

CHARACTERISTICS OF BIOCHAR PRODUCED FROM CELLULOSE FOR ATMOSPHERE CO₂ CAPTURE

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Abstract Biochar (BioC) production, from biomass, is attractive due to its low cost and relevant physicochemical characteristics. Within this context, the objective of the present work was to produce BioC from cellulose of *Pinus elliotti*, with different pyrolysis parameters, to use it on the CO₂ adsorption, from atmosphere. As main results, the produced BioC presented a porous structure, with a fibrous characteristic, due to the raw material used (cellulose). In the same way, those P800 presented specific surface area and total pore volume higher than those P600, due to the higher pyrolysis temperature applied. Due to these characteristics, P800 presented a greater ability to adsorb CO₂. Thus, a potential use for BioC was identified in this work.

Keywords: cellulose, *Pinus elliotti*, biochar, CO₂ adsorption.

1 Introduction

Graphene stacking gives rise to the structure of graphite and other carbon allotropes such as nanotubes, presents many fields of application and properties (ZARBIN; OLIVEIRA, 2013). In addition to the graphene and derivatives structures, there are forms of amorphous carbon, such as carbon black, activated carbon, glassy carbon, biochar, among others. Biochar (BioC) is a carbon-rich material, produced from the pyrolysis of organic feedstocks in the total or partial absence of oxygen. The thermochemical conversion of biomass for the production of BioC is a common method and presents high efficiency in terms of product quality and yield (LAZZARI et al., 2018). Furthermore, this organic material, usually becomes more attractive due to its low cost, viability, abundance and non-toxicity (BAKIERSKA et al., 2014; CHANG; CHEN; JIAO, 2010) (ZHANG et al., 2019) (YU et al., 2019). BioC morphological carbonaceous structure includes the amorphous carbon structure and the graphitic condensed structure, which are the non-carbonized fraction and the completely carbonized fraction of BioC, respectively. (CHEN et al., 2018).

Cellulose is a qualified raw material for the preparation of carbonaceous materials, because it is available in abundance and usually high quality, in addition to be a renewable resource. (DUNNIGAN et al., 2018; LAZZARI et al., 2018; YAMADA et al., 2017; HAN et al., 2016). Using a controlled temperature and an inert atmosphere, the carbohydrate structure of the biomass, from cellulose, decomposes into carbonaceous solid residues (called biochar). Moreover, condensable vapors (bio-oil) and non-condensable vapors (H₂, CO, CH₄, CO₂ and C_xH_y) are obtained from the obtention process of BioC, which may be interesting in the obtention of bio-gases.

Due to that, BioC from pyrolysis is highly carbonaceous and has a high energy and added value, being used for many purposes. One application of this biomass is in the production of activated carbon, which is widely used as an adsorbent, due to its high specific surface area and defined pore structure, as well as its high chemical resistance and adsorption capacity for organic compounds. (SKOUTERIS et al., 2015; LEE et al., 2013; BASU, 2010).

Then, the objective of the present work was to evaluate the influence of the pyrolysis temperature on the physical and morphological properties of BioC, formed from the cellulose of *Pinus elliotti*. Finally, the CO₂ capture efficiency was measured for both obtained BioC.

2 Materials and methods

Initially, bleached cellulose pulp, from *Pinus elliotti* was ground in a knife mill and dried in an oven at 105 °C for 24 hours. Then, pyrolysis was carried out in a bench reactor, which operates in a batch system. A detailed description of this equipment may be found at Perondi et al. (2017).

Two tests were carried out, in order to evaluate the effect of the temperature (800 and 600°C) used for the BioC preparation. BioC from it were named according to the final operational temperature, i.e., P800 and P600, respectively. The tests were carried out under an inert gas (N₂) flow with a flow rate of 150 mL min⁻¹, heating of 2 °C min⁻¹ and an isotherm time of 60 min.

For the evaluation of cellulose pulp and BioC morphology, Field Emission Scanning Electron Microscopy (FEG-SEM) were carried out, using a Tescan brand equipment – model FEG Mira 3 (Czech Republic). All samples were previously coated with Au, and the acceleration voltage applied was 15 kV.

