CHAPTER 10

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Effect of pyrolysis temperature on physicochemical properties of biochars made from two different bamboo species

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ABSTRACT
Due to its high photosynthetic efficiency and conversion into biomass, bamboo has great potential for the production of coal for agricultural use (biochar). This work compared the coals produced at different pyrolysis temperatures from the stem of two species of wide occurrence in the south of the country: Phyllostachys aurea (an exotic species) and Guadua sp. (southern Brazil). The results showed differences between the two species, starting with the lignin and volatile content of the stems in natura, and the exotic species showed higher levels of lignin and lower levels of extractives. These differences are reflected in the pyrolysis process and in the chemical characteristics of the coals, and the exotic species produces coals with higher carbon contents.

Keywords: Biochar, Slow pyrolysis, TGA, DRIFT.

1 INTRODUCTION

The use of coals as soil conditioner (biochar or *biochar*), in addition to an interesting strategy to store carbon in a stable form, contributes to the increase of water retention capacity in the soil and decreases nutrient losses by leaching (Sohi et al., 2010). To be economically sustainable, biochar production must be associated with the use of underutilized biomass waste and energy generation. In several countries in Asia and Africa, bamboo is an important raw material for various industrial and energy uses. In Brazil, although still little explored and studied, bamboo has great potential for use due to its high efficiency of conversion into biomass, with more than 130 native species occurring in its territory. Few works on the coal produced by species of these genera are published. This work compared the chemical characteristics of the raw material and coals produced from three different temperatures with two species of bamboo: *Phyllostachys aurea* (an exotic species) and *Guadua* sp. (native to Brazil).

2 MATERIAL AND METHODS

The two bamboo species were obtained in the Irati National Forest, PR: an exotic *Phyllostachys aurea* and another native *Guadua* sp., probably *angustifolia*. The samples of one individual of each species, with undetermined age, were dried in an oven at 110°C for 24 hours, ground and sieved at 2 mm. Pyrolysis was performed in an adapted muffle furnace, under low oxygen concentration, at 350, 450 and 550 degrees, with a heating rate of 10 °C $^{min-1}$, for 1 h at the final temperature. The *in natura* samples were analyzed for lignin and extractive contents, according to ABNT NBR 7989/03 and NBR 14853/02, respectively. The coals were submitted to immediate analysis to determine the contents of moisture, ash, volatile material and fixed carbon, according to the ABNT NBR 8112/86 standard. The thermogravimetric analysis of the in *natura and* pyrolysed samples was performed in a DTG – 60H analyzer (Shimadzu), under N2, with a flow of 50 cm3 $^{min-1}$ $^{and\ a\ heating\ rate\ of\ 10}$ °C min-1 from room temperature to 600 °C. The pH was determined according to Rajkovich et al (2011). Elemental analysis of all samples was performed using an analyzer PE2400 CHNS/O (Perkin Elmer). Infrared spectroscopy by diffuse reflectance in the region 4000-400 cm-1 $^{\text{was performed in IR-660 equipment (Varian) with EasyDiff accessory (Pike), acquiring 64 scans per spectrum with resolution of 4}}$ cm-1. The samples (1%) were diluted in KBr spectroscopic grade. The spectra were recorded by absorbance, with correction of the baseline, and smoothed by the Savitzky-Golay method.

3 RESULTS AND DISCUSSION

P. aurea presented the highest percentage of lignin (26%) and the lowest percentage of extractives (1.7%). The lignin content of *Guadua* sp. nov. (19%) is within the range found by Brito et al. (1987) but, for *P. aurea*, the value is above those mentioned in this study (20%) and close to the lignin content mentioned for *Eucalyptus urophylla* (25%). Gomide et al. (1981) showed that the lignin content tends to increase with the age of the bamboo, while the extractive content decreases. This fact and the different lignin extraction methodologies could explain the differences found in the literature for these characteristics. Brito et al. (1987), for example, studied samples of G. angustifolia from approximately three years of age and found lignin content of 20.1%. Xavier et al. (2005) found the content of 36.7% of lignin in P. *aurea*, without defined age. Charcoal yields ranged from 52.1% to 31% for exotic bamboo and between 39.6% and 31.1% for native bamboo (Table 1), decreasing with increasing carbonization temperature. At 550°C, the yield of the two species was similar, but the immediate analysis showed a high ash content in the coals of *Guadua* sp., especially in the coals obtained at 450 and 550 degrees. The high ash content in bamboo coals is associated with the chemical composition of the stems, which in these species has high silica contents (Brito et al., 1987).

