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EFFECT OF EXTRACTIVES AND CARBONIZATION TEMPERATURE ON ENERGY CHARACTERISTICS OF WOOD WASTE IN AMAZON RAINFOREST

Keywords:
Biomass
PCA
Thermal decomposition
Energy

ABSTRACT: The objective of this study was to evaluate the effect of extractives soluble in hot water, besides final carbonization temperatures, on the gravimetric yield and properties of charcoal for waste of three native forest species from the Amazon region. Waste cuttings of Ipé, Grapia and Maçaranduba species, from the machine processing for joinery of a company in the State of Pará, were used. Carbonization was carried out in an adapted electric furnace with a heating rate of 1.67°C min^{-1} and final temperatures of 500, 600 and 700°C. The waste was carbonized fresh after extraction in hot water to remove extractives. Gravimetric yields were analyzed, as well as chemical features and high heating value. In the evaluation of the experiment, arranged in a factorial scheme with three factors (species x temperature x material with and without extraction), and Principal Component Analysis used too. The presence of extractives (soluble in hot water) from wood waste had little influence on the gravimetric yield and immediate chemical composition of charcoal; however, it showed a greater high heating value and lower contents of hydrogen and nitrogen. The increase in the final carbonization temperature reduced the gravimetric yield in charcoal, the content of volatile materials and hydrogen, with a higher content of fixed carbon, carbon and high heating value. The treatments with the best energy characteristics were obtained from Ipé and Maçaranduba charcoals with extractives produced at 600°C, in addition to Ipê and Maçaranduba charcoals with and without extractives obtained at 700°C.

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EFEITO DOS EXTRATIVOS E TEMPERATURA DE CARBONIZAÇÃO NAS CARACTERÍSTICAS ENERGÉTICAS DE RESÍDUOS MADEIREIROS DA AMAZÔNIA

Palavras chave:
Reaproveitamento
Resíduo de madeira
Decomposição térmica
Energia

RESUMO: O objetivo foi avaliar o efeito dos extrativos solúveis em água quente e temperatura final de carbonização no rendimento gravimétrico e propriedades do carvão vegetal em resíduos de três espécies florestais nativas, provenientes da região amazônica. Foram utilizados resíduos de aparas das espécies de ipê, garapa e maçaranduba, provenientes do processamento de usinagem da marcenaria de uma empresa do estado do Pará. As carbonizações foram realizadas em forno elétrico adaptado utilizando uma taxa de aquecimento de 1,67°C min^{-1} e temperaturas finais de 500, 600 e 700ºC. Os resíduos foram carbonizados in natura e após extração em água quente para remoção dos extrativos. Foram analisados os rendimentos gravimétricos, as análises químicas e o poder calorífico superior. A presença de extrativos solúveis em água quente dos resíduos das madeiras pouco influenciaram no rendimento gravimétrico e na composição química imediata do carvão vegetal, contudo apresentou maior poder calorífico superior, menor teor de hidrogênio e nitrogênio. O aumento da temperatura final de carbonização reduziu o rendimento gravimétrico em carvão vegetal, o teor de materiais voláteis e de hidrogênio, havendo aumento do teor de carbono fixo, teor de carbono e poder calorífico superior. Os tratamentos com as melhores características energéticas foram os carvões de Ipê e Maçaranduba com extrativos produzidos a 600ºC, além do carvão de Ipê e Maçaranduba com e sem extrativos obtidos a 700ºC.

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INTRODUCTION

The Amazon region is one of the main producing regions of tropical wood in the world, only behind countries as Malaysia and Indonesia (ORGANIZACIÓN INTERNACIONAL DE LAS MADERAS TROPICALES - OIMT, 2011). The main economic activities are the exploration and wood processing industry, as well as mining (VERÍSSIMO; SOUZA JR, 2006). The gross revenue of the wood industry in the Amazon was US$ 1,075 billion in 2013 (VERÍSSIMO; PEREIRA, 2014).

Forests have great importance in the context of carbon dioxide capture from the atmosphere (FIGUEIREDO et al., 2015), and it is one of the factors favoring the effort to try to keep the preservation of the Amazon rainforest. However, this does not occur and a significant amount of trees is annually torn down by various companies for wood exploitation.

