucalyptus, justifying, therefore, the low coefficient of variation for these properties. However, even if such variations between genetic materials are minimal for elemental chemical composition, when the objective is the production of charcoal, the species with the highest levels of carbon and hydrogen should be preferred (Pereira et al., 2013a).

It is observed that nitrogen and sulfur contents ranged from 0.02 to 0.14 and 0.01 to 0.06, respectively (Figure 2). Similar values were found by Juízo et al. (2017) studying genetic materials of eucalypts. According to Trugilho et al. (2015), these values can be considered low in relation to fossil fuels, mainly with coal, which contributes to charcoal being considered more environmentally interesting for the steel sector.

The total extractive contents had an average value of 4.96%, while the total lignin presented an average value of 30.85% and for holocellulose was found to be 64.05% (Figure 3).

It is verified that only the total extractive content had coefficient of variation considered average, and the others presented low coefficient of variation. The major variations in extractive content in relation to lignin and holocellulose contents can be explained, mainly due to the fact that the concentration of these compounds in the wood varies according to the genetic material, age, silvicultural treatments, climatic conditions, soil and fertilization, besides the relation between the amount of heartwood and sapwood (Carneiro et al., 2017b).

The extractives of the wood are composed of chemical groups of different natures, among them are present the fatty acids, phenols, steroids, resins, among other organic compounds (Rowell et al., 2005). The extractives of phenolic origin, for example, have high carbon content, which can contribute to the increase of the calorific value of wood and charcoal, and increase the yield the of charcoal (Carneiro et al., 2017b).

Cellulose and hemicelluloses have low resistance to thermal degradation when compared to lignin, with maximum mass peaks losses in the pyrolysis process at the temperature

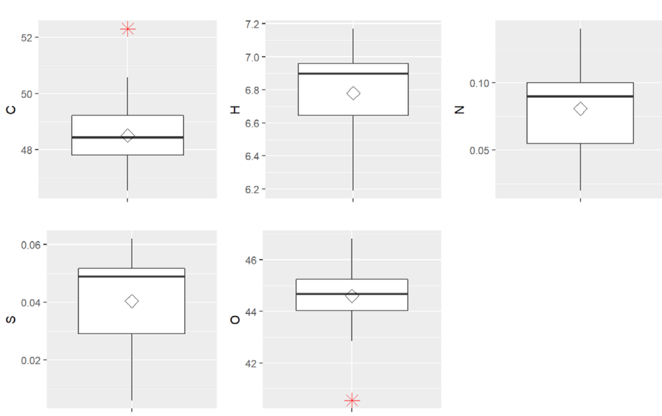

Figure 2. Variation of the elemental chemical composition of the genetic materials studied. C, H, N, S, O = Carbon, Hydrogen, Nitrogen, Sulfur and Oxygen content (%).

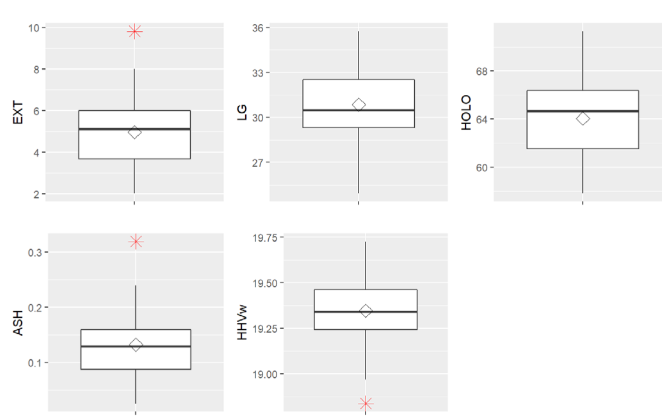

Figure 3. Variation of the structural chemical composition and higher heating value of the wood of the studied genetic materials. EXT = Extratives content (%); LG = Total lignin content (%); HOLO = holocelulloses content (%); ASH = Ash contnt of wood (%); HHVw = Higher heating value of wood (MJ kg^{-1}).

range of 275-350°C (Yang et al., 2007). Lignin, on the other hand, presents high resistance to the thermal degradation, due to the presence of greater number of C-C and C=C bonds in its condensed structure, besides presenting a high percentage of elemental carbon and low oxygen content when compared to holocellulose (Haykiri-Acma et al., 2010).

