Influence of Chemical Composition of *Eucalyptus* Wood on Gravimetric Yield and Charcoal Properties

Bárbara L. Corradi Pereira,[a,]* Angélica de C. O. Carneiro,[a] Ana Márcia M. L. Carvalho,[a] Jorge L. Colodette,[a] Aylson Costa Oliveira,[a] and Maurício P. F. Fontes [b]

The objective of this study was to assess the chemical properties of wood from six clones of *Eucalyptus* spp. relative to charcoal yield and its properties, determine the correlations between the evaluated parameters and identify a clone of *Eucalyptus* having the greatest potential for charcoal to steelmaking use. The study of chemical properties included analysis of elemental composition, contents of cellulose, hemicelluloses, lignin, and ash, the syringyl/guaiacyl ratio (S/G), and the index of crystalline cellulose in the wood. The pyrolysis of wood was done in an electric laboratory oven. The gravimetric yield in charcoal, the content of volatile matter, fixed carbon and ash, higher heating value, and elementary composition were determined. Data were subjected to an analysis of variance, and after the difference between them was established, the Tukey test was applied. The Pearson correlation was employed as well. The results indicated that the contents of carbon, oxygen, and hydrogen in the wood significantly affected the charcoal yields and its higher heating value. Higher rates of crystalline cellulose favored the gravimetric yield in charcoal. The S/G ratio contributed more to the charcoal yield when compared to total lignin content.

Keywords: Crystalline cellulose; Syringyl/guaiacyl ratio; Charcoal quality

*Contact information: a: Departamento de Engenharia Florestal, Universidade Federal de Viçosa, Viçosa, Minas Gerais, Brazil, 36570-000; b: Departamento de Solos, Universidade Federal de Viçosa, Viçosa, Minas Gerais, Brazil, 36570-000;*Corresponding author: babicorradi@gmail.com*

INTRODUCTION

Brazil is the only country that produces charcoal on a large scale to be used in industry; the country is known to be the greatest producer and consumer of the product. About 17.8 million cubic meters of charcoal from planted forests are produced annually in the country (ABRAF 2013). Consumption is primarily focused on the internal market; only 0.1% of the charcoal production is exported. (ABRAF 2013).The main destinations are the sectors of pig iron and steel manufacturing, which consume 72% of the produced charcoal, iron alloy, which consumes 12% of the produced charcoal, followed by residential uses (residential cooking and heating), other industrial uses (excluding the steel industry), and the production of cement, chemicals, food, and ceramics (EPE 2012). A good part of the secondary products, iron and steel, for example, is exported, demonstrating the importance of the international scenario for the forest sector in Brazil.

Eucalyptus is the genus most commonly used in reforestation programs in Brazil in order to meet the demand of various forest-based industries. Conditions relating to soil and climate as well as land ownership, together with the historical policies of investment in research and development have led to the highest average productivity, 40.7 m^3/ha·year in 2011 (ABRAF 2013). The potential of *Eucalyptus* as a producer of wood quality, allied with advances in silviculture practices, optimizing forest management, and genetic improvement provides Brazil with a comparative advantage in the production of raw materials from planted forests.

The selection of superior genetic material in *Eucalyptus* spp. for charcoal production is based on research on the technological properties of the wood (Trugilho *et al.* 2001; Botrel *et al.* 2007; Santos *et al.* 2011, 2012). Those species and/or clones were selected with characteristics suitable for this purpose, such as high wood density and high lignin content, which ought to be combined with a rapid increase in wood volume. Estimates of wood dry mass, lignin dry mass, carbon mass, and elementary composition are also commonly used parameters in the evaluation of eucalyptus clones for charcoal production.

Botrel *et al.* (2007) affirms that in addition to the analysis of wood, it is also necessary to consider the final production performance of, in this case, charcoal. Thus, the improvement of the raw material in conjunction with the obtained product provides more effective responses. Clonal plantation forestry practices enable the reduction in the variability of the wood properties. Such uniformity subsequently gives rise to an increased charcoal yield based on carbon, as well as desirable properties with respect to its use based on heating value, density, and content of fixed carbon.

Slow pyrolysis of wood or carbonization is a physicochemical process in which the wood is heated at a very slow heating rate in a non-oxidizing atmosphere, and wood residence time is about 4 to 5 days (Mohan *et al.* 2006). The process has a main product, a solid residue rich in carbon, charcoal, and a volatile fraction consisting of non-condensable gasses and condensable organic vapors. In slow pyrolysis (carbonization), wood is heated to temperatures around 450 °C. At this temperature it is possible to connect higher yields of charcoal to quality required in the steelmaking.

Studies have shown that wood decomposition begins at 200 °C, reaches a maximum rate of mass loss at 350 °C, and continues above 500 °C, illustrating the complex contributions of all the chemical constituents (Müller-Hagedorn *et al.* 2003; Poletto *et al.* 2010). Lignin is the most important chemical component of the wood when aiming to produce charcoal. Due to its high level of aromaticity, size, and arrangement of its structure, it has a higher resistance to thermal degradation when compared to cellulose and hemicelluloses (Haykiri-Acma *et al.* 2010).

The cited literature indicates the influence of wood quality on the properties of charcoal (Trugilho *et al.* 2001; Botrel *et al.* 2007; Santos *et al.* 2011). However, there is a lack of studies that investigate the chemical composition of wood; both structural and elemental, to check its influence on the charcoal properties and to better understand the process of pyrolysis of wood.

The objective of this study was to evaluate the chemical properties of wood from the *Eucalyptus* clones, the charcoal yield, and the properties of the charcoal in order to determine the correlations between the properties of wood and those of the resulting charcoal. An additional objective was to identify a clone of *Eucalyptus* having the greatest potential for charcoal to steelmaking use.

EXPERIMENTAL

Material

Six clones of *Eucalyptus* spp. from a clonal test were used (Table 1).

Table 1. General Information about the Different Genetic Materials Studied

Clone	Genetic Material	Origin (Company)	Total Height (m)	Mean Diameter* (cm)	Annual Increment ($m^3.ha^{-1}.year^{-1}$)
1	*Eucalyptus camaldulensis*	Plantar S.A/ Curvelo, MG, Brazil	23.9	15.41	39.6
2	*Eucalyptus urophylla* Hybrid	Gerdau S.A/ Três Marias, MG, Brazil	22.9	14.82	32.4
3	*Eucalyptus grandis* Hybrid	Suzano/ Teixeira de Freitas, BA. Brazil	24.0	16.69	40.7
4	*Eucalyptus urophylla* Hybrid	Gerdau S.A/ Três Marias. MG, Brazil	23.7	15.48	35.9
5	*Eucalyptus urophylla*	V & M Florestal/ João Pinheiro, MG, Brazil	19.9	15.54	31.5
6	*Eucalyptus camaldulensis*	Gerdau S.A/ Três Marias, MG, Brazil	25.0	15.76	40.3

* Diameter at Breast Height (DBH), 1.30 m above ground level.

The six clones of *Eucalyptus* spp. were planted with a spacing of 3.8 x 2.4 m. Plants were then fertilized with 100 g NPK formulation 06:30:06 + 0.5% zinc per plant. Trees were harvested at the age of 7.5 years.

The clones were obtained from a forestry company, located in Lassance, Minas Gerais, Brazil, whose UTM coordinates are: 513262.29W and 7999059.47S. Zone 23S, Datum SAD 69.

The clonal test was conducted in the Brazilian "Cerrado" biome, which is characterized by seasonality; the summer is hot and humid and the winter is cold and dry. The site climate is classified as Köppen Aw, tropical rainy. The average annual temperature is 24 ºC and the annual rainfall index is between 750 and 2000 millimeters (mm) with an annual average of 1800 mm, with precipitation concentrated from October to March. This data was provided by the forestry company that monitors the temperature and precipitation throughout the year.