Table 1. Immediate analysis of charcoal samples of two bamboo species (Exotic, *Phyllostachys aurea* and Native, *Guadua sp.*) pyrolyzed at 350, 450 and 550ºC.

Tabela 1. Análise imediat*a das amostras de carvões de duas espécies de bambu (Exótico, *Phyllostachys aurea* e Nativo, *Guadua sp.*) pirolisadas a 350, 450 e 550°C.

Tratamento	Umidade (%)	Cinzas (%)	Voláteis (%)	C. Fixo (%)	pH	Rendimento (%)
Exótico – *Phyllostachys aurea*						
350°C	3,4	3,5	41,2	51,9	8,0	52,1
450°C	3,4	2,7	36,5	57,4	9,5	34,3
550°C	3,9	4,3	31,3	60,5	9,5	31,0
Nativo – *Guadua sp.*						
350°C	4,8	5,0	31,6	58,7	8,2	39,6
450°C	5,0	11,7	24,3	59,1	9,1	34,2
550°C	4,1	9,6	23,9	62,5	9,9	31,1

* média de 3 repetições

The pH of the samples showed similar values for both species, increasing with the final carbonization temperature. The elemental analysis of the coals shows increasing levels of C with the increase of the carbonization temperature (Table 2).

Table 2. Elemental analysis* of fresh culms and charcoal from two bamboo species (*Phyllostachys aurea* and *Guadua sp.*).

Tabela 2. Análise elementar* dos colmos *in natura* e dos carvões de duas espécies de bambu (*Phyllostachys aurea* e *Guadua sp.*).

Amostra	C%	H%	N%	O%	H/C	O/C
BE350	68,46 (0,41)	4,50 (2,12)	0,33 (3,03)	26,71 (1,08)	0,07	0,39
BE450	70,90 (1,39)	3,94 (3,03)	0,25 (4,00)	24,91 (4,42)	0,06	0,35
BE550	73,75 (1,96)	3,63 (2,68)	0,25 (6,19)	22,38 (6,97)	0,05	0,30
BEin**	44,43 (0,26)	5,81 (1,99)	0,20 (5,00)	49,55 (0,18)	0,13	1,12
BN350	67,06 (0,28)	4,36 (0,87)	1,01 (0,57)	27,57 (0,73)	0,06	0,41
BN450	69,43 (0,30)	4,02 (0,90)	0,93 (0,62)	25,63 (0,80)	0,06	0,37
BN550	67,81 (1,24)	3,32 (2,11)	0,90 (1,11)	27,97 (3,23)	0,05	0,41
BNin**	39,24 1,53)	5,08 (2,31)	0,56 (4,10)	55,11 (0,99)	0,13	1,40

* *Média de três repetições;* ** material *in natura;* Números entre parênteses = coeficiente de variação % BEx = bambu exótico, *P.aurea*, x = temperatura de pirólise; BNx= bambu nativo, *G.sp.*,x = temperatura de pirólise;

The reduction of the O/C and H/C ratios reveals the process of defunctionalization and aromatization of the carbonaceous structure, respectively, after pyrolysis. In the thermogravimetric curves (Figure 1), the mass loss is observed at ~110°C, corresponding to the water loss in all samples. In addition, three more thermal events are observed in the pyrolyzed samples at 350 and 450°C and two thermal events in the pyrolyzed sample at 550°C, for both bamboos (exotic and native). The first mass loss is related to the degradation of hemicellulose and cellulose and starts at 330°C and 340°C for coals obtained at 350°C from exotic and native bamboo, respectively. In the samples pyrolyzed at 450°C, this event is shifted to lower values (325°C and 315°C for exotic and native bamboo), indicating that the increase in pyrolysis temperature causes the loss of smaller and/or more labile molecules in the coals. This fact is also indicated by the absence of this peak in the pyrolyzed samples at 550°C, where the first mass loss occurs at higher temperatures (450 and 415°C, for exotic and native bamboos, respectively).

Figure 1. Mass loss and differential thermodynamic curve (DTA) of in natura samples and the coals of two bamboo species (A. exotic *P.aurea*; B. native Guadua sp.