The higher heating value of wood ranged from 18.84 to 19.73 MJ kg^{-1}, with a coefficient of variation of 0.93%. The energy released in the thermal degradation of wood is associated with enthalpy of carbon, hydrogen and sulfur. Due to the low concentration of sulfur in the genetic materials studied, the low variation of carbon and hydrogen contents contributed to a low coefficient of variation of the higher heating value of wood (Trugilho et al., 2015).

The average charcoal gravimetric yield of the genetic materials evaluated was 34.63%, with a coefficient of variation of 3.74% (Figure 4).

Some of the properties of wood that most influence charcoal yield, according to Carneiro et al. (2017a) and Juizo et al. (2017), are the lignin, carbon and hydrogen contents. The coefficients of variation found for such wood properties were low, which may justify the low coefficient of variation obtained for the yield. A higher gravimetric yield in charcoal is associated with a lower mass and energy loss of the carbonization process.

The average apparent relative density of charcoal was equal to 0,32 g cm^{-3} with coefficient of variation of 12.11%. It can be verified that the ash content of charcoal varied from 0.11 to 0.70%. The volatile matter content presented an average of 34.05%, with coefficient of variation of 6.85%, and the fixed carbon content varied from 69.32 to 77.23%. During carbonization a partial degradation of the volatile materials occurs, resulting, therefore, in the concentration of fixed carbon and ashes in the final product (Van Der Stelt et al., 2011; Koppejan et al., 2015).

The presence of ash reduces the calorific value of charcoal, as well as contributing to blast furnace wear. Volatile

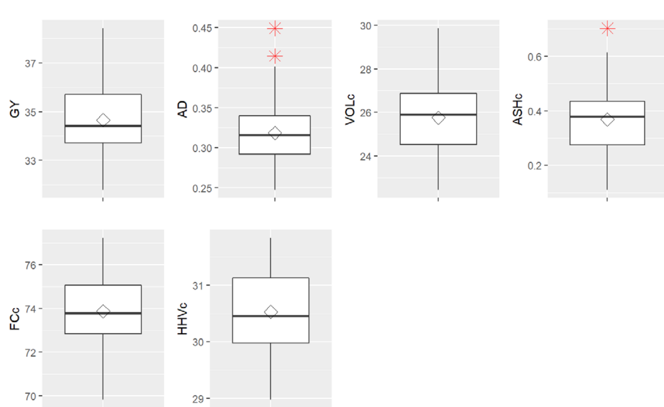

Figure 4. Variation of charcoal properties of the studied genetic materials. GY = Gravimetric yield of charcoal (%); AD = Aparent density (g cm^{-3}); VOLc = Volatile matter contents of charcoal (%); ASHc = Ash contents of charcoal (%); FCc = Fixed carbon content of charcoal (%); HHVc = Higher heating value of charcoal (MJ kg^{-1}).

materials, on the other hand, act on the flame stability and combustion rate of the charcoal in the blast furnace. However, a high content of volatile materials may mean lower reducing efficiency of the iron ore reduction process.

Whereas fixed carbon is a parameter related to the volume utilization of the blast furnace, in which a higher fixed carbon content results in a smaller volume occupied by charcoal, which provides larger spaces for the ore to be reduced (Oliveira et al., 2013).

For the production of charcoal for steel industry use it is recommended that the ash content is less than 1% and the fixed carbon content is between 70 and 80% (Carneiro et al., 2017b). Considering the values recommended by these authors, it was verified that all the genetic materials met the specifications.

The higher heating value of charcoal varied from 29.98 to 31.83 MJ kg^{-1}. The higher heating value of charcoal is higher than that of wood due to the partial degradation of cellulose and hemicelluloses, increasing the concentration of the components more stable to degradation (lignins), thus concentrating carbon contents in charcoal (Phanphanich & Mani, 2011). The 1% increase in the biomass carbon concentration can raise its higher heating value by up to 0.39 MJ kg^{-1} (Jenkins et al., 1998). Therefore, the low coefficient variation of the carbon and lignin contents of the wood may explain the low variability for the higher heating value of charcoal.

In the initial degradation range of the wood (100 to 200°C), it is observed that the loss of mass was smaller when compared to the others, with values varying from 0.30 to 0.96% (Figure 5). This temperature range is called the zone of thermal stability of the wood, where the components of the wood are thermally stable, provided that the wood it is not exposed for a long period.