The predominant soil is Oxisol, which is porous, permeable, well drained, and as a consequence, strongly leached. Most of the texture is sandy and sandy clay, about 25% clay, in the layer of 0 to 40 cm from the surface.

A total of 3 trees, representative of the population from each clone, were used as samples, and the selection was made excluding the trees that had visual defects or were at the edges of the planting area.

Preparation of the Samples

Transversal sections of wood of each tree were collected in portions corresponding to the basis (0%), 25, 50, 75%, and at the top (100%) of merchantable height (minimum diameter of 7 cm), which refer to cumulative height of the tree. Two opposite wedges were obtained from each transversal section, through medulla, heartwood, and sapwood. These portions of wood were used to obtain a composite sample that would be representative of the entire tree. The composite samples were used for analysis.

To perform X-ray diffraction and determine chemical and elementary composition, the wood composite samples were transformed into sawdust using a laboratory Wiley mill according to the TAPPI standard 257 om-52 (TAPPI 1998). Samples of sawdust fractions that were classified between the superposed sieves with 40 and 60 mesh (ASTM 1982) were used for structural chemical analysis and X-ray diffraction. For the elementary chemical composition, a fraction selected between the superposed sieves with 200 and 270 mesh was used (Paula *et al*. 2011; Santos *et al*. 2012).

The pyrolysis of wood was carried out in an electric laboratory oven using approximately 350 g of oven-dry wood (±103 °C). Oven-dried wood was used because it is known that moisture content can affect the charcoal yield and its properties. The samples were inserted in a metallic cylindrical container having a volume of about 0.003 m^3. Laboratory oven temperature control was performed manually. The initial temperature was 100 ºC, and the final temperature was 450 ºC, remaining stable in the last 60 min; therefore, the pyrolysis time was 4.5 h, which corresponds to an average heating rate of 1.67 $ºC \cdot min^{-1}$. These experiment conditions were used according to Trugilho *et al*. (2001), Botrel *et al.* (2007), and Neves *et al*. (2011).

After pyrolysis, the gravimetric yield on charcoal was determined based on the dry mass of the wood. The carbonized samples (charcoal) were ground using a pestle and mortar. For proximate analysis and higher heating value (HHV), samples that were classified between the superposed sieves with 40 and 60 mesh were used, according to ABNT NBR 8112 (ABNT 1986) and ABNT NBR 8633 (ABNT 1984). For the elementary composition, a fraction selected between the superposed sieves with 200 and 270 mesh was used.

Elemental Chemical Composition of Wood

The elementary analysis of wood was done according to the methodology described by Paula *et al*. (2011) and Protásio *et al.* (2012a), as well as instructions contained in the equipment manual for the Elemental Vario Micro Cube CHNS-O model. A mass equivalent to 2.0 mg of dry sawdust was used in a specimen holder made of tin.

The chemical elements carbon (C), nitrogen (N), hydrogen (H), and sulfur (S) were identified using a thermal conductivity detector, for which each element has a specific peak and interaction. The oxygen value was determined as the sum of C, N, H, and S subtracted from 100.

Atomic H/C and O/C ratios of Eucalyptus wood were determined following Pach *et al.* (2002) and Ascough *et al*. (2010):

$$\text{Atomic H/C Ratio} = \frac{\text{number of H atoms}}{\text{number of C atoms}} = \frac{\%H/1}{\%C/12} \quad (1)$$

$$\text{Atomic O/C Ratio} = \frac{\text{number of O atoms}}{\text{number of C atoms}} = \frac{\%O/16}{\%C/12} \quad (2)$$

Structural Chemical Composition of Wood

The determination of absolutely dry content was done according to the standard TAPPI 264 om-88 (TAPPI 1998).

The extractives content of wood was determined according the standard TAPPI 204 om-88 (TAPPI 1998) using a determination method of total extractives, only substituting ethanol/benzene with ethanol/toluene.

Soluble and insoluble lignin content was determined following specialized standards (Goldschimid 1971; Gomide and Demuner 1986). An acidic hydrolysis was made with sulfuric acid 72% in 0.3 g of sawdust at 30 ºC for 1 h. After this, the mixture was diluted to 3% and submitted to another hydrolysis at 2 atm pressure and 121 ºC for 1 h. The insoluble lignin content was determined by filtration and the soluble lignin content by UV spectroscopy. Total lignin was obtained by the sum of insoluble and soluble lignin.

To determine the content of cellulose and hemicelluloses, percentages of carbohydrates (sugar) were calculated according to Wallis *et al*. (1996). The content of cellulose was determined by considering the glucose percentage, excluding the portion of that value attributable to the content of mannose, whose glucose units in glucomannans are present in a ratio of 1:1 relative to mannose (Rowell *et al.* 2005). Percentages of hemicelluloses were calculated from the difference between the mass of extractives-free wood and the sum of cellulose and total lignin.

The ash percentage in wood was determined according to the standard TAPPI T-15 wd-80 (TAPPI 1998).

The syringyl/guaicyl ratio (S/G) of lignin was determined by means of liquid chromatography after oxidation of sawdust free of extractive with nitrobenzene, as described by Lin and Dence (1992).

To evaluate the crystalline cellulose, wood samples were characterized by X-ray diffraction following procedures described in the literature (Fengel and Wegner 1989). The analysis of X-ray diffraction was carried out at room temperature with a Diffractometer X-ray System model X' Pert PRO (PANanlytical) using a Ni filter and Co-ka radiation (λ = 1.78890 Å), angular variation of 5-50 (2θ), velocity of 3º/min, voltage of 40 kV, and current of 30 mA.

The index of crystalline (IC) of the cellulose was calculated by the method of Segal *et al*. (1959), which is determined by the ratio between the peak of the maximum (2θ = 26.15°) and minimum (2θ = 20.91°) intensity of diffraction after the baseline correction. The software Origin 8.0 was used (ORIGINLAB 2007).

Charcoal Properties

The higher heating value of charcoal was determined according to the methodology described by the standard ABNT NBR 8633 (ABNT 1984) using an adiabatic calorimeter bomb IKA300.

Proximate analysis of charcoal that corresponds to the content of volatile matter, ash, and fixed carbon on a dry basis was determined according to the standards ABNT NBR 8112 (ABNT, 1986) and ASTM D 1762-84 (ASTM, 2007).

For the determination of elementary composition (carbon, nitrogen, hydrogen, sulfur, and oxygen), the same procedure adopted for the elementary chemical composition of wood was used.

Fixed carbon yield was determined according to Antal *et al.* (2000) and also used by Oyedun *et al.* (2012):

$$\text{Fixed Charcoal Yield} = \frac{\text{Charcoal yield x (100}-\text{\%volatile matter}-\text{\% char ash)}}{100-\text{\% wood ash}} \qquad (3)$$

Statistical Analysis

The experiment was conducted according to a randomized design with six treatments (clones) with three replicates (tree-sample), giving a total of 18 sampling units.

Data normality was verified by Lilliefors test and homogeneity of variance by Hartley, Cochran, and Bartlett; these assumptions were fulfilled.

Data were subjected to analysis of variance, and when significant differences were established, treatments were compared through Tukey test at 5% probability.

Correlation between the evaluated properties was determined by Pearson's correlation coefficient (r). The Student's *t* test was used to establish if the correlation coefficient is significantly different from zero. The Pearson correlation was considered significant when the p-value was less than 0.05.

RESULTS AND DISCUSSION

Elementary Chemical Composition of Wood

For the elementary chemical composition, the analysis of variance indicated that the clone effect was significant at a 95% level of confidence only for the nitrogen content, as shown in Table 2. It was found that the average contents of carbon, hydrogen, and oxygen were 45.41, 5.80, and 48.67%, respectively. It is noteworthy that the contents of these elements presented significant differences at a 90% level of confidence (Table 2).