In 2009, in the Legal Amazon, comprising the Brazilian states of Pará, Amazonas, Maranhão, Goiás, Mato Grosso, Acre, Amapá, Rondônia, Roraima and Tocantins, 2,226 logging companies were identified. These companies extracted around 14.2 million cubic meters of native wood, the equivalent to 3.5 million trees and, among the various exploited species, *Apuleia leiocarpa* (Vogel) J.F.Macbr. (Grapia), *Manilkara huberi* (Ducke) Chevalier (Maçaranduba) and *Tabebuia serratifolia* (Vahl) Nichols (Ipé), are mentioned. The processing of 14.2 million cubic meters of roundwood resulted in the production of 5.8 million m^3 of lumber (INSTITUTO DO HOMEM E MEIO AMBIENTE DA AMAZÔNIA, 2010), thus generating 8.4 million m^3 waste.

Much of this wood waste is generated in the processing of lumber, and the percentage generated in relation to processed wood depends on the type of raw material, the end product and technological conditions, besides the process used. Moreover, the abundance of raw material in certain regions contributes to the low use of wood and causes the greatest waste generation (HILLIG et al., 2009).

According to Goulart et al. (2012), native species have potential for many uses and studies should be conducted to infer the best purpose of each species. This is not different for the wood waste of these species, which may have potential to be energetically used in the production of heat, steam or electricity in thermal power plants. Another use is in the form of solid fuel, such as charcoal. In addition to enabling the rational destination of wood waste as an energy source, it adds value to this residue and ceases to be an aggravating factor for the environment (RUISHENG et al., 2014). Bach et al. (2016) also emphasize the importance of biomass as a renewable and zero-carbon resource.

Wood species and final carbonization temperature are important variables that influence the quality of charcoal, since different products with different physical and chemical characteristics are generated as a function of the different reactions caused by these two variables (TRUGILHO; SILVA, 2001).

In the Amazon region, large amounts of native wood are transported by the Amazon river to be further mechanically processed, thus with a large amount of wood waste generated, that can be used for different purposes, such as energy production. Due to the importance that there is in the possibility of using this waste as an energy source, this study aimed to evaluate the effect of extractives soluble in hot water and final carbonization temperature on the gravimetric yield and properties of charcoal on the waste of three forest native species from the Amazon region.

MATERIAL AND METHODS

Raw material

Waste cuttings (small pieces of wood) from the mechanical processing of three forest species were used; they were obtained during processing in a wood joinery of the company SEMASA Industry Trade and Export of Madeira Ltda., located in the metropolitan region of Belém, state of Pará, Brazil. Waste of the species *Apuleia leiocarpa* (Vogel) J.F.Macbr. (Grapia), *Manilkara huberi* (Ducke) Chevalier (Maçaranduba) and *Tabebuia serratifolia* (Vahl) Nichols (Ipé) were used separately.

The wood pieces were ground in a Wiley mill for the generation of sawdust, with a granulometry between 40 and 60 mesh. They were placed in plastic bags opened and packaged in a climate room at 20 ± 2°C temperature and 65 ± 3% relative humidity, until constant mass, with average moisture of 12%.

The insoluble lignin content (Klason) was determined according to the procedure described by Gomide and Demuner (1986). The content of lignin soluble in sulfuric acid was determined by spectrophotometry, using the equation described by Goldschimid (1971). Total lignin was taken as the sum of soluble and insoluble lignins. The ash content was determined according to Brazilian Regulatory Standard 13999 (2003). The holocellulose content was obtained by the difference of total lignin, extractives and ash contents.

Removal of extractives

The wood was divided into two batches per species, one with and without extraction in hot water. The extraction followed the designationof American Society for

Testing and Materials – ASTM D – 1110-84 (2013), which standardizes the solubility test of wood in hot water.

After acclimation, an adaptation of ASTM D – 1110-84 (2013) was carried out, being approximately 60g of sawdust were kept under extraction in a thermostatic bath with 2 liters of distilled water for 3.5 hours at the boiling temperature under normal pressure conditions. After extraction, the samples were filtered into crucibles with porosity 2 and dried in an oven at a temperature of 103 ± 2°C, in which the determination of the content of extractives in hot water was also performed. The fresh sawdust and that obtained after the extraction in hot water were conditioned in a climate room at 20 ± 2°C temperature and 65 ± 3% relative humidity, until constant mass.

Process for the production and yield of charcoal (carbonization)

For the production of charcoals, 20 g of dry wood and of that obtained after the extraction in hot water were used, with a particle size of 40-60 mesh. Approximately 20g of sawdust were used in each crucible to perform carbonization, and eight crucibles were prepared per species (eight replicates).

