

Production of activated carbon from fast-pyrolysis biochar

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Abstract

Thermochemical conversion of lignocellulosic biomass via fast-pyrolysis technique has become an interesting alternative to produce valuable bio-based products, such as the bio-oil. This alternative, for instance, can increase even more the profitability of such well-consolidated pulp and paper industries by turning it into more energetically self-sufficient process. Besides bio-oil, the fast-pyrolysis process results in many byproducts with high economic and environmental benefits. Biochar is one of these byproducts, and it can be activated by physical and chemical methods to use for water treatment and for environmental remediation. This study investigates the activation of biochar obtained from the fast-pyrolysis of wood biomass. The biochar was collected from a pilot-plant of bio-oil production and then activated via physical route (CO_2) at 800°C for 30 and 60 minutes; and via chemical route (H_3PO_4) at 450, 550 and 650°C for 60 minutes. The activated carbon was characterized by product yield, proximate analysis, surface area and thermogravimetric analysis. The chemical routes with H_3PO_4 were more efficient than the physical routes with CO_2 . The chemical activation at 450°C presented the highest product yield (80.47%) followed by a decrease in the yield to 71-75% with the increase of the temperature. The fixed carbon content increased after both physical and chemical activation, remaining around 91%. On the other hand, the volatile matter decreased significantly, especially in the physical routes. The surface area increased from 17.94 (untreated biochar) to 450-655 m^2/g , confirming the improvement of the porosity, mainly in the biochar activated by H_3PO_4 at 450°C and by CO_2 for 60 minutes. All biochar activated by chemical routes presented similar residual mass at 600°C, whereas the material physically activated with CO_2 presented lower residual mass, especially the one treated for 30 minutes. Overall, these results provide an alternative to produce a high added-value material from a fast-pyrolysis byproduct, encouraging the exploration of thermochemical conversion of lignocellulosic biomass.

Keywords: Biochar activation; biorefinery; surface area; thermochemical conversion; bio-oil.

Introduction

The energy self-sufficiency and the substitution of fossil fuels through the reuse of biomass are two of the main targets currently focused by pulp and paper industries. The fast-pyrolysis process is an interesting alternative to substitute the fossil fuels in the energy production. Besides the energy production, this technology of thermochemical conversion produces solid (biochar), liquid (bio-oil) and gaseous products [1], which can be converted in biochemicals and intermediate liquid streams [2].

The reuse of these products – as the biochar – is part of the concepts proposed in the biorefinery, especially the full enhancement of the biomass source with minimum loss of energy and mass [3]. The biochar is a good source to use for carbon sequestration [4] and as sorbent to abate organic pollutants [5]. Furthermore, biochar can be used as precursor for activated carbons with higher surface area [2, 6].

The conversion of biochar into activated carbon can be made by physical or chemical methods. The physical activation consists of the partial gasification of the biochar by an oxidant, such as steam or dioxide carbon at 700-900°C. On the other hand, the chemical activation occurs through the impregnation of the

biochar with a chemical, such as $ZnCl_2$ and H_3PO_4 followed by a carbonization step under inert atmosphere [7]. Both activation methods are good alternatives to improve the surface structure of the biochar and properties like surface area, pore volume and polarity, contributing to extend the number of applications.

In this study, we investigated the biochar from fast-pyrolysis pilot-plant of bio-oil as source to produce activated carbon under different conditions. Our purpose was to enhance the reuse of a byproduct from fast-pyrolysis process in a pulp and paper industry based on the concepts of bioeconomy. The activated carbon was produced by physical and chemical methods using CO_2 and H_3PO_4 , respectively, and they were characterized through the product yield, proximate analysis, surface area and thermogravimetric analysis.

Experimental

Raw material

Biochar was collected in a fast-pyrolysis pilot-plant of bio-oil production (BIOWARE, Brazil). The reactor was set to operate in fluidized bed, temperature of $500^\circ C$ for 5 seconds and 100 mm H_2O of pressure. The biomass used for bio-oil production was eucalypt wood fines rejected from a pulp and paper industry.

Activated carbon production

Activated carbon was produced using chemical and physical activations under different conditions. The chemical activation was performed with phosphoric acid (H_3PO_4). The mass ratio of H_3PO_4 to biochar was 2:1. The biochar was soaked and mixed for 15 minutes with 100 mL aqueous solution containing 40 g of H_3PO_4 . Then, this mixture was oven-dried for 24 hours at $103^\circ C$ followed by chemical activation in a muffle furnace at $450^\circ C$, $550^\circ C$ and $650^\circ C$ for 1 hour. The material obtained was washed with a solution containing 10% HCl and hot water until to reach neutral pH in the water, followed by drying in an oven at $103^\circ C$ until to reach constant mass.

The physical activation was performed in a muffle furnace equipped with manometer, gas control valve and a 25 cm-length quartz tube. The biochar was activated with dioxide carbon (CO_2) at $850^\circ C$ for 30 and 60 minutes with a heating rate of $15^\circ C/min$. The CO_2 flow was set in 200 mL/min.