Samples' elemental analysis was evaluated in terms of mass percentage of some chemical elements on the combustible materials structure, such as carbon, hydrogen, nitrogen, sulfur and oxygen. This analysis was performed following ASTM D5373/02 (carbon, hydrogen and nitrogen) and ASTM D4239-14e2 (sulfur) standards. The equipment with the brand of ELEMENTAR instruments and Vario Macro model was used for this analysis.

Moisture content and volatile matter content were determined by gravimetric measurements. Ash content was determined using an alumina crucible, with a standard weight. The measurements were performed using a muffle furnace with the used cellulose pulp into the crucible, weighted until the constant mass remained. The total carbon content was determined by the differences between the sum of % of moisture, volatile matter, char and total sample weight.

The specific surface area was measured by the Brunauer, Emmet and Teller method (BET) using the Quanta chrome Instruments equipment (model 1200e), managing the N₂ adsorption/desorption process at -196 °C. The *Pinus elliotti* sample underwent a degassing process, conducted under N₂ flow (no vacuum) and a temperature of 105 °C, for a period of 20h. BioC samples (P800 and P600) underwent a degassing process, conducted under vacuum and at a temperature of 380 °C, for a period of 20h.

BioC CO₂ adsorption capacity was determined in a Netzsch STA 449 F3 Jupiter® thermobalance. Approximately 10 mg of BioC was used for each run. The test started with a flow of 50 mL min⁻¹ of N₂ and a temperature of 120°C for 60 minutes, to eliminate possible volatile compounds present in the biochar. Then, the temperature was decreased to 25°C and the CO₂ replaced the N₂ (flow of 50 mL min⁻¹). The experiment was maintained for 30 minutes with CO₂ flow. The values corresponding to the CO₂ adsorption mass were collected every 1.5 seconds and the result was expressed in mg of CO₂ per g of cryogels. To evaluate the adsorption cycles, the procedure was repeated five times.

3 Results and discussion

Table 1 presents the results obtained for the cellulose characteristics and its BioC. The yield of products from the pyrolysis process is linked to the operational parameters (heating

rate, temperature and residence time) used during the process. The highest yield of BioC (27%) was obtained with the lowest temperature (600 °C). This occurs because at low temperatures and especially at low heating rates, the removal of volatile compounds is slow, allowing a secondary reaction that occurs between the char and volatile particles, favoring the formation of a secondary char (ALHO, 2012). Furthermore, when temperature increases there is decreases on the oil and char yield, which promotes an increase in the yield of gases. According Guerrero et al. (2005), the char yield decreases with increasing pyrolysis temperature and increases with decreasing heating rate. The authors obtained a yield of 24% of char, at a heating rate of 10 °C min⁻¹ and temperature of 600 °C. Alho (2012) also reported the same trend for *Pinus* and *Eucalyptus* species.

Table 1 – Immediate and elemental analysis of cellulose from *Pinus elliotti* and its BioC, produced at temperatures of 800 and 600 °C.

	Cellulose <i>Pinus elliotti</i>	P800	P600
Biochar (%)	-	20.87	27.74
Oil (%)	-	26.58	27.17
Gases (%)	-	52.55	45.10
Moisture (% m/m)	5.34 ± 0.17	4.83 ± 0.07	2.53 ± 0.14
Ash (% m/m)	1.20 ± 0.05	5.71 ± 0.09	7.52 ± 0.69
Volatiles (% m/m)	86.74 ± 0.47	6.96 ± 0.74	11.78 ± 0.22
Fix carbon (% m/m)	6.73 ± 0.49	84.90 ± 2.62	79.48 ± 2.63
N (% m/m)	0.29 ± 0.03	0.37 ± 0.08	0.29 ± 0.009
C (% m/m)	34.11 ± 0.07	82.11 ± 0.11	75.95 ± 4.58
H (% m/m)	6.71 ± 0.04	2.12 ± 0.13	3.45 ± 0.23
S (% m/m)	0.32 ± 0.05	0.46 ± 0.05	0.52 ± 0.03
O* (% m/m)	58.57 ± 0.05	14.94 ± 0.001	19.79 ± 0.21
Specific surface area (m ² g ⁻¹)	2.56	361.5	180.56
Total volume of porous (cm ³ g ⁻¹)	0.0043	0.017	0.012

Note: * Calculated by difference.