Carbonization was carried out in a muffle furnace, adapted to this activity, at the Bioenergy Laboratory of Department of Forestry Sciences, Federal University of Lavras/DCF/UFLA. A heating rate of 1,67 °C min^{-1} was used, at final temperatures of 500, 600 and 700°C, with a residence time of 30 minutes for all cases. The gravimetric yield in charcoal was determined in relation to dry mass.

Characterization of charcoals

The chemical characterization of charcoals was carried out according to the procedures of the Brazilian Regulatory Standard 8112 (ABNT, 1986), while the high heating value was determined according to the procedure described in NBR 8633 (ABNT, 1984).

For elemental analysis, the charcoals were sieved, and the fraction used was the one that passed through a 200-mesh sieve and was retained on that with 270 mesh. The quantification of contents of carbon, hydrogen and nitrogen, in relation to wood dry mass, was held in a universal analyzer. The analyzer uses helium and oxygen, respectively, as carrier and ignition gases. 2-mg samples were placed in tin capsules and were completely incinerated at 1200°C.

Statistical analysis

In the evaluation of the experiment, a completely randomized design was used, arranged in a factorial scheme with three factors (species x temperature x material with and without extraction), eight replicates for gravimetric yield and four replicates for high heating value chemical and elemental analyses. When the variance analysis were significant, for qualitative factors (species and, material with and without extraction), the Tukey test ($p < 0.05$) was used, while linear regression (simple model) was used for the quantitative factor (temperature).

Principal Component Analysis - PCA was also used. An m × n matrix (where m is the number of samples and n is the number of variables) was used in the PCA. For each Amazon species with the materials with and without extractives, using the final carbonization temperature, the matrices were formed. The treatments were identified as Garapa – G, Ipé – I, Maçaranduba – M, materials with extractives – C, without extractives – S, final carbonization temperatures of 500, 600 and 700°C, and totaling 18 samples per matrix. Data were autoscaled and PCA was performed.

RESULTS AND DISCUSSION

Gravimetric yield and immediate chemical analysis

The summary of the analysis of variance of the gravimetric yield and quality of charcoal indicated the effects of the interactions species x temperature and species x extraction were significant for the gravimetric yield in charcoal, while triple the interaction was significant for the contents of volatile materials and fixed carbon (Table 1). A significant interaction indicates that there is dependence among the factors and the deployment and evaluation of an effect inside the other must be analyzed. For the ash content, the effects of species and extraction were significant.

The highest yields in charcoal from wood waste with and without extractives were those of grapia and ipé, respectively. Only grapia had a significant difference in charcoal yield for the material with and without extractives

TABLE 1 Summary of the analysis of variance for charcoal yield, content of volatile materials, fixed carbon and ash.

Variation factor	Degrees of freedom	Mean square			
		Charcoal yield	Volatile materials	Fixed carbon	Ash
Species (Sp)	2	8.86*	2.13*	211.20*	185.66*
Temperature (Temp)	2	223.37*	988.36*	957.74*	0.29 ns
Extraction (Ext)	1	18.46*	0.56 ns	7.59*	4.03*
Sp x Temp	4	2.22*	3.52*	5.10*	0.21 ns
Sp x Ext	2	10.72*	3.37*	3.25*	0.04 ns
Temp x Ext	2	2.00 ns	1.97*	1.94*	0.16 ns
Sp x Temp x Ext	4	0.14 ns	1.44*	2.48*	0.18 ns
Error	126	0.66	0.15	0.23	0.09
CV (%)		2.87	2.82	0.58	10.84

*Significant by F test ($p < 0.05$); ns: not significant ($p > 0.05$);

in hot water, and it is possible to infer that the absence of extractives soluble in hot water of this material negatively affected the yield in charcoal (Table 2).

TABLE 2 Mean values and multiple comparison test for the deployment of the interactions between the gravimetric yield in charcoal (%).

Interaction extraction x species			
Extraction	Grapia	Ipé	Maçaranduba
With extractive	29.46 Aa	28.57 Ba	27.96 Ca
Without extractive	27.66 Bb	28.52 Aa	27.65 Ba
Interaction temperature x species			
Temperature (°C)	Grapia	Ipé	Maçaranduba
500	30.46 AB	31.16 A	30.11 B
600	28.31 A	28.35 A	27.48 B
700	26.90 A	26.12 B	25.83 B

Same capital letters in each row and lowercase in each column do not differ by Tukey test at significance ($p < 0.05$).