From 200 to 300°C there was a mean mass loss of 13.00%, with values varying from 11.06 to 15.07%. In this temperature range most of the mass loss can be attributed to thermal degradation of the hemicelluloses (Pereira et al., 2013b).

It is verified that in the temperature range of 300 to 450°C the greatest mass loss of wood occurs, with values varying from 55.49 to 66.00%. Considering that the wood is composed of 48% cellulose, it is possible to affirm that most

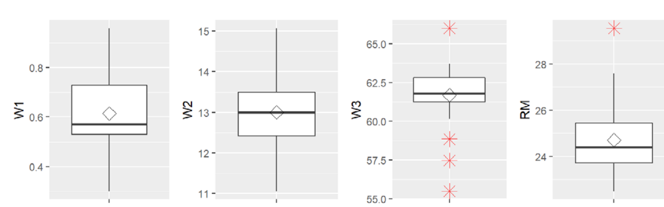

Figure 5. Values of weight loss in Eucalyptus wood in function of temperature ranges and residual mass at 450 °C. W1 = Weight loss from 100 to 200 °C (%); W2 = Weight loss from 200 to 300 °C (%); W3 = Weight loss from 300 to 450 °C (%). RM = Residual mass (%).

of the cellulose was degraded in this temperature range, and that the partial degradation of the lignin contributed to the mass loss values found in this range. Thus, the degradation of thermal lignin occurs over a wide temperature range, starting at temperatures near 160°C until temperatures above 450°C (Yang et al., 2007).

The observed values for the residual mass at 450°C ranged from 22.49 to 29.55% (Figure 5). The residual mass of the thermogravimetric analysis is related to the gravimetric yield in charcoal, where the genetic materials more resistant to the thermal degradation present a higher yield in charcoal (Pereira et al., 2013b).

As for the correlations between the parameters of the thermogravimetric analysis and the properties of wood and charcoal, it is observed that the loss of mass in the temperature range of 300-450 °C was the one that presented a greater number of significant correlations with the properties of both the wood and charcoal (Table 2).

Table 2. Correlations between values of the mass loss of eucalypts wood and the properties of wood and charcoal.

Variables	Weight loss			Residual mass (%)
	100-200°C	200-300°C	300-450°C	
AMI	-0.30 p=0.14	0.64* p=0.01	-0.26 p=0.20	0.10 p=0.64
BD	0.49* p=0.01	-0.16 p=0.43	-0.13 p=0.52	-0.31 p=0.13
FW	0.20 p=0.34	-0.01 p=0.95	-0.43* p=0.03	-0.22 p=0.29
C	0.25 p=0.23	0.22 p=0.28	-0.44* p=0.03	-0.32 p=0.12
H	-0.12 p=0.56	-0.16 p=0.44	0.01 p=0.95	-0.48* p=0.01
N	0.43* p=0.03	0.26 p=0.20	-0.08 p=0.683	0.17 p=0.41
S	0.02 p=0.9	-0.13 p=0.52	0.17 p=0.43	-0.10 p=0.64
O	-0.23 p=0.26	-0.19 p=0.36	0.35* p=0.08	0.44* p=0.03
EXT	0.28 p=0.17	0.25 p=0.23	-0.61* p=0.00	-0.12 p=0.57
TL	0.22 p=0.29	0.10 p=0.63	-0.40* p=0.05	0.00 p=0.98
HOLO	-0.32 p=0.12	-0.22 p=0.29	0.50* p=0.01	0.07 p=0.74
ASHm	-0.26 p=0.21	-0.08 p=0.71	0.55* p=0.01	-0.14 p=0.51
CY	0.43* p=0.03	0.05 p=0.82	-0.60* p=0.00	0.21 p=0.32
AD	0.19 p=0.37	0.09 p=0.66	-0.50* p=0.02	-0.20 p=0.33
VOLc	0.24 p=0.24	0.11 p=0.60	-0.38* p=0.06	0.05 p=0.80
ASHc	-0.00 p=0.99	-0.189 p=0.37	0.22 p=0.29	-0.26 p=0.20
FCc	-0.24 p=0.25	-0.10 p=0.64	0.36* p=0.07	-0.03 p=0.88
HHVc	-0.02 p=0.90	0.25 p=0.23	0.06 p=0.78	-0.07 p=0.75

* Significant correlations at 10% probability. AMI = Annual mean increment; BD = Basic density of wood; FW = Fiber wall fraction; C, H, N, S, O = Carbon, Hydrogen, Nitrogen, Sulfur and Oxygen content; EXT = Extratives content; TL = Total lignin content; HOLO = Holocellulose content; ASHm = Ash content of wood; CY = charcoal yield; AD = Aparent density of charcoal; VOLc = Volatile matter of charcoal; ASHc = Ash content of charcoal; FCc = Fixed carbon of charcoal; HHVc = Higher heating value of charcoal.