The content of fixed carbon and carbon on BioC increased, when compared to the raw material, for both immediate and elemental analysis. This occurs because, during pyrolysis, there is a decrease in the concentration of hydrogen and oxygen, due to dehydration, decarboxylation and condensation reactions. The concentrations of fixed carbon and carbon found in the biochar (P800) were 84.90 and 82.11%, respectively. Alho (2012) also found similar results (being 80.8 and 82.68% for the species of *Pinus taeda*).

Biomass' moisture can affect the pyrolysis process, as well as the quality and physical properties of the pyrolyzed products. Then, it is suggested that the thermochemical conversion of biomass should be carried out with samples that present moisture levels below 15%

(SHAH; KHAN; KUMAR, 2018; NANDA et al., 2013). In this regard, *Pinus elliotti* sample presented a humidity of $\approx 5.34\%$.

Ash is the solid residue generated after the complete combustion of raw material. In the case of pyrolysis, the ash is associated with the inorganic compounds presented on the raw material. In this way, the ash composition is directly related to the raw material used in the thermal process. Biomass ash, in general, may contain silicon, aluminum, iron, calcium and small amounts of magnesium, titanium, sodium and potassium. Its chemical composition is an important parameter to be considered during the thermochemical conversion, as it can generate operational problems, such as the formation of slag at high temperatures, which reduces the process' efficiency (NANDA et al., 2013; BASU, 2010). The ash content found for the *Pinus elliotti* was $1.20\% \pm 0.05$. This low value makes the material attractive for thermochemical conversion purposes.

Volatile matter, composed of moisture, light hydrocarbons (CO , CO_2 and H_2) and tar, is the condensable and non-condensable vapor released when the material is heated. The amount released is dependent on the rate of heating and the temperature to which it is subjected (BASU, 2010). Regarding the results for specific surface area, the increase in temperature, promoted an increase in the specific surface area, especially the biochar P800 with the highest specific surface area ($361 \text{ m}^2 \text{ g}^{-1}$). The same trend was observed for the total pore volume.

Figure 1 presents the SEM images of cellulose (Fig. 1a) and its BioC (Fig. 1b, c). It's possible to see that cellulose presents long and flat micro fibers, with a thickness of about 50 micrometers, a result close to those from Macedo et al. (2017). The length of the fibers cannot be measured because they are long, but long-fiber cellulose, originating from coniferous species, has a length between 2 and 5 millimeters. (IBÁ, 2019).

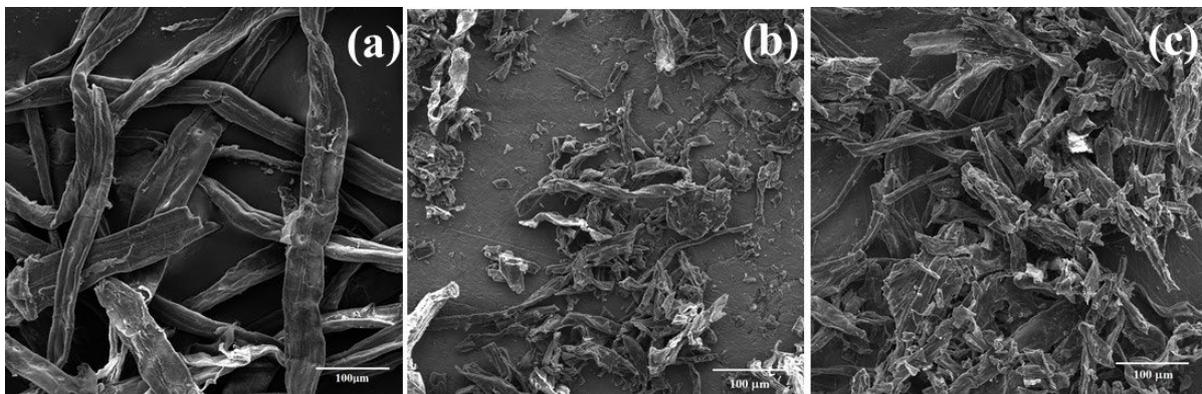


Figura 1 – SEM images of (a) cellulose *Pinus elliotti* and biochars from cellulose: (b) P800 and (c) P600. Scale: 100 μm .