By the evaluation of the effect of temperature within species, it was observed that the regression analysis was significant for all species. The adjustment of simple regression models showed high coefficients of determination and tended to reduce charcoal yield with increasing carbonization temperatures (Figure 1). The reduction in yield at high temperatures is due to the continuation of the release of volatile material from charcoal mass (TRUGILHO; SILVA, 2001; VIEIRA et al., 2013).

Fiber cell wall is structurally constituted by three primary compounds, cellulose, hemicelluloses, and lignin. When pyrolysis process is led up to the temperature of 450°C, it may occur total or partial thermal decomposition of the cellulose and hemicelluloses (YANG et al., 2007), causing a reduction in cell wall thickness of charcoal fiber. In the present work temperatures were carried out above 450°C, which may have caused a thermal degradation of the lignin and consequently a reduction of the gravimetric yield.

For the significant interaction between species x temperature x extraction in the contents of volatile material and fixed carbon, it was decided to evaluate the effect of extraction in hot water for each species within the final carbonization temperatures (Table 3).

The content of volatile material was statistically equal for all three species and for the material with and

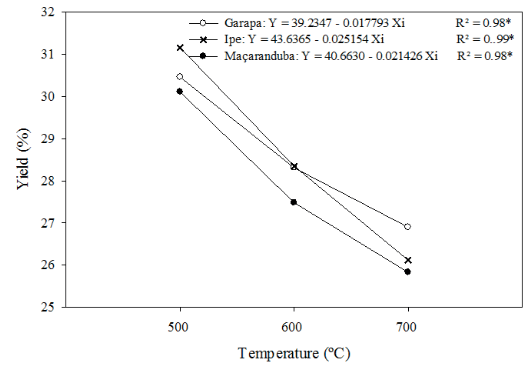

FIGURE 1 Functional relationship between the final carbonization temperature and gravimetric yield for the three species.

without extractives in hot water, when wood waste was carbonized at a final temperature of 600°C. At 500°C in Grapia and 700°C in Maçaranduba presented statistical difference in the content of volatile matter for the material with and without extractives, besides an increase in the content of this material without extractives.

Norgate et al. (2012) and Mathieson et al. (2012) state that steel industries in many countries prefer to use wood with a low content of volatile matter in their processes, since these materials volatilize at low temperatures, and charcoal with a high content of fixed carbon is preferred, due to having high heat resistance (CHENG et al., 2016). There was little variation in the content of volatile material between wood waste with and without extractives.

Grapia charcoal showed a lower content of fixed carbon at all carbonization temperatures. This fact can be explained by the lower content of lignin presented by the waste of this species. Wood rich in lignin contributes to a higher gravimetric yield in charcoal and high content of fixed carbon (RIAZ et al., 2016). This is due to the high content of carbon present in the lignin structure (RAGAN; MEGONNEL, 2011). Only Maçaranduba charcoal showed no statistical difference in the content of fixed carbon for materials with and without extractives at the three final carbonization temperatures. At 600°C,

TABLE 3 Mean values and multiple comparison test for the deployment of the interactions between the contents of volatile materials and fixed carbon..

T (°C)	Extraction	Content of volatile materials (%)			Content of fixed carbon (%)		
		G	I	M	G	I	M
500	With extractive	20.13 Bb	21.11 ABa	21.66 Aa	74.11 Ba	77.25 Ab	76.81 Aa
	Without extractive	21.18 ABa	20.16 Ba	21.59 Aa	73.01 Ba	78.50 Aa	77.76 Aa
600	With extractive	11.39 Aa	11.79 Aa	11.55 Aa	82.31 Ba	86.31 Aa	87.21 Aa
	Without extractive	12.14 Aa	11.64 Aa	12.33 Aa	81.90 Ba	87.04 Aa	87.17 Aa
700	With extractive	10.57 Aa	8.69 Ba	8.06 Bb	82.78 Bb	89.51 Ab	90.64 Aa
	Without extractive	8.71 Ab	7.35 Bb	8.25 Aa	85.24 Ba	91.33 Aa	90.82 Aa

T: Temperature; G: Grapia; I: Ipé, M: Maçaranduba. Within each temperature, the same capital letters in each line and lowercase in each column do not differ by Tukey test ($p < 0.0$ 5).

the content of fixed carbon did not show statistical differences for the three species and for the material with and without extractives in hot water.