Traces of sulfur were also verified for the wood clones 1, 2, and 3: 0.015%, 0.003%, and 0.009%, respectively for each clone. The other clones showed no detectable sulfur contents.

Table 2. Mean Values of Nitrogen, Carbon, Hydrogen, and Oxygen of *Eucalyptus* spp. Wood in Percentage and H/C and O/C ratios

Clone	Nitrogen *	Carbon**	Hydrogen**	Oxygen[a]**	H/C	O/C
1	0.10ab (0.01)	45.70ab (0.56)	5.86ab (0.07)	48.32ab (0.63)	1.54 (0.003)	0.79 (0.020)
2	0.11ab (0.01)	45.92ab (0.86)	5.91ab (0.09)	48.06ab (0.93)	1.54 (0.007)	0.79 (0.030)
3	0.12a (0.01)	44.80ab (0.84)	5.70ab (0.10)	49.38ab (0.93)	1.53 (0.003)	0.83 (0.031)
4	0.10ab (0.01)	43.76b (1.90)	5.58b (0.26)	50.55a (2.17)	1.53 (0.011)	0.87 (0.075)
5	0.09b (0.01)	47.11a (1.89)	5.96 a (0.23)	46.83b (2.12)	1.52 (0.003)	0.75 (0.073)
6	0.10ab (0.01)	45.19ab (0.53)	5.82ab (0.06)	48.89ab (0.59)	1.55 (0.005)	0.81 (0.019)

[a]Calculated by difference; *Significant of 5% of probability; **Significant of 10% of probability. (...)Standard deviation; Means in the column followed by the same letter do not differ at 5% of probability by the Tukey Test.

According to Unger *et al.* (2001), in disregard of minor quantities of nitrogen and other elements such as sulfur, wood is considered to be comprised of approximately 50% carbon, 6% hydrogen, and 44% oxygen. Trugilho *et al*. (2012) determined the wood elementary chemical composition of 15 *Eucalyptus* clones for bioenergy, and the authors found 47.21 to 49.93% of carbon, 4.88 to 6.12% of hydrogen, 0.30 to 2.43% of nitrogen, and 43.11 to 46.02% of oxygen. These values are in agreement with those found in the present study.

Even if the differences are minimal, when the objective is the generation of energy from wood, either through combustion, pyrolysis, or gasification, those species with higher percentages of carbon and hydrogen should be preferred. According to Trugilho *et al*. (2012), the elemental composition is important for the characterization of fuel because the energy generated by thermal degradation is associated with the enthalpy of carbon, hydrogen, and sulfur. This is due to the fact that carbon and hydrogen are the elements that contribute most to the calorific value of fuel (Demirbas and Demirbas 2004; Protásio *et al*. 2011). By contrast, oxygen is generally present in plant-based fuels, and its presence decreases the calorific value of fuel (Huang *et al*. 2009; Protásio *et al*. 2011). Therefore, low H/C and O/C ratios are desirable for the use of wood for energy.

The Van Krevelen diagram (Fig. 1) shows the differences in the elemental composition of typical solid fuels, plotting H/C *vs*. O/C ratios. In the diagram, the information about the wood of eucalyptus clones and charcoal are also presented.

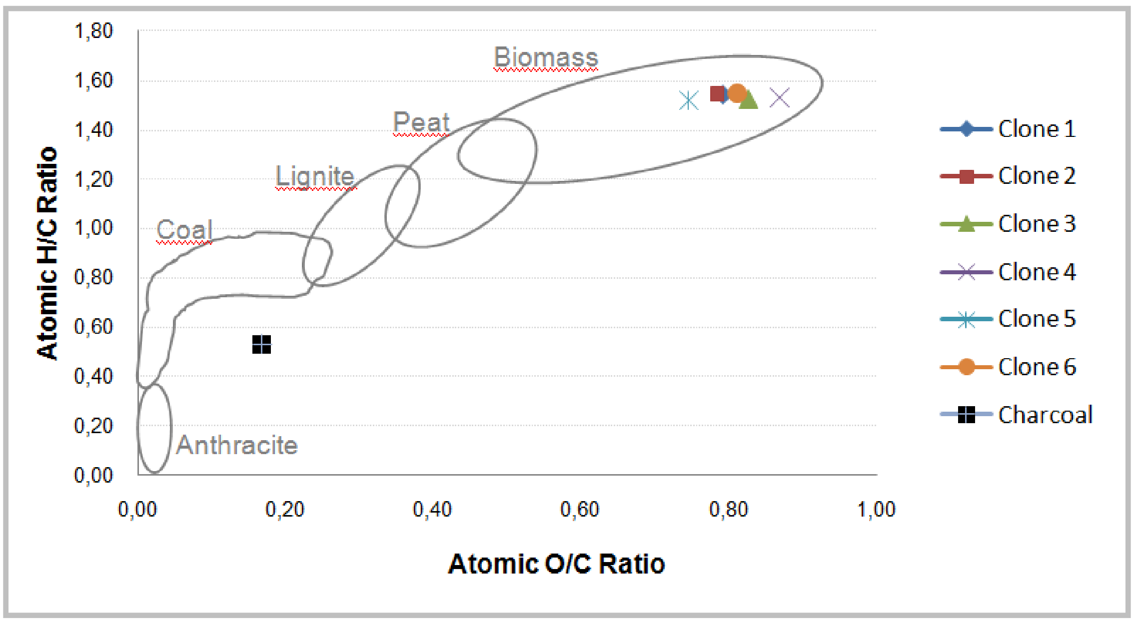

Fig. 1. Van Krevelan diagram showing atomic O/C and H/C ratios of *Eucalyptus* spp. wood and charcoal. Comparison data was obtained from Van Loo and Koppejan (2008).

Wood showed variation from 1.52 to 1.55 for H/C and 0.75 to 0.87 for O/C, and clone 5 showed the lowest values for both ratios. This is because the wood of clone 5 showed the highest percentages of hydrogen and carbon and a lower percentage of oxygen.

It is clear that wood compared to charcoal contains more oxygen. It can be seen that carbon content increases, while oxygen and hydrogen contents decrease as lignocellulosic structures are degraded during pyrolysis.

Besides the energy capacity of renewable fuels, environmental aspects must also be considered, with regard to the quantities of sulfur and nitrogen. If the raw material has high levels of nitrogen, then the formation of nitrous oxides and nitric acid may occur during pyrolysis and its release into the atmosphere can cause negative environmental impacts (Yuan *et al*. 2011). Emissions of sulfur oxides are minimal, due to lower levels of sulfur found in the majority of biomass fuels (Baxter and Koppejan 2004).

The low levels of nitrogen and sulfur in the wood, 0.09 to 0.12% and 0 to 0.01%, respectively, contribute so that the charcoal will be environmentally more advantageous than the use of mineral coal.

Structural Chemical Composition of Wood

In Table 3, the mean values for the chemical components of wood in the *Eucalyptus* clones are evaluated. In addition, results of the multiple comparison tests are indicated by the letters.

