CHARACTERISTICS OF BIOCHAR PRODUCED FROM CELLULOSE FOR CAPTURE OF ATMOSPHERIC CO_2

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Received October 3, 2022

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, intended for use in CO_2 adsorption from the atmosphere. As main results, the produced BioC presented a porous structure, with a fibrous characteristic, due to the raw material used (cellulose). Also, the biochar prepared at 800 °C (P800) presented higher specific surface area and total pore volume than that prepared at 600 °C (P600), due to the higher pyrolysis temperature applied. On the other hand, P600 presented a higher conversion of cellulose to BioC. Due to these characteristics, P800 presented greater ability to adsorb CO_2. Thus, a potential use for BioC was identified in this work.

Keywords: cellulose, *Pinus elliotti*, biochar, CO_2 adsorption

INTRODUCTION

Graphene stacking gives rise to the structure of graphite and other carbon allotropes, such as nanotubes, yielding materials with specific properties that find application in various fields.[1] In addition to graphene and derivatives structures, there are forms of amorphous carbon, such as carbon black, activated carbon, glassy carbon and 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.[2] Furthermore, this organic product becomes even more attractive due to the low cost, viability, abundance and non-toxicity of the raw materials.[3-6] The morphological carbonaceous structure of BioC includes the amorphous carbon structure and the graphitic condensed structure, which are the non-carbonized fraction and the completely carbonized fraction of BioC, respectively.[7]

Cellulose is a suitable raw material for the preparation of carbonaceous materials, because it is available in abundance and usually high quality, in addition to being a renewable resource.[8-11] Using a controlled temperature and an inert atmosphere, the carbohydrate structure of the cellulosic biomass decomposes into carbonaceous solid residues (called biochar). Moreover, condensable vapors (bio-oil) and non-condensable vapors (H_2, CO, CH_4, CO_2 and C_xH_y) are obtained from the preparation 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.[12,13,14] Thus, the objective of the present work was to evaluate the influence of the pyrolysis temperature (600 and 800 °C) on the physical and morphological properties of BioC, formed from the cellulose of *Pinus elliotti*. Finally, the obtained BioC products were investigated in terms of their CO_2 capture efficiency.

EXPERIMENTAL

Initially, commercial bleached cellulose pulp, from *Pinus elliotti* (supplied by the company Trombini (Brazil) 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 in the previous report of Perondi *et al*. (2017).[15]

Two tests were carried out, in order to evaluate the effect of the temperature (800 and 600 °C) used for the preparation of BioC. The obtained biochar products were named according to the final operational temperature, *i.e*., P800 and P600, respectively. The tests were carried out under an inert gas (N_2) flow, with a flow rate of 150 mL min^{-1}, heating rate 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.

Elemental analysis of the samples was performed and the mass percentage of some chemical elements in the combustible materials structure, such as carbon, hydrogen, nitrogen, sulfur and oxygen, was determined. This analysis was performed following ASTM D5373/02 (carbon, hydrogen and nitrogen) and ASTM D4239-14e2 (sulfur) standards. Elementar® Instruments equipment, 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, the cellulose pulp was placed into the crucible, and repeatedly weighed until constant mass was obtained. The total carbon content was determined by the difference between the sum of % of moisture, volatile matter and char and total sample weight.

The specific surface area was measured by the Brunauer, Emmet and Teller method (BET), using Quanta Chrome Instruments equipment (Model 1200e), managing the N_2 adsorption/desorption process at -196 °C. The *Pinus elliotti* sample underwent a degassing process, conducted under N_2 flow (no vacuum) and a temperature of 105 °C, for a period of 20 h. BioC samples (P800 and P600) underwent a degassing process, conducted under vacuum and at a temperature of 380 °C, for a period of 20 h.