The mean contents of lignin, extractives, ash and holocellulose of Ipé wood are, respectively, 33.47; 10.50; 0.65 and 55.38%. The values are 29.50; 10.05; 1.93 and 58.52% for Grapia wood and, for Maçaranduba wood, they are 34.68; 7.36; 0.33 and 56.63%. The higher lingnin content of maçaranduba and ipé corroborated with the higher fixed carbon content in relation to garapa.

Regression analysis was significant for the contents of volatile materials and fixed carbon in all species (Table 4). The coefficients of determination were high, especially for the material without extractives. It was possible to observe a reduction in the contents of volatile materials with increased carbonization temperatures, and the opposite effect was observed for the content of fixed carbon. Oliveira et al. (2010) found the same trend for *Eucalyptus pellita* at 5 years of age. These authors observed a higher degradation of wood constituents at the highest temperatures, which leads to a reduction in volatile materials. Trugilho and Silva (2001) also obtained a reduction in the contents of volatile materials with increasing temperatures.

The contents of fixed carbon are inversely proportional to the contents of volatile materials, since the removal of volatiles in charcoal causes a relative increase in the concentration of fixed carbon. The higher the final pyrolysis temperature, the higher the concentration of carbon in charcoal (PROTÁSIO et al., 2014).

The ash content showed a significant variation between species and material with and without extractives in hot water (Table 5). The waste of Garapa charcoal had the highest ash content. The final carbonization temperature did not affect the ash content. Ash contents in charcoals from wood with extractive were higher than those of charcoals from wood without extractives in hot water. This may have occurred due to the solubilization of these mineral components by hot water.

TABLE 5 Contents of ash and fixed carbon in charcoal from three species with a pre-treatment at three temperatures.

Treatment	Ash content %			Mean
	Grapia	Ipé	Maçaranduba	
With extractive	6.28	1.77	1.35	3.13 a
Without extractive	5.93	1.27	0.73	2.64 b
Mean	6.11 A	1.52 B	1.04 C	2.89

Same lowercase letters in each column within each species do not differ by Tukey test ($p < 0.05$).

Elemental chemical analysis and heating value

It is found that the triple interaction (species x temperature x extraction) was significant for elemental carbon (Table 6). The interaction between the factors temperature x extraction was significant for hydrogen, carbon and high heating value (HHV), with a significant interaction between species x temperature for HHV. For nitrogen, there was a significant interaction between species x extraction. A deployment of interactions and an evaluation of an effect inside the other were carried out to assess the dependence between the factors.

The highest contents of elemental carbon occurred in Ipé and Maçaranduba species, since the waste of these species showed a higher content of lignin, compared to Garapa (Table 7). The carbon content at a temperature of 700°C was higher in the material without extractives,

TABLE 6 Summary of the analysis of variance of carbon elements, hydrogen, nitrogen and high heating value.

Variation factor	DF.	Mean square			
		Carbon	Hydrogen	Nitrogen	High heating power
Species (Sp)	2	239.924*	0.106 ns	0.422*	1,635,419.05*
Temperature (Temp)	2	232.353*	6.704*	0.042ns	1122291.68*
Extraction (Ext)	1	30.355*	0.650*	14.204*	558624.50*
Sp x Temp	4	2.749 ns	0.134 ns	0.008 ns	32386.68*
Sp x Ext	2	1.025 ns	0.161 ns	0.043*	532.16 ns
Temp x Ext	2	17.639*	0.615*	0.009 ns	11756.29*
Sp x Temp x Ext	4	7.304*	0.108 ns	0.012 ns	1659.21 ns
Error	54	2.169	0.101	0.006	2785.88
CV (%)		1.80	13.69	7.51	0.68

CV: Coefficient of variation; *Significant by F test ($p < 0.05$); ns: not significant; DF: degree of freedom.

TABLE 4 Equation adjusted for the effect of the three temperatures in the content of volatiles and fixed carbon at three species.