Table 3. Mean Values of Cellulose, Hemicelluloses, Lignin, Extractives, Ash, and S/G ratio of *Eucalyptus* spp. Wood

Clones	Cellulose (%)	Hemicelluloses[a] (%)	Lignin[a] (%)	Extractives (%)	Ash (%)	S/G
1	47.6 ab (0.60)	22.1 ab (0.33)	30.3 ab (0.49)	4.3 ab (0.24)	0.16 ab (0.02)	2.75 b (0.09)
2	46.1 b (0.13)	22.5 a (0.41)	31.4 a (0.32)	5.0 a (0.42)	0.14 ab (0.01)	2.95 a (0.05)
3	48.2 a (0.25)	22.0 ab (0.71)	29.8 bc (0.74)	4.1 b (0.20)	0.12 ab (0.01)	2.75 b (0.00)
4	48.8 a (0.68)	22.4 ab (0.30)	28.8 c (0.77)	4.7 ab (0.21)	0.10 b (0.02)	2.33 c (0.08)
5	48.4 a (1.13)	21.9 b (1.03)	29.7 bc (0.24)	4.8 ab (0.11)	0.11 ab (0.04)	2.70 b (0.05)
6	47.2 ab (0.64)	22.4 a (0.89)	30.4 ab (0.33)	3.1 c (0.29)	0.18 a (0.05)	2.35 c (0.09)

[a] Wood free of extractives. S/G= Syringyl/Guaicyl ratio. (...)Standard deviation. Means in the column followed by the same letter do not differ from each other at a probability level of 5% by the Tukey test.

When planning to use wood for the charcoal production, wood with lower percentages of cellulose and hemicelluloses should be preferred because these components present low resistance to thermal degradation, having maximum peaks of mass loss at approximately 275 ºC for hemicelluloses and 350 ºC for cellulose (Yang *et al.* 2007; Shen *et al.* 2010). Thus, these components do not contribute significantly to the charcoal yield, but they do contribute significantly to condensable and non-condensable gases.

In regards to the lignin content, which is the most important component when the purpose of wood is the production of charcoal, clones 1, 2, and 6 showed great potential. This is due to the high resistance to thermal degradation of lignin when compared to cellulose and hemicelluloses because of high level of aromaticity, size, and arrangement in lignin structure (Haykiri-Acma *et al.* 2010). A minimum lignin content of 28% is required by large companies that produce charcoal; thus, a *Eucalyptus* clone must meet this threshold to be considered for planting. Lignin contents that were verified in the clones under the study are considered satisfactory for the charcoal production and are in accordance with other studies in which the *Eucalyptus* clones were studied for the same purpose. For example, Santos *et al*. (2011) and Arantes *et al*. (2011) reported mean values of total lignin of 32.00 and 29.75%, respectively.

The chemical composition of wood influences the charcoal quality and yield; high lignin contents have contributed to higher gravimetric yield in charcoal and higher content of fixed carbon (Vale *et al*. 2010; Protásio *et al*. 2012b). This fact is related to the higher resistance to thermal degradation of lignins when compared to holocelluloses, mainly due to the larger number of C-C and C=C bonds present in its structure and because the lignin has a high percentage of elementary carbon and low oxygen when compared to other chemical components of wood (Rowell *et al.* 2005).

The extractives contents verified in this study have also been confirmed in the work by Santos *et al*. (2011), who found mean contents of 5.0% of extractives for four clones of 7-year-old *Eucalyptus* spp. This result can also be observed in the study done by Arantes *et al*. (2011) who obtained mean extractives contents of 2.91% for a clone of *E. grandis* x *E. urophylla* at an age of 6 years.

Wood extractives are a group of cell wall chemicals that include lipids, phenolic compounds, terpenoids, fatty acids, resin acids, steryl esters, sterol, waxes, and many other minor organic compounds (Rowell *et al.* 2005). The presence of extractives may increase or decrease the charcoal gravimetric yield. This fact depends on the chemical composition of extractives (Santos *et al.* 2011), especially their C/H ratio and, therefore their thermal stability.

According Shebani *et al*. (2008), *Eucalyptus* woods contain more polar extractives, comprised of tannins, gums, sugars, starches, and colored matter. A majority of these compounds degrade within the range 200 to 500 ºC (Grønli *et al.* 2002; Shebani *et al.* 2008) due to the chemical nature of extractives in young *Eucalyptus* trees. The degradation of polar extractives can result in a reduction of charcoal gravimetric yield, as verified in this study.

Despite the significant differences in the ash content between the clones, the values obtained are considered low. The maximum value found was 0.18%, which was also reported by Soares (2011) when evaluating a 7-year-old clone of *E. grandis* x *E. urophylla*. According to Barcellos *et al*. (2005) the mineral content of *Eucalyptus* wood corresponds, in general, to less than 1%. The presence of a high content of inorganic components in wood is also not desirable in charcoal production. Inorganic components are not degraded during pyrolysis, and therefore are undesirable during the use of charcoal in the production of any types of iron alloys. Specifically, the iron alloys become brittle and less malleable and become more prone to the propagation of cracks and fissures.

The S/G ratio presented variations of 2.33 (clone 4) to 2.95 (clone 2). Clone 6 also had a low S/G ratio of 2.35, whereas that of clones 1, 3, and 5 had an intermediate S/G ratio around 2.70. According to the results, the clones that presented lower S/G ratios also stood out as a source of raw material for charcoal production. For such regard, clone 4 should not be considered. Although it had a low S/G ratio, this clone did not stand out in lignin content, for example, which is an important property when the wood is intended for charcoal production.

These observations are consistent with the few existing studies, verifying that the lowest S/G proportion led to higher gravimetric yield in charcoal (Santos 2010; Soares 2011). However, this relation is not yet well established, and there is a need for further research on this subject.

The fact that lower S/G ratios are associated with higher charcoal yield can be attributed to its guaiacyl units having only one methoxyl group ($-OCH_3$) bond to C3, where there is a steric hindrance for bonds. In these aromatic units, the C5 positions are available to make bonds, and such bonds have high stability, whether it is a C-bond or an ether bond. Therefore, when there are larger amounts of units in this type of lignin composition, they are characterized by higher polymerization, then higher quantity of energy is required to break the bonds and hence more stable during the pyrolysis of wood. The syringyl units have a methoxyl group bonded to the C3 and C5 carbons. Since these positions are sterically hindered for bond formation, the lignin of type guaicyl-syringyl that have higher proportions of these units will be less condensed and consequently less stable to thermal degradation.

Figure 2A shows the X-ray diffraction results referring to the wood clones. Figure 2B shows the index of crystalline cellulose of wood of the evaluated clones, calculated from the diffractograms.

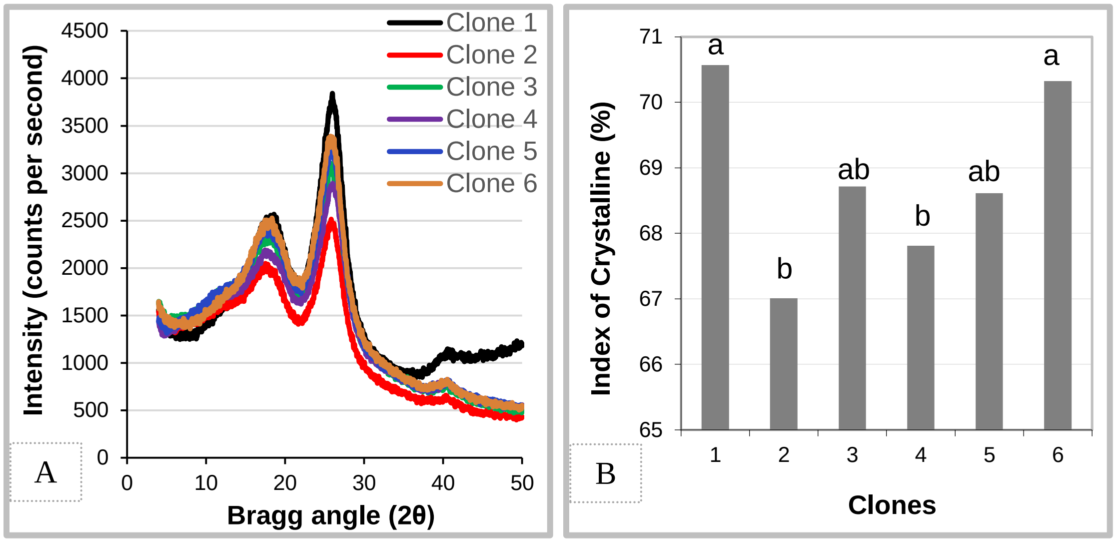

Fig. 2. (A) X- ray diffractions of *Eucalyptus* spp., wood clones 1 and 2. (B) Mean values of Index of crystalline of *Eucalyptus* wood. Standard Deviations: Clone 1 = 0.33; Clone 2 = 0.42; Clone 3 = 1.53; Clone 4 = 0.10; Clone 5 = 0.71; Clone 6 = 0.11. Means followed by the same letter do not differ at 5% probability according to the Tukey test.

