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Original Article

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Elementary, Chemical and Energy Characteristics of Brazil Nuts Waste (*Bertholletia excelsa*) in the State of Pará

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ABSTRACT

This study aimed to determine the chemical and energetic composition of Brazil nut waste in the city of Castanhal-PA. Some of the material was crushed, sifted and stored for acclimatization and analysis. Molecular and immediate chemical analyses were performed on the raw material according to NBR standards. Another part was charred in Muffle furnace, with heating rate of 1.67 °C.min-1 and temperature of 450 °C for 60 minutes. For biomass, 55.76% of lignin and 2.61% of minerals were found. Means of 65.67% for volatiles were also found; 2.08% of ashes and 21.64% of fixed carbon. In the elementary, means of 53.54% of carbon and 0.11% of sulfur were found. For charcoal, 25.81% of volatiles were found; 1.76% of ashes and 67.50% of fixed carbon. Residues have high levels of lignin, fixed carbon and low ash contents, demonstrating potential for direct burning for energy, charcoal, activated carbon and biochar.

Keywords: biomass, lignin, charcoal, carbon.

1. INTRODUCTION

Biomass consists of organic material of animal or vegetable origin, and is considered an alternative source of energy. According to Werther et al. (2000) and Saini et al. (2015), agricultural residues present high energy potential, since after carbonization, biomass transforms into charcoal.

Brazil is considered as one of the largest agricultural producers, consequently generating large amounts of waste, which has potential for bioenergy (Vieira et al., 2012; Scatolino et al., 2018). Among these agricultural products, Brazil nuts, known as *Bertholletia excelsa* species, are one of the main products exported from the Amazon (Lorini et al., 2018).

Brazil nut belongs to family *Lecythidaceae* and grows in a wide area of South America (Brito et al., 2010), mainly in the region of the State of Pará, Brazil. "Castanheira do Pará", the name given in Brazil to this tree, can be found in the Brazilian Amazon, and in countries like Peru, Colombia, Venezuela and Ecuador. The tree is large, and can reach height of 50 m or more (Melo et al., 2018). The fruit is a large capsule, known as a hedgehog, within each hedge there may be about 8-26 "chestnut" with their own individual shell. One tree can produce about 300 or more of these hedgehogs with fruits (Kainer et al., 2006). The seed core contains 63-70% oil, which can be used to make soap and 17% of protein (Chunhieng et al., 2008).

Yearly, thousands of tons of Brazil nuts are exported (Bonelli et al., 2001; Homma, 2004). In 2010, production increased by 7.7%, with a trend of linear growth in the last three years (Silva et al., 2013). This variation is due to the great demand for the product, mainly by companies related to foreign trade.

It is estimated that for each ton of clean chestnut, 1.4 tons of residues are produced, consisting of bark and the so-called hedgehog, the chestnut fruit. Thus, the total of shells and hedgehogs generated exceeds 56 thousand tons. The aim of this work was to determine the elementary, chemical and energetic composition to indicate the potential use of Brazil nut biomass waste.

2. MATERIAL AND METHODS

Agroindustrial Brazil nut wastes (*Bertholletia excelsa*) were collected in the municipality of Castanhal, located in the northeastern region of the State of Pará. These residues are constituted of shells and urchins originated from processing to obtain chestnut almonds.

Some of the fresh material was stored for later carbonization. The other part was packed in sealed and identified plastic bags. Then, the biomass was crushed and sieved in a set of sieves with grain size of 40, 60, 100, 200 and 270 mesh to carry out analyses. The granulometrically classified materials were stored in an air conditioning room, with temperature conditions of 20 ± 2 °C and humidity of 65 ± 3%, until reaching constant mass, with mean humidity of 12%.

In the chemical analyses, ABNT NBR 7989/2010 (ABNT, 2010a) was used for lignin quantification, ABNT NBR 14853/2010 (ABNT, 2010b) for total secondary components (extractives) and ABNT NBR 13999/2003 (ABNT, 2003) to determine inorganic constituents (minerals) of the residue. The holocellulose content was determined by difference in relation to the other chemical constituents as total extractives, lignin and minerals.

For elementary analysis (CHNS), the fraction that passed through the 200-mesh sieve was used and was retained in the 270 mesh, indicated for the follow-up of the analysis. Carbon, hydrogen, nitrogen, sulfur and oxygen (by difference) contents were determined in an Elemental universal analyzer, model Vario Micro Cube. The analyzer uses, as drag and ignition gases, helium and oxygen, respectively. The 2-mg and three replicate samples were packed in tin capsules and completely incinerated at 1200 °C.

The chemical characterization of charcoals and biomass was carried out according to procedures and standards described by Moulin et al. (2017), taking into account adaptation of heating values. All chemical analyses were carried out in triplicate to calculate the mean values, standard deviation and variation coefficient, with values being obtained in the form of descriptive statistics.

For the production of vegetal coals, fresh material with mean humidity of 12%, was used for all residues. The charcoal was produced in a Muffle-type furnace adapted to this function, with heating rate of 1.67 $°C.min^{-1}$, at temperature of 450 °C, with residence time of 60 minutes. Cooling occurred naturally and gradually after the furnace reached the final carbonization temperature and time. The choice of carbonization conditions was based on the methodology described by Nobre et al.

(2015), in which Amazonia wood wastes were used to produce activated carbon.

3. RESULTS AND DISCUSSION

The results obtained in the chemical and elementary biomass analyses are described in Tables 1, 2 and 3.

For the chemical composition, biomass exhibited mean values of 55.76% of lignin, 4.54% of extractives, 2.61% of minerals and 37.09% of holocellulose. Among the results, it is worth highlighting lignin, which presented high value, favoring the production of activated carbon, since it is the substance most resistant to thermal degradation, when compared to cellulose and hemicelluloses.