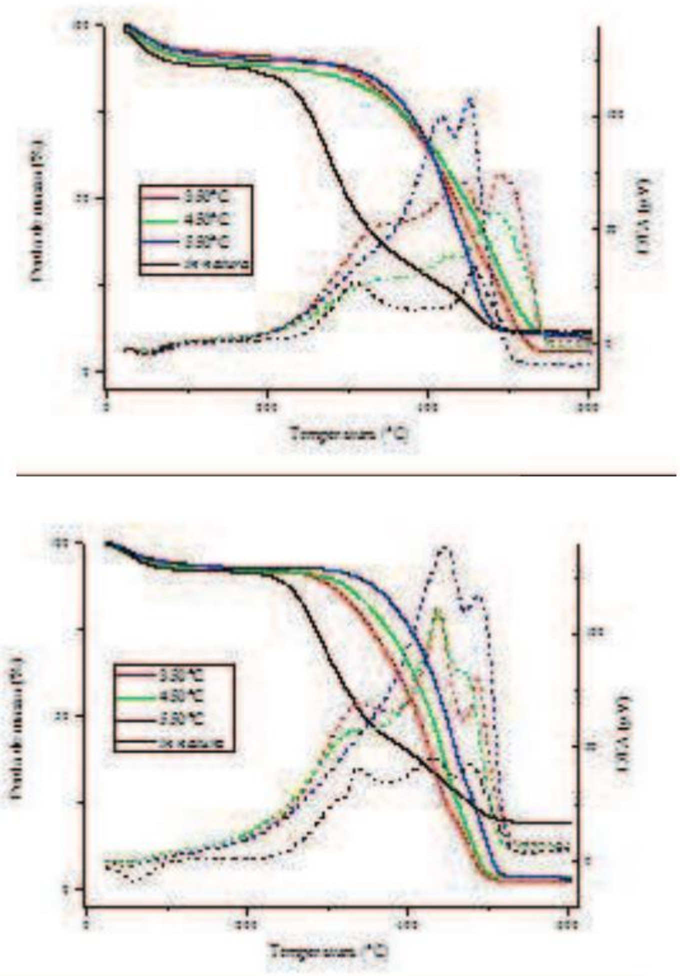

Figura 1. Perda de massa e curva termo diferencial (DTA) de amostras in natura e dos carvões de duas espécies de bambu (A. exótico *P.aurea;* B.nativo *Guadua sp.*)

The increase in the degradation temperature in the pyrolysed samples at 550°C corresponds to the degradation of cellulose residues and the beginning of lignin degradation and indicates that the materials produced at this temperature are more thermally resistant, that is, more aromatized, than the pyrolysates at lower temperatures. This behavior is observed in the pyrolyzed samples of both species. The last mass loss corresponds to the degradation of lignin and occurs at higher temperatures. In the exotic bamboo sample, this loss occurs at higher temperatures, probably due to the greater amount of this component in the in natura sample, in relation to the native bamboo, which agrees with the results of the chemical analysis. The spectra (Figure 2 and 3) of bamboos in natura are typical of lignocellulosic materials, with characteristic bands of O-H and N-H stretch (~3300 cm-1, Leng et al. 2011), oxygenated functional groups (C-O of polysaccharides, ~1039 cm-1, Niemeyer et al. 1992), ketones, aliphatic aldehydes (~1730 cm-1, Golonka et al. 2005), amides (1660-1630 cm-1, Golonka et al. 2005; Stevenson 1994). In the spectra of the two bamboo species, bands at ~1510 cm-1 (aromatic C=C stretch - vibration of aromatic rings, Wu et al. 2011) are present that disappear in the spectra of coals. In these, other bands are present, attributed to aliphatic C-H stretching (~2930 cm-1, Stevenson 1994) and symmetrical stretching of CH3 in methoxyl (~2863 cm-1, Sharma et al. 2004). The bands at ~1695 cm-1 indicate carboxylic groups (stretches in aromatics, Leng et al., 2011). These groups arise at the lowest pyrolysis temperatures (350 and 450°C). The intensity of this band decreases at 550°C with respect to the 1602 cm-1 band of aromatic structures (Golonka et al., 2005), also indicated by the bands at 3050 cm-1 (aromatic C-H stretch, Leng et al., 2011). These bands result from the carbonization process, since they are not present in the material in natura, become more intense with the increase in temperature and at 550°C dominate the spectrum, reflecting a highly aromatic material, without reactive functional groups.

Figure 2: Absorbance spectra of exotic bamboo *Phyllostachis aurea* in natura (BE IN) and cabornized at 350, 450 and 550 ºC.