Despite the interference of the amorphous regions of celluloses, the presence of peaks corresponding to the crystallographic planes in the following Bragg angle (2θ) was observed: 18.2 (plane 101); 26.1 (plane 002); and 40.9 (plane 040). The X-ray results exhibited peaks characteristic of the crystalline planes characteristic of lignocellulosic materials, where the reflection can be seen (002) as more intense for all the clones.

Clone 1 and 6 presented the highest index of crystallinity, 70.6 and 70.3%, respectively, and the wood clones 2 and 5 were found to have the lowest index of crystallinity, 67.0 and 67.8%, respectively. Meanwhile, the clones 3 and 5 presented intermediate mean values, 68.7 and 68.67.

It is assumed that wood having a higher index of crystallinity will be more resistant to thermal degradation, which would contribute to higher charcoal yield. This hypothesis is based on studies that demonstrate that the amorphous region of cellulose is more susceptible to heat action and have lower thermal stability compared to crystalline regions (Kim *et al.* 2010; Poletto *et al.* 2012). According to Poletto *et al.* (2012), this occurs due to a higher amount of hydrogen bonding between cellulose chains that can result in a more condensed structure with higher index of crystalline and thermal stability. Moreover, the intermolecular hydrogen bonds stabilize the cellulose molecules and may inhibit thermal expansion (Hidaka *et al.* 2010), improving the thermal stability of wood.

In the present study, it was found that wood with a higher index of crystallinity also presented higher charcoal yield, such as clones 1 and 6, while the clones with a lower index of crystalline (clones 2 and 4) obtained the lowest charcoal yield. However, it cannot be affirmed that the crystallinity directly influences the charcoal yield in isolation, since the clones with a higher index of crystalline presented higher wood density, higher lignin content, and lower S/G ratio, factors that together can contribute to the increased charcoal yield.

Clone 6 showed a low S/G ratio, high crystallinity index, low contents of extractives, high contents of lignin, and the highest annual increment (Table 1). Thus, according to the results for the chemical properties of wood, clone 6 showed superior characteristics for the production of charcoal in relation to the others.

Gravimetric Yield in Charcoal

The mean gravimetric yield in charcoal obtained for the different clones are considered satisfactory (Table 4), according to research developed by Trugilho *et al.* (2001), Botrel *et al.* (2007) and Santos *et al*. (2011). Antal *et al.* (2000) found that the average commercial charcoal yield does not exceed 30%, not only due to the fact that the raw material influences the charcoal yield, but also due to the process of conversion that was used.

Table 4. Gravimetric Yield in Charcoal (%) and their Correlations(r) with the Wood Properties, Regardless of the Clone

Gravimetric Yield in Charcoal						
Clones	1	2	3	4	5	6
GYC (%)	34.96 ab$^{(0.47)}$	34.71 ab$^{(0.09)}$	34.93 ab$^{(0.44)}$	34.33 b$^{(0.72)}$	35.40 ab$^{(0.23)}$	35.76 a$^{(0.55)}$

Pearson Correlations(r): Gravimetric Yield in Charcoal and Wood Chemical Properties									
Variable	C	H	O	Extractives	Lignin	Cellulose	Hemicelluloses	IC	S/G
GYC	0.50*	0.61*	-0.51*	-0.51*	0.31	-0.32	-0.20	0.50*	-0.58*

GYC = Gravimetric yield in charcoal. Means in line followed by the same letter do not differ at 5% probability of Tukey Test. $^{(...)}$Standard deviation. * Significant correlations at 5% probability ($p<0.05$).

The wood properties determine the charcoal quality and yield together with the production process used. In this study, the chemical composition exerted great influence on the charcoal yield.

The chemical composition of wood influenced the gravimetric yield in charcoal expressively, contributing to the best performance in charcoal production. The wood presented a set of chemical properties with high total lignin content, low extractives content, high index of crystalline, and low S/G ratio.

The carbon and hydrogen contents were positively correlated with the charcoal yield, and the oxygen presented a negative correlation. This is possibly due to the disruption of less stable bonds during the pyrolysis, such as the C-O-C bond with oxygen loss, and therefore oxygen content contributed negatively to gravimetric yield in charcoal. It is to be expected that structures that contain C-C or C=C bonds with lignin will give larger charcoal yields.

Although there was a positive tendency in the relation between the lignin content and negative between the cellulose content with the charcoal yield, as can be seen in Table 4, both showed no significant correlation. Trugilho *et al*. (2001) found no significant correlation between lignin content and charcoal gravimetric yield. For this reason, these authors argue that despite the importance of the high lignin content for charcoal production, this characteristic cannot be used alone as a parameter for the classification of wood for energy purposes.

In the present study, the effects of the S/G ratio and the index of crystalline had dominant effects on the charcoal yield. It was observed that the highest index of crystalline and lowest S/G ratio promoted an increase in the charcoal yield. The structure of crystalline cellulose and the highest proportions of guaiacyl units contributed to increase the resistance of thermal degradation of wood and, consequently, the increase of charcoal yield.

In other words, the results showed that the quality of lignin (S/G ratio) is more relevant than the lignin contents to charcoal production. Wood with high thermal stability is preferable if the objective is a high yield into charcoal, and therefore low S/G ratio should be sought.

Properties of Charcoal

The Higher Heating Value (HHV) of charcoal (Table 5) is superior to wood because most of the components that have less stable bonds in wood are degraded during pyrolysis, favoring the compounds that have bonds that are more resistant to the heat action, such as the aromatic rings present in the lignin structure. Lignin's fundamental units are linked by a multitude of inter-unit bonds including ether and carbon–carbon linkages (Rowell *et al.* 2005), whereas energy contained in the C–C bond is higher than C–O or C–H bonds (Phanphanich and Mani 2011). The relative increase in carbon content due to thermal degradation, directly results in higher calorific value (Phanphanich and Mani 2011), as lower H/C and O/C atomic ratios, implying that the charcoal became more aromatic and carbonaceous than wood (Fu *et al*. 2011), as shown in Fig. 1. The average values of H/C and O/C for charcoal were 0.531 and 0.168, respectively.

It is noteworthy that the calorific value of charcoal from the clones evaluated presented an energetic mean increase of 61.3%.

Table 5. Higher Heating Value of Charcoal (kcal.kg^{-1}) and their Correlation with the Chemical Properties of Wood, Regardless of the Clone

Higher Heating Value of Charcoal						
Clones	1	2	3	4	5	6
HHV (kcal.kg^{-1})	7413.1 b (23.50)	7502.1 ab (115.50)	7490.1 ab (100.55)	7069.7 c (59.04)	7616.3 a (54.74)	7547.1 ab (15,91)

Significant Correlations (r): Higher Heating Value of Charcoal and Wood Chemical Properties				
Variables	Carbon	Hydrogen	Oxygen	Lignin
HHV	0.58* (p value=0,011)	0.58* (p value=0,011)	-0.58* (p value=0,011)	0.49* (p value=0,039)

HHV charcoal= Superior Calorific Value of charcoal in kcal.kg^{-1}. Means in the line followed by the same letter do not differ at 5% probability by Tukey test. (...)Standard deviation. *Significant correlations at 5% probability (p<0.05).