Species	Equations adjusted to wood with extractives			
	Content of volatile materials	R^2	Content of fixed carbon	R^2
Grapia	$\hat{Y}i = 42.6775 - 0.047743Xi$	0.81*	$\hat{Y}ii = 53.7225 + 0.043359Xi$	0.79*
Ipé	$\hat{Y}i = 51.1245 - 0.062099Xi$	0.92*	$\hat{Y}ii = 47.5775 + 0.061312Xi$	0.92*
Maçaranduba	$\hat{Y}i = 54.5572 - 0.067997Xi$	0.93*	$\hat{Y}ii = 43.4022 + 0.069146Xi$	0.92*
	Equations adjusted to wood without extractives in hot water			
	Content of volatile materials	R^2	Content of fixed carbon	R^2
Grapia	$\hat{Y}i = 51.4169 - 0.062337Xi$	0.93*	$\hat{Y}ii=43.3853 + 0.061118Xi$	0.93*
Ipé	$\hat{Y}i = 51.4916 - 0.064064Xi$	0.96*	$\hat{Y}ii = 47.1686 + 0.064172Xi$	0.96*
Maçaranduba	$\hat{Y}i = 54.0643 - 0.066674Xi$	0.95*	$\hat{Y}ii = 46.0390 + 0.065290Xi$	0.94*

*Significant by F test (< 0.0 5). $\hat{Y}i$: estimate of the content of volatile materials, $\hat{Y}ii$: estimate of the content of fixed carbon, Xi: Final carbonization temperature.

TABLE 7 Elemental carbon of the species at three temperatures and materials with and without extraction in hot water.

Elemental Carbon (%)				
Extraction	Temperature (°C)	Grapia*	Ipé	Maçaranduba*
With extractive	500	74.27 B	80.55 A	79.80 A
	600	79.11 B	85.22 A	84.92 A
	700	79.03 B	85.46 A	83.26 A
Without extractive	500	75.77 B	81.62 A	78.38 A
	600	80.92 B	85.11 A	83.92 A
	700	81.02 B	87.96 A	88.61 A

Same capital letters in each row do not differ by Tukey test ($p < 0.05$). *There was a statistical difference among species between the material with and without extractive at a temperature of 700°C.

in all waste. This result may reflect volatilization (ignition) of a mineral present in the waste at this carbonization temperature (TRUGILHO; SILVA, 2011).

Table 8 shows that regressions for the carbon content at the three temperatures were significant and with high determination coefficients, except for Maçaranduba waste with extractives. It can be stated that there is an increasing trend of elemental carbon in charcoal as a function of the final carbonization temperature, for wood both with and without extractives in hot water.

Charcoal produced using wood with no extractives in hot water showed a higher hydrogen content at 500 and 600°C, although there was no difference for the temperature of 700ºC, (Table 9). The regressions for hydrogen content were significant and it is possible to infer that there is a tendency to reduce this chemical constituent with increasing temperatures, either in the presence or absence of extractives in hot water. Maia et al. (2011) state that this fact is due to the reactions resulting from pyrolysis, which is a drastic process of dehydration, decarboxylation and condensation.

In biomass, low amounts of nitrogen are desirable, since they result in environmental pollution, with the formation of some compounds after biomass combustion, such as nitrogen oxides (BILGEN; KAYGUSUZ, 2008; KUMAR et al., 2010). In this study, the content of nitrogen was higher in Ipé wood (Table 10).

Higher nitrogen contents were observed in charcoals from wood without extractives in hot water. It can be observed that this element is not washed during wood extraction, which caused its highest concentration in charcoal without extractives.

TABLE 9 Mean values, multiple comparison test for the deployment of temperature and extraction interactions, equations adjusted to hydrogen for the three temperatures.

Hydrogen (%)			
Interaction extraction x temperature (°C)			
Extraction	500	600	700
With extractive	2.62 b	2.20 b	1.86 a
Without extractive	3.04 a	2.52 a	1.69 a

Equations adjusted to temperatures			
With extractive	R^2	Without extractive	R^2
$\hat{Y}i = 4.4955 - 0.003781Xi$	0.35*	$\hat{Y}i=6.4768 - 0.006766Xi$	0.91*

Same lowercase letters in each differ by Tukey test ($p < 0.05$). $\hat{Y}i$: estimate of hydrogen, Xi: Final carbonization.

TABLE 10 Average values and multiple comparison test for the deployment of nitrogen interactions.

Nitrogen (%)			
Interaction extraction x species			
Extraction	Grapia	Ipé	Maçaranduba
With extractive	0.50 Cb	0.80 Ab	0.65 Bb
Without extractive	1.48 Ba	1.68 Aa	1.46 Ba

Same capital letters in each row and lowercase in each column do not differ by Tukey test ($p < 0.05$).