According to Brito & Barrichelo (1977) and Santos et al. (2016) high lignin contents may be correlated with higher fixed carbon content, volatile substances and consequently higher gravimetric coal yield.

The values obtained for the content of volatile materials, fixed carbon and ash (immediate chemical composition), are shown in Table 2.

These values are close to those found by Netto et al. (2006), who obtained 71.04% of volatile materials, 1.88% of ashes and 27.07% of fixed carbon. The low ash content is a positive factor for the production of activated carbon, considering that mineral components cause an unfavorable effect on the adsorption process, preferentially adsorbing water, due to the hydrophilic character (Moreno-Castilla, 2004). Raw materials with higher carbon content and lower ash content may be considered more suitable for the production of activated carbon (Chen et al., 2013).

The amount of fixed carbon, ash and volatiles, directly affect the quality of activated carbon (Melo et al., 2015; Apaydin-Varol & Erülken, 2015). In addition, it is possible to estimate the yield of coal to be obtained (Oliveira et al., 2010; Schröder et al., 2007).

Studies by Bonelli et al. (2001) indicate that Brazil nut residues have characteristics that demonstrate their capacity to be transformed into charcoal and consequently activated carbon, with immediate chemical composition of 76.1% of volatile materials, 22.2% of fixed carbon and only 1.7% of ashes.

Table 1. Mean chemical composition, standard deviation (SD) and variation coefficient (VC) values of Brazil nut residues.

Chemical composition	Lignin (%)	Extracts (%)	Minerals (%)	Holocellulose* (%)
Mean	55.76	4.54	2.61	37.09
SD	6.64	0.28	0.17	0.06
VC	11.91	6.35	6.81	0.20

*Values obtained by difference; SD = standard deviation; VC = variation coefficient.

Table 2. Immediate chemical composition for Brazil nut biomass.

Chemical composition	Moisture (%)	Volatile (%)	Ashes (%)	Fixed Carbon* (%)
Mean	10.61	65.67	2.08	21.64
SD	0.14	0.30	0.04	0.29
VC	1.41	0.46	2.21	0.90

*Values obtained by difference between the other constituents; SD = standard deviation; CV = coefficient of variation.

Table 3. Mean elementary analysis, standard deviation (SD) and variation coefficient (VC) values for Brazil nut biomass.

Elements	C (%)	H (%)	N (%)	S (%)	-O (%)*	O/C
Mean	53.54	5.69	1.57	0.11	37.01	0.69
SD	0.81	0.07	0.05	0.01	0.93	0.03
VC	1.52	1.31	2.87	7.30	2.52	4.00

*Values obtained by difference between the other constituents, discounting the amount of minerals of the immediate composition (Table 2); SD = standard deviation; VC = variation coefficient.

Table 4. Immediate chemical composition of produced charcoal.

Chemical composition	Moisture (%)	Volatiles (%)	Ashes (%)	Fixed carbon (%)*
Mean	4.93	25.81	1.76	67.50
SD	0.25	1.07	0.28	0.98
VC	0.05	0.04	0.16	0.01

*Values obtained by difference between the other constituents; SD = standard deviation; VC = variation coefficient.

Table 5. Mean elementary analysis, standard deviation (SD) and variation coefficient (VC) values of carbons at carbonization temperature of 450 °C.

Elements	C (%)	H (%)	N (%)	S (%)	-O (%)*	O/C
Mean	72.50	3.46	1.94	0.16	19.86	0.27
SD	1.27	0.07	0.01	0.00	1.35	0.02
VC	1.75	1.94	0.73	2.72	6.80	8.54

*Values obtained by difference between the other constituents, discounting the amount of minerals of the immediate composition (Table 2); SD = standard deviation; VC = variation coefficient.

These authors also presented the elementary chemical characteristics of this material, which corroborate the suggestion for use as precursors in the production of charcoal and activated carbon, having 50.0% of carbon, 5.8% of hydrogen, 0.7% of nitrogen and 43.5% of oxygen.

The values obtained for carbon, hydrogen, nitrogen and sulfur contents found for the four species through elementary analysis are shown in Table 3.

In the immediate chemical composition of charcoal, means of 4.93% of moisture, 25.81% of volatiles, 1.76% of ashes and 67.50% of fixed carbon were found, in addition to gravimetric yield of 41.67%, standard deviation of 1.20 and variation coefficient equal to 2.88. This occurs because the residue has a high content of lignin and carbon, which gives more resistance to the thermal degradation of the material during the carbonization process. Another relevant factor is the oxygen content, which also contributes to coal yield. The lower oxygen content allows for less combustion of the material during the carbonization process, because combustion occurs or is increased due to the amount of oxygen present in the material to be charred and in the furnace where it will be pyrolysed.

The values found for the chemical composition of charcoal produced from Brazil nuts residual biomass are described in Table 4.

Nogueira et al. (2014) show that charcoal produced from chestnut residues has the necessary amounts to be used as a precursor of activated carbon, finding values for immediate chemical analysis with 4.71% of humidity, 20.79% of volatile materials, 0.87% of ashes and 78.33% of fixed carbon.

Elementary analysis (CHNS-O) values for coal produced at 450 °C can be seen in Table 5.

It was observed that, in coal, carbon contents are higher and hydrogen contents are lower when compared to original biomasses (Table 3). Pyrolysis allows obtaining product with high carbon content due to the volatilization of hydrogen, oxygen and nitrogen containing compounds (Sekirifa et al., 2013).

4. CONCLUSION

The analyses performed showed the energy potential of Brazil nuts residues, and results showed high levels of lignin, fixed carbon, volatile substances and low ash content, determining potential for the use of Brazil nut biomass for direct burning, production of good quality activated carbon and also biochar.

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