The CO_2 adsorption capacity of the obtained BioC 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 N_2 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 CO_2 replaced the N_2 (flow of 50 mL min^{-1}). The experiment was maintained for 30 minutes with CO_2 flow. The values corresponding to the CO_2 adsorption mass were collected every 1.5 seconds and the result was expressed in mg of CO_2 per g of BioC. To evaluate the adsorption cycles, the procedure was repeated five times.

RESULTS AND DISCUSSION

Table 1 presents the results obtained for the cellulose characteristics and the obtained BioC samples. 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 at the lower 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 secondary char.[16] Furthermore, when temperature increases, there is a decrease in the oil and char yield, which promotes an increase in the yield of gases. According Guerrero *et al*. (2005),[17] the char yield declines with rising 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 *et al*. (2012)[16] also reported the same trend for *Pinus* and *Eucalyptus* species.

The content of fixed carbon and carbon on BioC increased, when compared to the raw material, as determined by both immediate and elemental analyses. 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. Other researchers have also found similar results for biochar prepared from the species of *Pinus taeda*, specifically of 80.8 and 82.68%.[16]

The moisture content of biomass can affect the pyrolysis process, as well as the quality and physical properties of the pyrolyzed products. Therefore, it is recommended that the thermochemical conversion of biomass should be carried out with samples that present moisture levels below 15%.[18,19] Considering this, the samples of *Pinus elliotti* used in this work presented a moisture content of ≈5.34%.

Table 1
Immediate and elemental analyses of cellulose from *Pinus elliotti* and its BioC produced at temperatures of 800 °C (P800) and 600 °C (P600)

Parameter	*Pinus elliotti* cellulose	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
Fixed 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

* Calculated by difference

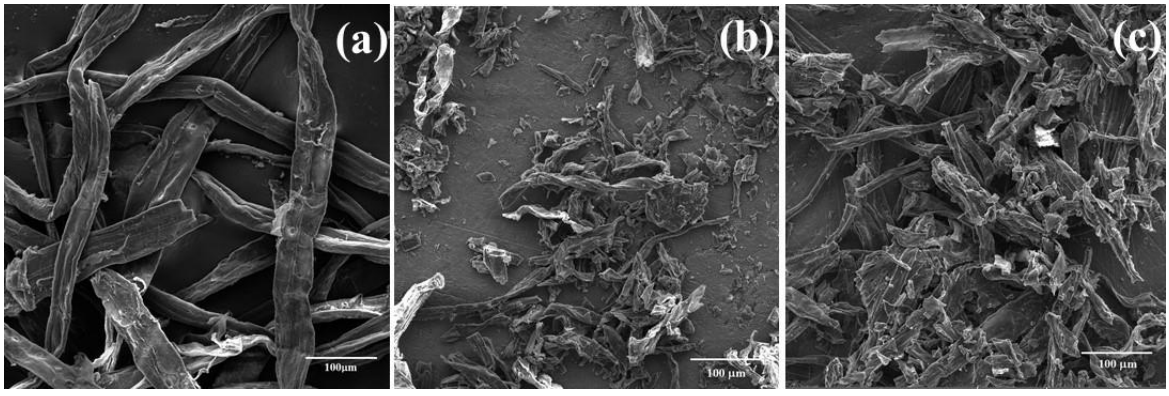

Figure 1: SEM images of (a) *Pinus elliotti* cellulose and biochars obtained from cellulose: (b) P800 and (c) P600 (at a scale of 100 µm)

Ash is the solid residue generated after the complete combustion of the raw material. In the case of pyrolysis, the ash is associated with the inorganic compounds present in 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.[14,19] The ash content found for the *Pinus elliotti* was 1.20% ± 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.[14] Regarding the results for specific surface area, the increase in temperature, promoted an increase in the specific surface area, notably for the biochar P800, which presented higher specific surface area (361 $m^2 g^{-1}$). The same trend was observed for the total pore volume.