The heating value is the measure of the amount of energy released by wood during its complete combustion, and it is one of the main variables used for the selection of species with better features for energy purposes (SANTOS et al., 2011). In this study, the woods with the highest heating values were Ipé and Maçaranduba, with 7,907 aband 7,936 kcal·kg^{-1}, respectively. This fact is related to larger amounts of elemental carbon observed in these species. Protásio et al. (2011) found the same behavior for *Eucalyptus urophylla* waste at 6 years of age, *Toona ciliata* at 18 years and *Pinus* sp. at 35 years.

The extractives significantly influenced the heating value, as the lowest values were derived from the charcoal produced from wood without extractives in hot water (Table 11). Wood extractives are advantageous materials for energy production, since these components positively influence the heating value, particularly those which have some phenolic compounds in their composition (GUO et al., 2010; TELMO et al., 2010).

Regressions performed in relation to species and temperature, as well as for materials with and without extractives in hot water for different temperatures, were significant (Table 12) and evidence the existence of an

TABLE 8 Functional relationship between elemental carbon and final carbonization temperature.

Species	Equations adjusted to the content of carbon			
	With extractive	R^2	Without extractive	R^2
Grapia	$\hat{Y}i = 63.1650 + 0.023838\ Xi$	0.73*	$\hat{Y}i = 63.4683 + 0.026275\ Xi$	0.64*
Ipé	$\hat{Y}i = 69.0050 + 0.024563\ Xi$	0.78*	$\hat{Y}i = 65.8725 + 0.031700\ Xi$	0.78*
Maçaranduba	$\hat{Y}i = 72.2616 + 0.017325\ Xi$	0.43	$\hat{Y}i = 52.9391 + 0.051163\ Xi$	0.95*

*Significant by F test (< 0.0 5). $\hat{Y}i$: Estimate of the content of elemental carbon, Xi: Final carbonization temperature.

increased heating value trend with increasing temperatures, both for the three species, and for charcoal from wood with and without extractives in hot water. Different authors also found a positive relationship between the heating value and the final carbonization temperature (TRUGILHO; SILVA, 2001; PROTÁSIO et al., 2014).

TABLE 11 Average values and multiple comparison test for the deployment of heating value interactions.

Heating value (kcal·kg^{-1})			
Interaction temperature x species			
Temperature (°C)	Grapia	Ipé	Maçaranduba
500	7,291B	7,674A	7,612 A
600	7,594 B	8,074 A	8,132 A
700	7,525 B	7,974 A	8,062 A
Interaction extraction x temperature			
Extraction	500°C	600°C	700°C
With extractive	7,612 a	8,044 a	7,920 a
Without extractive	7,439 b	7,823 b	7,787 b

Same capital letters in each row and lowercase in each column do not differ by Tukey test ($p < 0.05$).

TABLE 12 Equations adjusted for the heating value at three temperatures and material with and without hot water extractives.

Species	Adjusted equations	R^2
Grapia	$\hat{Y}i = 6765.7500 + 1.173750\ Xi$	0.54*
Ipé	$\hat{Y}i = 7006.7916 + 1.500625\ Xi$	0.51*
Maçaranduba	$\hat{Y}i = 6585.3750 + 2.250625\ Xi$	0.63*
Extraction		
With extractive	$\hat{Y}i = 6934.5555 + 1.540833\ Xi$	0.47*
Without extractive	$\hat{Y}i = 6637.3888 + 1.742500\ Xi$	0.67*

*Significant by F test (< 0.0 5). $\hat{Y}i$: Estimate of the high heating value, Xi: Final carbonization temperature.

The two principal components account for approximately 81% of the variance in the original data; thus, it was decided to use only these two principal components for principal PCA.

The distribution of variables and treatments was analyzed together (Figure 2), and it was possible to observe four distinct groups. The first group involves Grapia charcoal with and without extractives in hot water, carbonized at 500°C (GC500 and GS500), which exhibit similarities regarding ash content, since this charcoal has a high content of these minerals, and the distance of these treatments between the vector ash content was unbalanced due to the high efficiency of these treatments.

The second group involves Grapia charcoal with and without extractives in hot water obtained at 600 and 700°C (GC600, GS600, GC700 and GS700), which had a high ash content. Grapia charcoal can be impractical for use in the energy sector due to its high mineral content since, according to the ash content, they can form foulings inside the equipment and pipes, damaging the process and production (KHAN et al., 2009).