Correlations were observed between the loss of mass in the temperature range of 300-450 °C and the properties of the wood: cell wall fraction, carbon content, oxygen, extractives, total lignin, holocelluloses and wood ash. In addition to the properties gravimetric yield, apparent density, volatile matter and fixed carbon of charcoal.

The association of the results of mass loss in the temperature range of 300-450 °C such properties of the wood and the charcoal makes that the thermogravimetric analysis presents potential of use as tool of pre-selection of genetic materials. Thus, the use of TGA in the pre-selection of materials is an alternative that can reduce costs for companies in the charcoal sector, since its use may mean a reduction in the number of properties of the genetic materials to be characterized.

A possible strategy in this sense would be to jointly use the results of average annual increment and basic density of wood, which are properties consolidated and widely used in the charcoal companies, with the values of mass loss at 300-450 °C in the thermograimetric analysis. By determining these three properties, it is possible to pre-select genetic material, aiming at a later complete characterization of the properties of these pre-selected genetic material.

Pre-Selection of Genetic Materials

These genetic materials were simultaneously selected, which presented mean values of mean annual increment and basic density above the median, and lower values for the mass loss of 300-450 °C in the thermogavemetic analysis (Table 3).

It can be observed in Table 2 that the genetic materials 9 (Hybrid of *E. urophylla* and *E. maidenii*), 10 (Hybrid of *E. urophylla* and *Eucalyptus* sp.), 19 (Hybrid of *E. urophylla*, *E. camaldulensis*, *E. grandis* and *Eucalyptus* sp.) and 21 (Hybrid of *E. urophylla*, *E. camaldulensis*, *E. grandis* and *Eucalyptus* sp.) presented potential for the three properties.

The complete characterization of the wood and charcoal properties of the pre-selected genetic materials for the production of charcoal is presented in Table 4. The presence of materials usually not used in the charcoal production, such as *Eucalyptus maidenii* hybrids is verified (Pereira et al., 2013a; Vital et al., 2013; Trugilho et al.; 2015; Pereira et al., 2016; Santos et al., 2016; Carneiro et al., 2017b; Rocha et al., 2017; Siebeneichler et al., 2017). In this way, the importance of the incorporation of genetic materials not usual for the charcoal production, in programs of improvement of these companies is evident.

In addition, the presence of genetic material from the breeding of four different species of eucalyptus in pre-selected individuals demonstrates how hybridization strategies have been fundamental for the development of potential clones for the production of charcoal.

Table 3. Mean values of mean annual increment, basic density and mass loss at 300-450 °C in the thermogavimetric analysis of the genetic materials studied.

Genetic material	Mean annual increment (m^3 ha^{-1} ano^{-1})	Basic density (g cm^{-3})	Weight loss 300-450°C (%)
1	32.07	0.59	61.46
2	44.79	0.60	61.26
3	51.03	0.53	62.46
4	34.60	0.56	66.00
5	29.98	0.60	61.09
6	55.77	0.52	60.70
7	60.01	0.55	63.33
8	44.11	0.54	62.54
9*	59.96	0.58	57.47
10*	48.46	0.56	55.49
11	49.27	0.59	63.68
12	47.50	0.55	62.80
13	43.98	0.61	62.44
14	38.13	0.55	62.38
15	43.69	0.57	63.20
16	37.12	0.55	63.37
17	44.62	0.55	61.79
18	59.56	0.55	62.30
19*	54.73	0.57	61.29
20	49.78	0.55	60.14
21*	57.67	0.58	58.85
22	48.64	0.55	61.67
23	59.30	0.55	63.26
24	38.41	0.58	61.38
25	33.31	0.57	61.72
Median	47.50	0.56	61.79

* The genetic materials with values above the median for annual mean increment and basic density, and values below the average for mass loss 300-450 °C.

Conclusions

The loss of mass in the temperature range of 300-450 °C, from the thermogravimetric analysis (TGA), presents the highest number of correlations between the properties of wood and charcoal, which allowed the use of this TGA variable in the pre-selection of genetic materials.