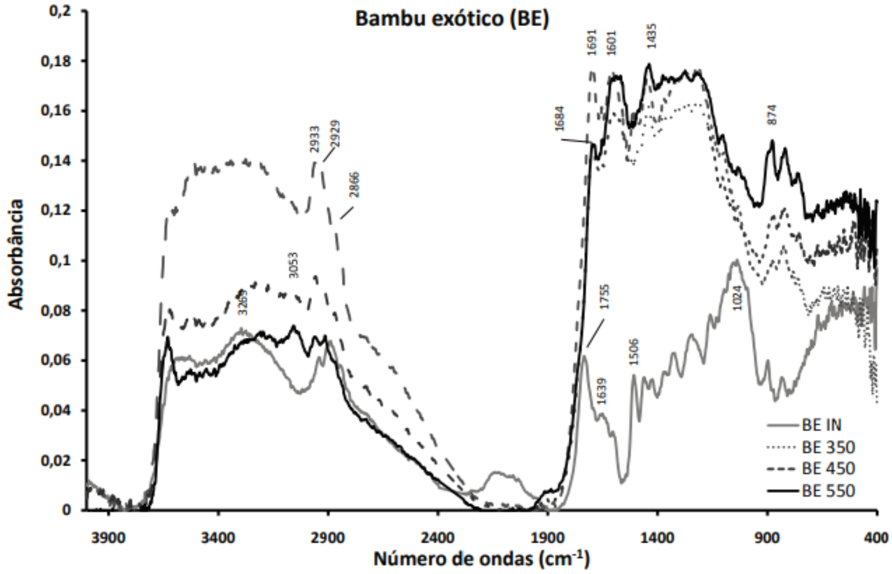

Figura 2. Espectros de absorbância do bambu exótico *Phyllostachis aurea* in natura (BE IN) e carbonizado a 350, 450 e 550°C.

Figure 3. absorbance spectra of native bamboo *Guadua sp*. in natura (BN IN) and carbonized at 350, 450 and 550 ºC.

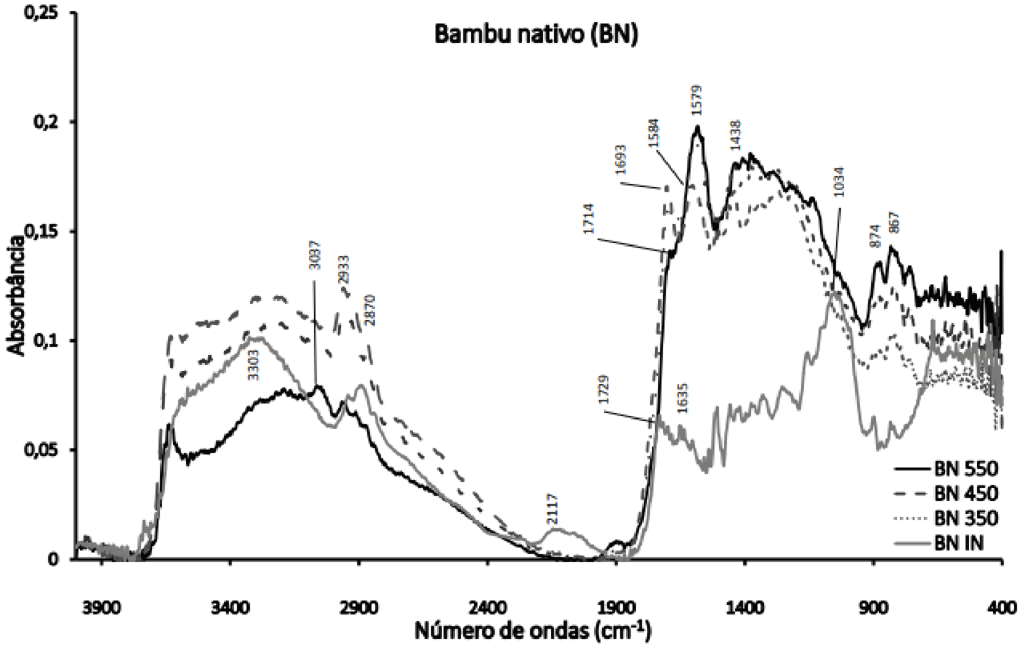

Figura 3. Espectros de absorbância do bambu nativo *Guadua sp*. in natura (BN IN) e carbonizado a 350, 450 e 550°C.

This change in molecular composition and structure can be expressed with relative, calculated indices of the spectra. The ratio between absorbance at ~3050 cm-1 and $^{\sim 2950}$ cm-1 indicates the relationship between aromatic and aliphatic structures. The higher this number, the greater the proportion of aromatics and, therefore, the greater the stability of the material against biological and biochemical decomposition. Another index is the ratio between the bands at ~1731-1695 $^{\text{cm-1 and} \sim 1610\text{-}1510}$ cm-1 that the higher it is, the greater the proportion of acid groups in relation to the aromatics. In Figure 4 it can be observed that with the increase in the temperature of carbonization, the stability of the material increases and the chemical reactivity decreases.