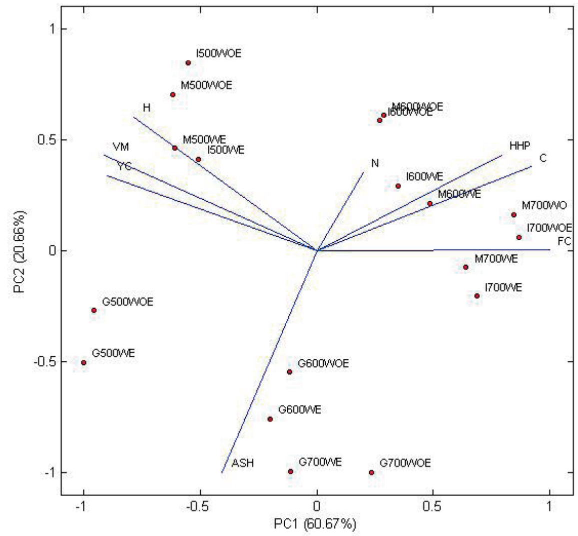

FIGURE 2 Dispersion of treatments depending on the scores and ranking diagram of eigenvectors of the first two principal components. Where, H: hydrogen, N: nitrogen, HHP: high heating value, C: carbon, FC: fixed carbon content, ASH: ash content, VM: content of volatiles, YC: yield in charcoal.

The third group is comprised by wood charcoals of Ipé and Maçaranduba with and without extractives in hot water, obtained at 600 and 700°C; these treatments showed similarities with the contents of fixed carbon, elemental carbon, high heating value and nitrogen. However, it is possible to visualize subgroups, where some had greater influence of variables such as Ipé and Maçaranduba wood charcoal with extractives obtained at 600°C (IC600 and MC600) and that had a greater high heating value, with averages of 8,192 and 8,239 kcal·kg^{-1}, respectively.

Another subgroup is formed by wood charcoal of Ipé and Maçaranduba with and without extractives in hot water obtained at 700°C, which is characterized by higher contents of fixed carbon and elemental carbon. The last subgroup is formed by charcoal wood of Ipé and Maçaranduba without extractives in hot water, carbonized at 600°C, characterized by a greater influence of nitrogen content. It is important to emphasize that the variable nitrogen is undesirable for the energy medium due to the formation of nitrogen oxides during the combustion of charcoal.

The fourth group consists of wood charcoal of Ipé and Maçaranduba with and without extractives in hot water, carbonized at 500°C. This group is characterized by having a high yield in charcoal and high contents of volatile materials and hydrogen. The yield in charcoal and the content of hydrogen are good parameters to qualify charcoal, but the content of volatile materials presents the opposite behavior, since high quantities of toxic substances are released during the combustion of charcoal (KABIR et al., 2010; SPARREVIK et al., 2015).

By analyzing the variables in order to qualify the treatments as a function of the energy characteristics of charcoal, the third group generally presented the best energy characteristics, especially the treatments ipé and maçaranduba with and without extractives carbonized at 700ºC with high values of fixed carbon content and carbon, Ipé and maçaranduba with extractives carbonized at 600ºC presented higher high heating value.

CONCLUSIONS

The presence of extractives, soluble in hot water, from wood waste positively influenced the gravimetric yield, only for Garapa charcoal. The immediate chemical composition of charcoal was little affected by the extractives. However, the waste with extractives showed higher ash content and high heating value and lower contents of hydrogen and nitrogen.

Temperature significantly affected the gravimetric yield and properties of charcoal. With the increase in the final carbonization temperature, a lower gravimetric yield in charcoal was observed; in the charcoal properties, it was found that the contents of fixed carbon, carbon and high heating value increased with increasing temperatures, and there was a reduction in the content of volatile materials and hydrogen.

For the studied wood species, the lowest gravimetric yield was found in the wood waste of Maçaranduba. In the wood waste of Garapa, a lower content of fixed carbon, carbon and high calorific value was observed, as well as higher ash content. There was higher nitrogen content in the waste wood of Ipé. The highest fixed carbon content of ipé and maçaranduba were due to their higher lignin content.

By principal component analysis, it was observed that the treatments with the best energy characteristics were: Ipé and Maçaranduba charcoals with extractives produced at 600°C, in addition to Ipé and Maçaranduba charcoals with and without extractives obtained at 700°C.

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