It was found that the total lignin content positively influenced the HHV of charcoal (Table 5). Basically the same correlation was also observed by Santos *et al*. (2011), who found a correlation coefficient equal to 0.59. It was also observed that the HHV of charcoal presented a significant correlation with elemental analysis of wood, a positive correlation with the carbon and hydrogen contents, and a negative correlation with the oxygen content. Such correlations can be due to the lignin that has more stable bonds to the thermal degradation. The C-C bonds are more stable than the C-O bonds, therefore requiring more energy for their degradation (Phanphanich and Mani 2011) and about 60% of the elementary carbon in its composition and 35% of oxygen (Pereira 2012).

The wood that was more lignified provided the charcoal production with a higher calorific value due to the preferential degradation of components rich in oxygen, cellulose, and hemicelluloses, and as a consequence, there was a concentration of carbon in charcoal. Hydrogen is the element of higher calorific value of wood and although it is present in small quantities, a higher percentage of hydrogen will contribute to an increase in the HHV of charcoal.

The charcoal with different clones evaluated in this study, in general, presented fixed carbon content and volatile matter slightly different from those desirable for the steel industry, 75 to 80% of fixed carbon and 20 to 25% of volatile materials (Table 6).

Table 6. Levels of Volatile Matter, Fixed Carbon, and Ash (%) in Charcoal and their Correlation with the Chemical Properties of Wood, Regardless of the Clone

Proximate Analysis of Charcoal						
Clones	1	2	3	4	5	6
VM (%)	26.72 a (0.49)	24.76 bc (0.34)	25.79 abc (0.78)	25.74 abc (0.25)	26.08 ab (0.96)	24.23 c (0.04)
FC (%)	72.93 c (0.44)	74.91 ab (0.32)	73.86 abc (0.78)	73.86 abc (0.36)	73.56 bc (0.96)	75.13 a (0.11)
CA (%)	0.35 b (0.06)	0.33 b (0.07)	0.35 b (0.02)	0.41 b (0.13)	0.36 b (0.04)	0.64 a (0,09)

Significant Correlations (r): Proximate Analysis of Charcoal and Wood Properties					
Variables	Extractives	Lignin	Cellulose	Hemicelluloses	Ash - Wood
VM	0.46*	-0.40	0.54*	-0.40	-0.15
FC	-0.32	0.48*	-0.57*	0.38	0.09
CA	-0.72*	-0.09	-0.09	0.34	0.54*

Means in line followed by the same letter do not differ at 5% probability by Tukey test. (...)Standard deviation. *Significant correlations, 5% of probability ($p<0.05$). VM= volatile matter, in %, CA = charcoal ash in % and FC= fixed carbon, in %.

It is notable that the ash content of charcoal in clone 6 was significantly higher than the other clones, but lower than the maximum desirable for the use of steel, which establishes that the ash content should be lower than 1%. The presence of ash in charcoal should be kept to a minimum to reduce its adverse effect on calorific value. Ash causes wear on the blast furnace and it influences the cleaning operations in the industry. It also tends to compromise the quality of pig iron, due to the phenomenon of segregation.

It is remarkable that among all of the properties evaluated, only the chemical composition of wood presented a significant correlation with the content of fixed carbon, volatile matter, and charcoal ash (Table 6).

It appears that the content of volatile matter presented a significant correlation with the extractives content and cellulose content. The wood clones with higher cellulose contents also presented higher volatile matter contents of charcoal; this is possibly due to the cellulose, which contributes less in fixed carbon. It is noteworthy that levels of fixed carbon and volatiles were inversely proportional.

It was observed that the fixed carbon content of charcoal was positively correlated with lignin content and negatively with cellulose content. The wood cellulose degrades at temperatures below the final temperature of pyrolysis (Yang *et al*. 2007) and contributes little to the concentration of carbon content in charcoal. On the other hand, the lignin, due to its thermal stability and higher carbon content in its composition, will contribute to the increase of fixed carbon in charcoal. Campos (2008), among other authors, reported a correlation coefficient of 0.8 between the fixed carbon of charcoal and lignin content.

There was a positive correlation between the wood ash and charcoal ash content since the inorganic compounds are noted as degraded during carbonization. This correlation was also found by Soares (2011), who found a correlation coefficient of 0.93.

The analysis of variance did not indicate significant differences between the elementary components of charcoal of *Eucalyptus* clones. Mean levels of 78.03% of carbon, 18.42% of oxygen, 3.45% of hydrogen, and 1.05% of nitrogen were observed (Fig. 3). All clones showed no detectable sulfur contents in charcoal. Probably, the contents of sulfur are volatilized during wood pyrolysis.

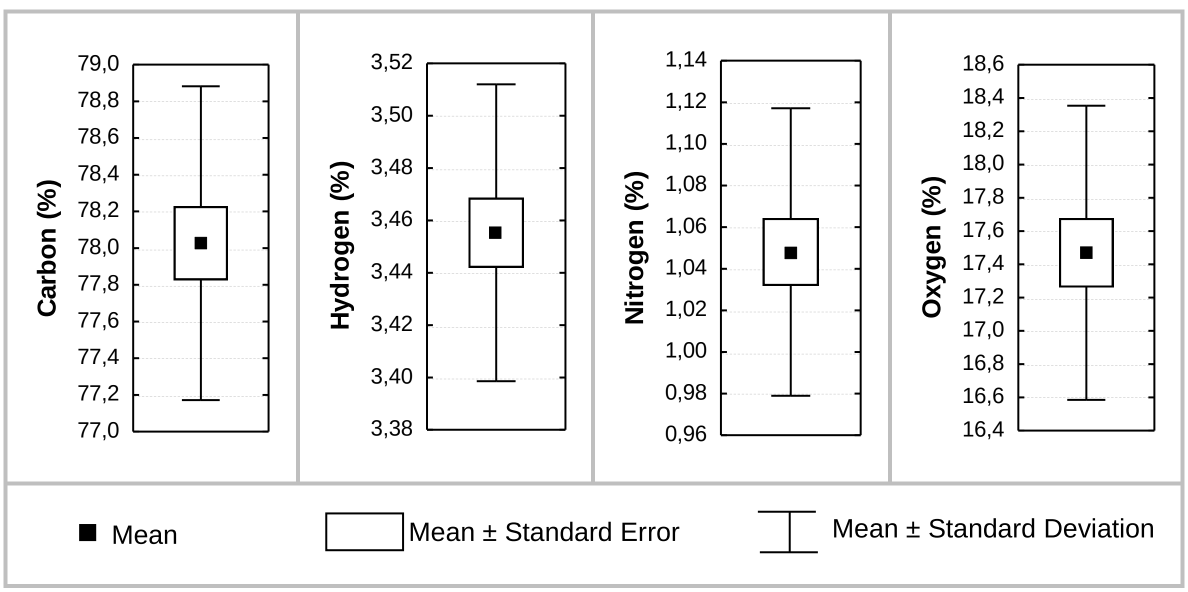

Fig. 3. Mean levels of carbon, hydrogen, nitrogen, and oxygen in charcoal

The results found are consistent with the mean values presented by Oliveira *et al*. (2010) and Soares (2011). The fixed carbon content in charcoal was less than the elementary carbon content, because the first analysis of carbon is eliminated in a volatile matter.

It is important that the carbonization of wood aims broadly to concentrate carbon and eliminate oxygen while consequently increasing the energy content of the final product. Considering that the wood clones evaluated presented mean contents of 45.41% of carbon, 48.67% of oxygen, and a mean gravimetric yield of charcoal of 34.90%, it can be inferred that the charcoal stored an average 60.0% of carbon from wood, while 86.8% of oxygen were volatilized.