Figure 4 - Relative presence of aromatic and aliphatic structures (A) and reactive and aromatic structures (B) as a function of carbonization temperature.

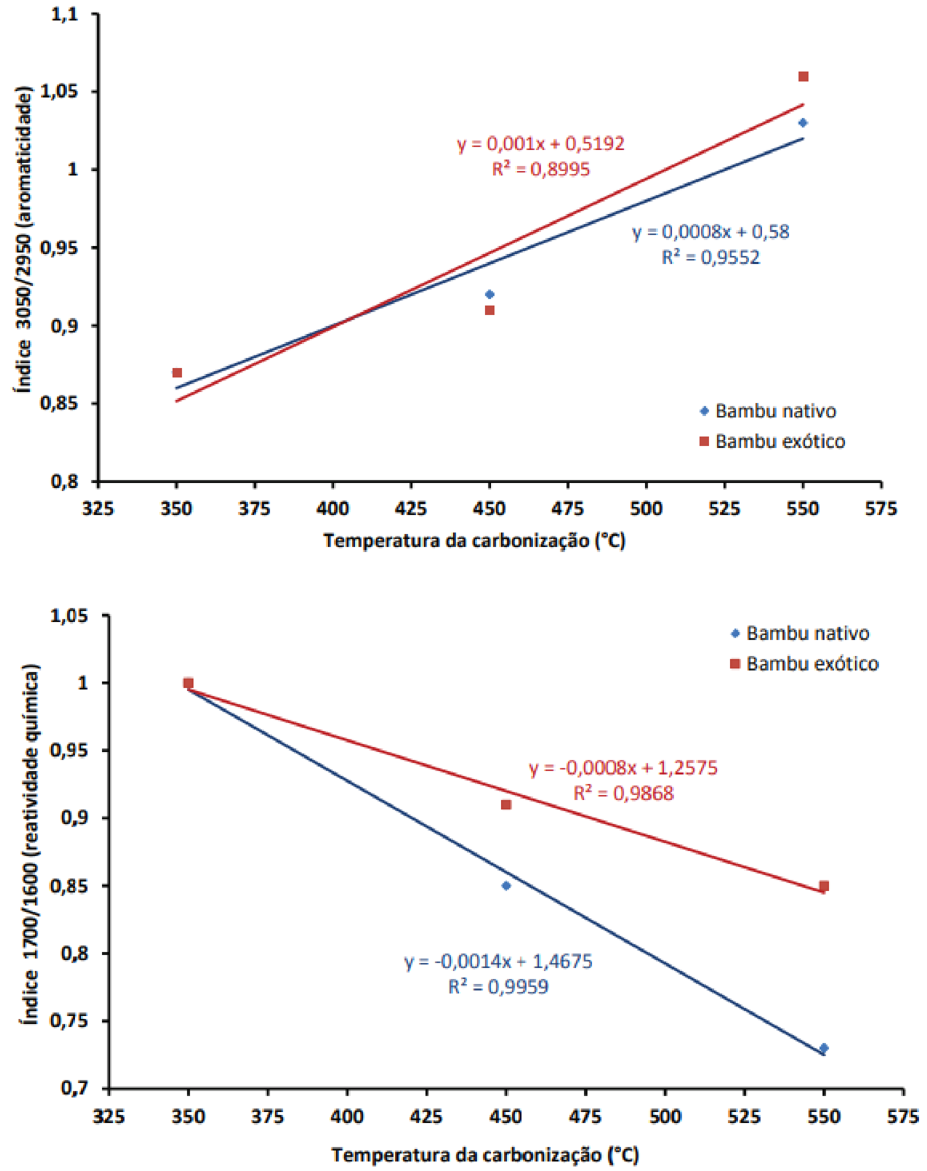

Figura 4. Presença relativa de estruturas aromáticas e alifáticas (A) e estruturas reativas e aromáticas (B) em função da temperatura da carbonização.

4 CONCLUSIONS

The stem coals of two bamboo species present characteristics potentially suitable for agricultural use. The coals obtained at 550 degrees showed higher carbon content. The coals of the two species showed differences in terms of ash and volatile content, with the native coal having higher ash contents and the exotic higher volatile content. As the pyrolysis temperature increases, coals have greater resistance to degradation and more aromatic character, with fewer functional groups than pyrolysed coals at lower temperatures. Such differences would lead to different neutralizing (ash) and ion exchange activities when used in the soil. Considering the higher ash and carbon contents in the coals of the two species, a higher carbon stock potential can be expected if *P. aurea coals* are incorporated into the soil.

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