The linear structure of cellulose shows a high tendency to form inter and intramolecular bonds. A portion of cellulose molecules aggregate forming microfibrils and from the agglomeration of these microfibrils, cellulosic fibers are formed. As a result, cellulose has high tensile strength and insolubility in most solvents (KLOCK et al., 2005).

On the other hand, the pyrolysis process broken and weakened cellulose, regardless the temperature employed for the BioC production. However, the fibrous structure was maintained, since it is possible to observe long and flat fibers. During the process of devolatilization, there is a gradual release of different volatile compounds, as the temperature increases, at a low heating rate. With this, cracks occur on the fibers' surface, causing their rupture. The carbonized particles formed by the devolatilization of *Pinus elliotti* contain complex pore structures and appears a micro-mesoporous structure.

The adsorption capacity of the produced BioC is shown in Figure 2. As can be seen in Figure 2(A), the adsorption capacity of CO₂ remains stable for up to 5 cycles, which shows that both BioC do not lose their efficiency after the desorption process. The maximum CO₂ adsorption capacity (Figure 2b) was 58 and 47 mg g⁻¹ for the P800 and P600, respectively. This capacity is reached within the first 5 minutes of testing. The difference between the specific surface area and the total pore volume, presented for each biochar (see Table 1), are perhaps the cause for the higher CO₂ adsorption capacity, presented by the P800, when compared to P600.

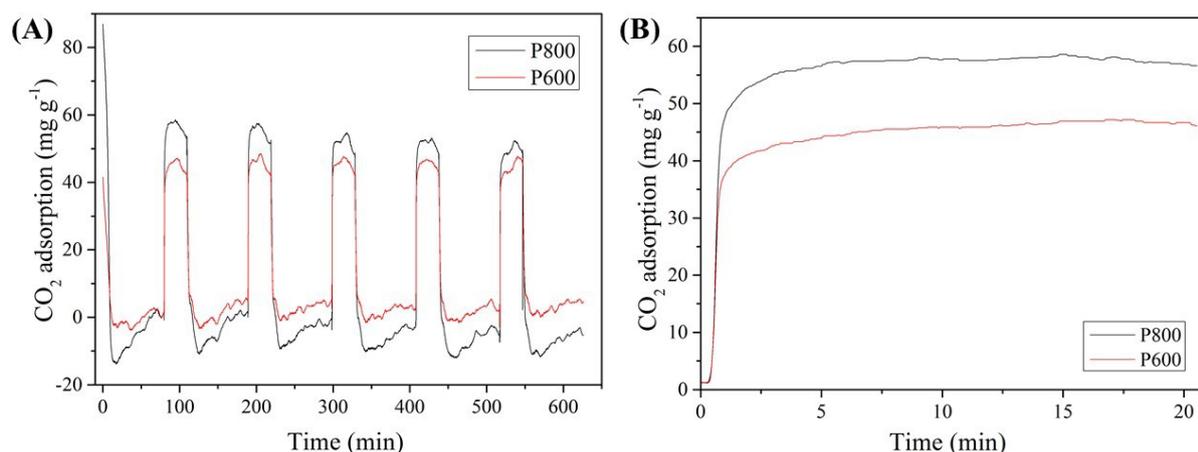


Figure 2 – (A) Cycles of adsorption and desorption of biochar P800 and P600. (B) Single adsorption cycle of P800 and P600 BioC.

4 Conclusions

This study presented the characteristics of two types of BioC, produced by two different pyrolysis routes. Cellulose from *Pinus elliotti* was used for the biomass production and there were differences, regarding morphological aspects, for those P800 and P600. Biochar yield decreased with increasing temperature and the specific surface area and the total pore volume increased with increasing temperature. The BioC's porous structure demonstrated that they have the capacity to be used as adsorbents and that they have stability in the adsorption capacity. Those P800 presented a greater capacity for the CO₂ adsorption, which may be related to the higher total volume of porous, porosity and Specific surface area, compared to P600.

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