As mentioned by Yang *et al*. (2007), part of the carbon present in lignin, cellulose, and hemicelluloses reacts with hydrogen and oxygen when submitted to pyrolysis and transforms into non-condensable gases, such as CO, CO_2, C_nH_n, and condensable gases. Most of the degraded carbon mainly showed C-O-C bonds that are characteristic of cellulose and hemicellulose, as well as remaining compounds containing carbons with C-C and C=C bonds that are characteristic of lignin. The oxygen present in wood has mainly single bonds to hydrogen or carbon, and during the thermal degradation of wood these are mostly lost. Therefore the oxygen bonds are present in small proportions of charcoal (Atkins and Jones 2006).

Figure 4 displays mean values of fixed-carbon yields of the evaluated eucalyptus clones. Clone 6 stood out compared to the others, and it presented 26.9% of fixed-carbon yield, followed by clones 5 (26.1%), 2 (26.0%), 3 (25.8%), 1 (25.5%), and 4 (25.4%).

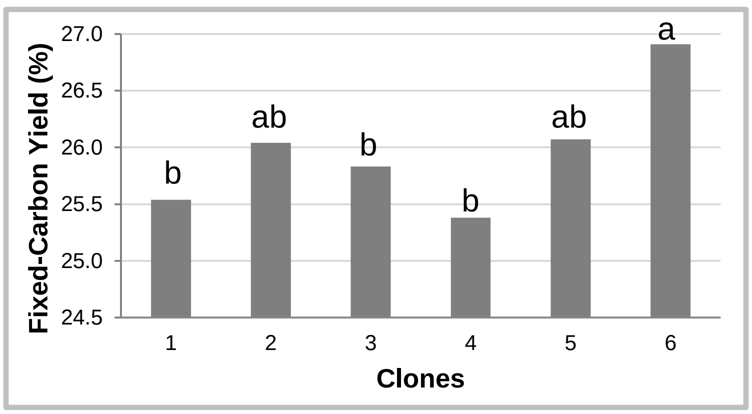

Fig. 4. Mean values of fixed carbon yield of *Eucalyptus* clones. Standard Deviations: Clone 1 = 0.42; Clone 2 = 0.15; Clone 3 = 0.21; Clone 4 = 0.43; Clone 5 = 0.50; Clone 6 = 0.41. Means followed by the same letter do not differ at 5% probability according to the Tukey test.

According to Oyedun *et al*. (2012), the fixed yield can be used as a measure of the efficiency of the process. This is an important property when it is intended to indicate a genetic material potential for charcoal production, as fixed carbon yield involves both productivity and quality related to charcoal. Botrel *et al.* (2007) found mean values equal to 25.97%, values close to those found in the present study.

CONCLUSIONS

1. Contents of carbon, oxygen, and hydrogen in wood are associated to the charcoal yield and its calorific value.
2. A higher index of crystalline cellulose favors the gravimetric yield in charcoal, but did not have an important influence on the charcoal properties.

3. Lower S/G ratio contributes more to the charcoal yield when compared to the total lignin content. Overall, a high lignin content contributes to charcoal properties, specifically HHV and fixed carbon.
4. A high extractives content negatively affects the charcoal yield.
5. The results for charcoal yield and its properties indicate the potential of Clone 6 to participate in hybridization and selection programs that aim to charcoal production.

ACKNOWLEDGMENTS

To the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG), the Conselho Nacional de Pesquisa e Desenvolvimento (CNPq), and the Thematic Group of Charcoal "G6".

REFERENCES CITED

Arantes, M. D. C., Trugilho, P. F., Lima, J. T.,Carneiro, A. C. O., Alves, E., and Guerreiro, M. C. (2011). "Longitudinal and radial variation of extractives and total lignin content in a clone of *Eucalyptus grandis* W. Hill ex Maiden x *Eucalyptus urophylla* S. T. Blake," *Cerne*, 17(3), 283-291.

American Society for Testing and Materials (1982). *Standard Methods of Evaluating Properties of Wood-base Fiber and Particles Materials*, Philadelphia, USA.

American Society for Testing and Materials (2007). *Standard Test Method for Chemical Analysis of Wood Charcoal*, Philadelphia, USA.

Antal Jr., M. J., Allen, S. G., Dai, X., Shimizu, B., Tam, M. S., and Grønli, M. (2000). "Attainment of the theoretical yield of carbon from biomass," *Ind. Eng. Chem. Res.* 39, 4024-4031.

Ascough, P. L., Bird, M. I., Scott, A. C., Collinson, M. E., Cohen-Ofri, I., Snape, C. E., and Le Manquais, K. (2010). "Charcoal reflectance measurements: Implications for structural characterization and assessment of diagenetic alteration," *Journal of Archaeological Science* 37(7), 1590-1599.

Associação Brasileira de Normas Técnicas (Brazilian Association of Technical Standards) (1984). "NBR 8633: Charcoal: Determination of the calorific value," ABNT, Rio de Janeiro.

Associação Brasileira de Normas Técnicas (Brazilian Association of Technical Standards). (1986). "NBR 8112: Carvão vegetal: Análise imediata," ABNT,Rio de Janeiro, 1986.

Associação Brasileira de Produtores de Florestas Plantadas – ABRAF, "Statistical Yearbook of ABRAF: base year 2012," Brasília, Brazil, 2013.

Atkins, P., and Jones, L. (2006). *Princípios de Química: Questionando a Vida Moderna e o Meio Ambiente,* Bookman, Porto Alegre.

Barcellos, D. C., Couto, L. C., Muller, M. D., and Couto, L. (2005)."The state of the art of eucalypt timber quality for energy production: a focus on silvicultural treatments," *Biomassa & Energia* 2 (2), 141-158.

Baxter, L., and Koppejan, J., (2004), "Biomass-coal co-combustion: Opportunity for affordable renewable energy," *Euroheat & Power*, Vol. 1/2004.

Botrel, M. C. G., Trugilho, P. F., Rosado, S. C. S., and Silva, J. R. M. (2007). "Genetic improvement of *Eucalyptus* charcoal properties," *Revista Árvore* 31(3), 391-398.

Campos, A. C. M. (2008). "Eucalyptus charcoal: Pyrolysis parameters effects upon wood and its chemical compounds and quality prediction with NIR spectroscopy," Dissertation (Master in Wood Science and Technology), Federal University of Lavras, Lavras, Brazil, 118 pp.

Demirbas, A., and Demirbas, H. (2004). "Estimating the calorific values of lignocellulosic fuels," *Journal Energy, Exploration & Exploitation* 20(1), 105-111.

Empresa de Pesquisa Energética. (2012). "*Balanço Energético Nacional 2012: Ano Base 2011*," Rio de Janeiro.

Fengel, D., and Wegener, G. (1989). *Wood: Chemistry, Ultrastructure, Reactions*, Gruyter, New York.

Fu, P., Yi, W., Bai, X., Li, Z., Hu, S., and Xiang, J. (2011). "Effect of temperature on gas composition and char structural features of pyrolyzed agricultural residues," *Bioresour. Technol*. 102, 8211-8219.

Goldschimid, O. (1971). "Ultraviolet spectra," In: Sarkanen, K. V., and Ludwig, C. H. (eds.), *Lignins*, Wiley Interscience, New York.

Gomide, J. L., and Demuner, B. J. (1986). "Determination of lignin in woody material: Modified Klason method," *O Papel* 47(8), 36-38.

Grønli, M. G., Várhegyi, G., and Di Blasi, C. (2002)."Thermogravimetric analysis and devolatilization kinetics of wood," *Ind. Eng. Chem. Res.* 41, 4201-4208.

Haykiri-Acma, H., Yaman, S., and Kucukbayrak, S. (2010). "Comparison of the thermal reactivities of isolated lignin and holocellulose during pyrolysis," *Fuel Processing Technology* 91, 759-764.