Through pre-selection, the genetic materials 9 (Hybrid of *E. urophylla* and *E. maidenii*), 10 (Hybrid of *E. urophylla* and *Eucalyptus* sp.), 19 (Hybrid of *E. urophylla, E. camaldulensis*, *E. grandis and Eucalyptus* sp.) and 21 (Hybrid of *E. urophylla*, *E. camaldulensis*, *E. grandis* and *Eucalyptus* sp.) presented potential for charcoal production.

The presence of a hybrid not commonly used for the production of charcoal (Hybrids of E. *urophylla* and E. *maidenii*), together with the presence of a hybrid of four species (Hybrid of E. *urophylla*, E. *camaldulensis*, E, *grandis* and *Eucalyptus* sp.), demonstrates, respectively, the importance of the research and development of nonconventional materials, and of new breedings in the programs of forest enhancement.

Pre-selection provides a reduction in the number of clones that have their wood and charcoal proprieties fully characterized, which can reduce the cost of breeding programs.

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Table 4. Proprieties of wood and charcoal in pre-selected materials.

Parameter	Genetic material											
	9			10			19			21		
	Mean	CV (%)	AMP	Mean	CV (%)	AMP	Mean	CV (%)	AMP	Mean	CV (%)	AMP
Properties of wood												
Mean annual increment (m^3 ha^{-1} ano^{-1})	59.96	1.17	1.33	48.46	7.22	6.99	54.73	13.35	13.29	57.67	6.55	7.47
Basic density (g cm^{-3})	0.58	2.43	0.03	0.55	2.30	0.02	0.57	0.66	0.01	0.58	0.73	0.01
Wall fraction (%)	63.31	7.04	8.81	58.98	3.30	3.51	65.26	8.74	10.30	68.88	7.47	9.90
Carbon content (%)	49.30	1.50	1.48	49.48	2.70	2.58	48.84	2.14	2.07	48.64	2.18	2.00
Hydrogen content (%)	6.77	1.70	0.23	6.55	3.15	0.38	6.72	4.81	0.56	6.49	5.82	0.69
Nitrogen content (%)	0.10	40.00	0.08	0.12	4.95	0.01	0.08	27.15	0.04	0.11	5.09	0.01
Sulphur content (%)	0.04	25.12	0.02	0.03	44.78	0.03	0.04	42.63	0.04	0.03	84.57	0.04
Oxygen content (%)	43.80	2.00	1.75	43.83	2.56	2.20	44.32	1.71	1.52	44.74	1.53	1.35
Total extractives (%)	6.10	13.16	1.59	6.77	12.66	1.66	6.47	14.62	1.89	8.36	15.80	2.57
Total lignin content (%)	33.33	4.90	3.25	32.70	4.12	2.66	31.12	8.19	5.07	31.33	3.03	1.90
Holocellulose content (%)	60.40	2.73	3.03	60.30	3.68	4.43	62.33	5.68	7.04	60.20	3.43	3.67
Ash content (%)	0.17	43.25	0.13	0.23	35.50	0.16	0.08	55.76	0.08	0.12	32.78	0.08
Higher heating value (MJ kg^{-1})	19.36	0.25	0.09	19.69	0.26	0.10	19.41	0.54	0.19	19.37	0.46	0.17
Properties of charcoal												
Gravimetric yield (%)	37.29	2.61	1.75	36.27	3.62	2.30	34.79	1.69	1.16	35.58	3.46	2.46
Apparently density (g cm^{-3})	0.37	12.37	0.08	0.36	4.84	0.03	0.30	3.30	0.02	0.38	16.66	0.11
Ash content (%)	0.31	32.37	0.18	0.35	29.04	0.19	0.28	30.28	0.14	0.27	54.58	0.30
Volatile matter content (%)	25.63	9.14	4.47	27.38	9.13	4.45	26.06	10.13	5.28	27.34	5.62	2.87
Fixed carbon content (%)	74.06	3.03	4.28	72.27	3.36	4.25	73.66	3.69	5.42	72.38	2.28	3.02
Higher heating value (MJ kg^{-1})	31.03	2.30	1.42	30.04	1.69	0.92	30.63	2.80	1.69	30.17	0.97	0.58

CV = Coefficient of variation (%); AMP = Amplitude of data

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