Figure 1 presents the SEM images of cellulose (Fig. 1a) and its BioC products (Fig. 1b, c). It may be noted that cellulose presents long and flat micro fibers, with a thickness of about 50 micrometers, a result close to those reported by Macedo *et al*. (2017).[20] 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.[21,22]

The linear structure of cellulose shows a high tendency to form inter and intramolecular bonds. A portion of cellulose molecules aggregate, forming microfibers, and from the agglomeration of these microfibers, cellulosic fibers are formed. As a result, cellulose has high tensile strength and insolubility in most inorganic solvents.[23]

On the other hand, the pyrolysis process broke and weakened cellulose, regardless of 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 surface of the fibers, causing their rupture. The carbonized particles formed by the devolatilization of *Pinus elliotti* contain complex pore structures and, as a result, a micro-mesoporous structure appears.

The CO_2 adsorption capacity of the produced BioC was investigated and the results are shown in Figure 2. As presented in Figure 2(A), the adsorption capacity towards CO_2 remains stable for up to 5 cycles, which shows that both BioC materials developed in this study maintain their efficiency after the desorption process. The maximum CO_2 adsorption capacity (Fig. 2B) was 58 and 47 mg g^{-1} for 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 CO_2 adsorption capacity obtained for P800, when compared to P600.

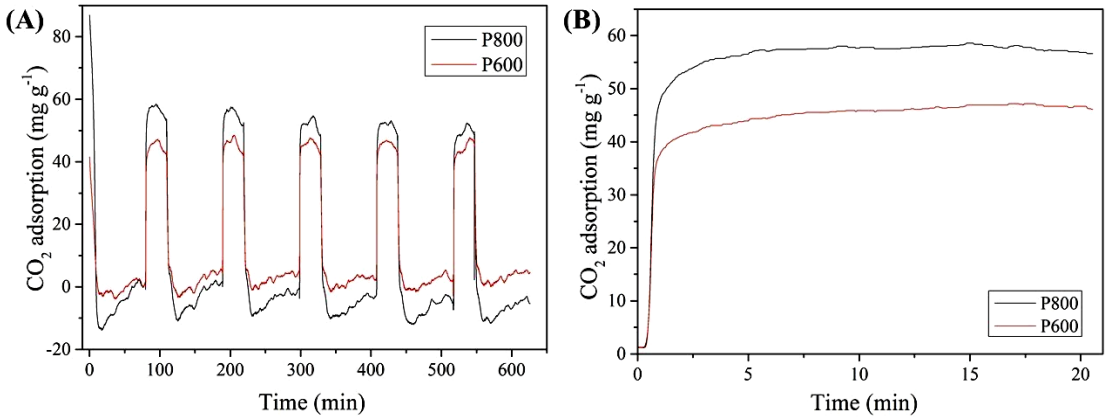

Figure 2: (A) Cycles of adsorption and desorption of biochars P800 and P600; (B) A single adsorption cycle of P800 and P600 BioC materials

CONCLUSION

This study investigated two types of biochar, produced by two different pyrolysis routes, and presented their characteristics. Cellulose from *Pinus elliotti* was used as raw material for the biochar production. Differences were found, regarding morphological aspects, between the biochar samples produced at different temperatures: P800 and P600. Furthermore, it was determined that the biochar yield decreased with increasing temperature. On the other hand, the specific surface area and the total pore volume increased with increasing temperature. The porous structure of the obtained biochar materials demonstrated that they are feasible alternatives to be used as adsorbents, since they present stability in their adsorption capacity. Sample P800 (biochar prepared at 800 °C) presented greater capacity for CO_2 adsorption, which may be related to the higher total volume of its porous structure, higher porosity and specific surface area, compared to sample P600 (biochar prepared at 600 °C).

ACKNOWLEDGEMENTS: Authors thank Federal University of Rio Grande do Sul (UFRGS), University of Caxias do Sul (UCS), Coordenação de Aperfeiçoamento de Pessoal de Nível Superior and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Instituto Euvaldo Lodi for the financial support.

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