Hidaka, H., Kim, U. J., and Wada, M. (2010)."Synchrotron X-ray fiber diffraction study on the thermal expansion behavior of cellulose crystals in tension wood of Japanese poplar in the low-temperature region," *Holzforschung* 64, 167-171.

Huang, C., Han, L., Yang, Z., and Liu, X. (2009). "Ultimate analysis and heating value prediction of straw by near infrared spectroscopy," *Waste Management* 29, 1793-1797.

Kim, U. J., Eom, S. H., and Wada, M. (2010). "Thermal decomposition of native cellulose: Influence on crystallite size," *Polymer Degradation and Stability* 95, 778-781.

Lin, S. Y., and Dence, C. W. (1992). *Methods in Lignin Chemistry*, Springer Verlag, Berlin.

Mohan, D., Pittman Jr, C. U., and Stelle, P. H. (2006). "Pyrolysis of wood/biomass for bio-oil: A critical review," *Energy & Fuels* 20, 848-889.

Müller-Hagedorn, M., Bockhorn, H., Krebs, L., and Müller, U. (2003). "A comparative kinetic study on the pyrolysis of three different wood species," *Journal of Analytical and Applied Pyrolysis* 68(1), 231-249.

Neves, T. A., Protásio, T. P., Couto, A. M., Trugilho, P. F., Silva, V. O., and Vieira, C.M.M. (2011). "Evaluation of eucalyptus clones in different places seeking to the production of vegetal charcoal," *Brazilian Journal of Forestry Research* 31(68), 319-330.

Oliveira, A. C., Carneiro, A. C. O., Vital, B. R., Almeida, W., Pereira, B. L. C., and Cardoso, M. T. (2010). "Quality parameters of *Eucalyptus pellita* F. Muell. wood and charcoal," *Scientia Forestalis* 38(87), 431-439.

Originlab Corporation. (2007). *ORIGIN version 8.0,* Origin Lab Corporation, Northampton.
Oyedun, A. O., Lam, K. L., and Hui, C. W. (2012). "Charcoal production via multistage pyrolysis," *Chinese Journal of Chemical Engineering* 20, 455-460.
Pach, M., Zanzi, R., and Björnbom, E. (2002). "Torrefied biomass a substitute for wood and charcoal," In: *Proceedings of 6th Asia-Pacific International Symposium on Combustion and Energy Utilization*, Kuala Lumpur.
Paula, L. R., Trugilho, P. F., Napoli, A., and Bianchi, M. L. (2011). "Characterization of residues from plant biomass for use in energy generation,"*Revista Cerne* 17(2), 237-246.
Pereira, B. L. C. (2012). "Wood quality of Eucalyptus for charcoal production," Dissertation (Master in Forest Science), Federal University of Viçosa, Viçosa, Brazil, 92 pp.
Phanphanich, M., and Mani, S. (2011). "Impact of torrefaction on the grindability and fuel characteristics of forest biomass," *Bioresource Technology* 102 (2011), 1246-1253.
Polleto, M., Dettenborn,, J., Pistor, V., Zeni, M., and Zattera, A. J. (2010). "Materials produced from plant biomass. Part I: Evaluation of thermal stability and pyrolysis of wood," *Materials Research* 13(3), 375-379.
Poletto, M., Zatterab, A. J., Fortea, M. M. C., and Santana, R. M. C. (2012). "Thermal decomposition of wood: Influence of wood components and cellulose crystallite size," *Bioresource Technology* 109, 148-153.
Protásio, T. P., Toloni, G. H. D., Guimarães Júnior, M., Bufalino, L., Couto, A. M., and Trugilho, P. F. (2012a). "Canonical correlations between chemical and energetic characteristics of lignocellulosic wastes,"*Cerne* 18(3), 433-439.
Protásio, T. P., Trugilho, P. F., Neves, T. A., and Vieira, C. M. M. (2012b). "Canonical correlation analysis between characteristics of *Eucalyptus* wood and charcoal," *Scientia Forestalis* 40(95), 317-326.
Protásio, T. P., Bufalino, L., Tonoli, G. H. D., Couto, A. M., Trugilho, P. F., and Guimarães Júnior, M. (2011). "Relation between higher heating value and elemental and mineral biomass plant components," *Brazilian Journal of Forestry Research* 31(66), 122-133.
Rowell, R. M., Pettersen, R., Han, J. S., Rowell, J. S., and Tshabalala, M. A. (2005). "Cell wall chemistry," In: *Handbook of Wood Chemistry and Wood Composites*, Rowell, R.M. (ed.), CRC Press, Boca Raton.
Santos, L. C., Carvalho, A. M. M. L., Pereira, B. L. C., Oliveira, A. C., Carneiro, A. C. O., and Trugilho, P. F. (2012). "Properties of wood and estimates of mass and energy of eucalyptus clones from different sites," *Revista Árvore* 36(5), 971-980.
Santos, R. C. (2010). "Quality parameters of wood and charcoal from eucalyptus clones," Doctorate in Wood Technology, Federal University of Lavras, Lavras, Brazil.
Santos, R. C., Carneiro, A. C. O., Castro, A. F. M., Castro, R. V. O., Bianche, J. J., and Cardoso, M. T. (2011). "Correlation of quality parameters of wood and charcoal of clones of eucalyptus," *Scientia Forestalis* 39(90), 221-230.
Segal, L., Creely, J. J., Martin, A. E., and Conrad, C. M. (1959). "An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer," *Textile Res. J.* 29, 786-794.

Shebani, A. N., Van Reenen, A. J., and Meincken, M. (2008). "The effect of wood extractives on the thermal stability of different wood species," *Thermochim. Acta* 471, 43-50.

Shen, R., Gu, S., and Bridgwater, A. V. (2010). "The thermal performance of the polysaccharides extracted from hardwood: Cellulose and hemicelluloses," *Carbohydrate Polymers* 82, 39-45.

Soares, V. C. (2011). "Thermal, chemical and physical behavior of wood and charcoal from *Eucalyptus grandis* x *Eucalyptus urophylla* at different ages," Doctorate in Wood Technology, Federal University of Lavras, Lavras, Brazil.

Tappi Technical Divisions and Committees. (1998). *TAPPI Test Methods*.

Trugilho, P. F., Bianchi, M. L., Rosado, S. C. S., Lima, J. T., and Napoli, A. (2012). "Elemental analysis of clones of eucalyptus wood," *Biomassa & Energia* 5(1), 53-58.

Trugilho, P. F., Lima, J. T., Mori, F. A., and Lino, A. L. (2001). "Evaluation of *Eucalyptus* clones for charcoal production," Cerne 7(2), 104-114.

Unger, A. Unger, W., Wagner, G., and Schniewind, A. P. (2001). *Conservation of Wood Artifacts*, Herrmann, B. (ed.), Springer Verlag, Berlin.

Vale, A. T., Dias, I. S., and Santana, M. A. E. (2010). "Relationships among chemical properties, physical and energy wood properties of five cerrado species," *Ciência Florestal* 20(1), 137-145.

Van Loo, S., and Koppejan, J. (2008). *The Handbook of Biomass Combustion and Co-firing*, Earthscan Publications, London, UK.

Wallis, A., Wearne, R., and Wright, P. (1996). "Chemical analysis of polysaccharides in plantation eucalyptus wood and pulps," *Appita J.*49(4), 258-262.

Yang, H., Yan, R., Chen, H., Lee, D.H., and Zheng, C. (2007). "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel* 86, 1781-1788.

Yuan, X., Zhou, Z., Li, J., Chen, X., and Wang, F. (2011). "HCN and NH_3 (NOx precursors) released under rapid pyrolysis of biomass/coal blends," *Journal of Analytical and Applied Pyrolysis* 92(2), 463-469.

Article submitted: March 05, 2013; Peer review completed: April 20, 2013; Revised version received: July 15, 2013; Accepted: July 16, 2013; Published: July 22, 2013.