Activated carbon characterization

The product yield of the activated carbon was determined for each condition of activation. The surface area (S_{BET}) was determined by B.E.T method and the proximate analysis was performed according to NBR 8112 standard. The thermogravimetric analysis (TGA) was performed in a Shimadzu DTG-60H equipment. Untreated biochar and activated biochar were heated from 20 to $600^\circ C$ in a N_2 inert atmosphere (50 mL/min gas flow) with heating rate of $10^\circ C/min$.

Results and Discussion

The chemical activation with H_3PO_4 presented the best results for the product yield (Figure 1A). All conditions adopted for the chemical activation resulted in yield higher than 70%, while the physical activation with CO_2 produced activated carbon with yield lower than 35%. The best yield was obtained for the chemical activation at $450^\circ C$, which is the lower temperature used in the activation. This suggests an influence of the temperature in the activated carbon yield, especially for the physical activation at $800^\circ C$. Very high temperatures can improve the porous structure of the material, which can decrease its yield and reduce its economic value [8].

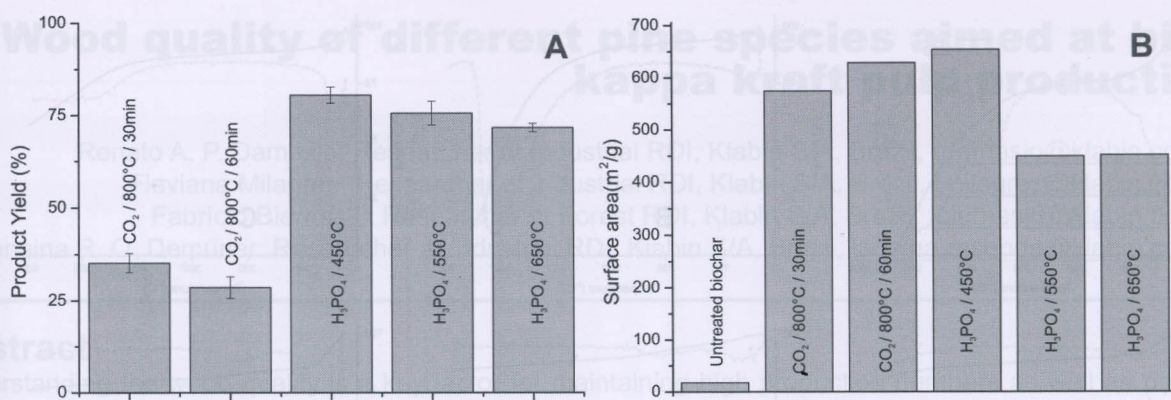


Figure 1. Product yield (A) and surface area (B) of untreated biochar and activated carbons.

On the other hand, the physical activation with CO₂ resulted in activated carbon with high surface area (Figure 1B). This significant increase of the surface area is related to the creation of microporous and mesoporous structures in the activated carbon due to the reaction between the biochar surface and the CO₂ [9]. The S_{BET} increased with increasing the time of activation, which was also observed by [10] in hickory and peanut hull hydrochars physically activated with CO₂. The S_{BET} of the activated carbon treated for 60 minutes was 9.35% higher than the activated carbon treated for 30 minutes. Regarding the chemical activation, the highest S_{BET} was found in the activated carbon at 450°C, followed by similar values of S_{BET} for the chemical activations at 550°C and 650°C.

The proximate analysis (Table 1) showed a similar increase of the fixed carbon regardless the physical or chemical activation. Both the volatile matter and ash content decreased substantially, mainly after the physical activation with CO₂. Regarding the chemical activation, both the volatile matter and ash content decreased with increasing the temperature. The lower contents of volatile matter and ash could be because the longer times of treatment, which support reactions of carbonization and release of volatile compounds [11].

Table 1. Proximate analysis of untreated biochar and activated carbons.

Treatment	Moisture (%)	Fixed carbon (%)*	Volatile matter (%)	Ash content (%)
Untreated biochar	10.93	79.51	3.97	5.59
CO ₂ / 800°C / 30min	7.53	91.78	0.54	0.17
CO ₂ / 800°C / 60min	7.78	91.71	0.41	0.12
H ₃ PO ₄ / 450°C	8.02	90.58	0.91	0.50
H ₃ PO ₄ / 550°C	7.92	90.9	0.82	0.36
H ₃ PO ₄ / 650°C	7.76	91.3	0.69	0.26

* The fixed carbon was determined by subtracting the percentages of moisture, volatile matter and ash.

Figure 2 illustrates the thermograms of untreated biochar and activated carbons. Most of the products presented a peak up to 100°C related to the loss of moisture. The activation of the biochar resulted in a product with higher thermal stability, especially for the activation with H₃PO₄. The residual mass of the activated carbons obtained by chemical activation presented residual mass between 16-25%, while the residual mass of the activated carbons obtained by CO₂ activation was 85% for 30 minutes and 45% for 60 minutes of treatment (Figure 2B-C). Regarding the physical activation, the treatment for 30 min presented an intense thermal degradation from 180 to 550°C, mainly due to the presence of organic matter from the precursor in the activated carbon. On the other hand, the CO₂ activation for 60 minutes presented a slighter thermal degradation from 320 to 530°C, confirming the higher thermal stability.

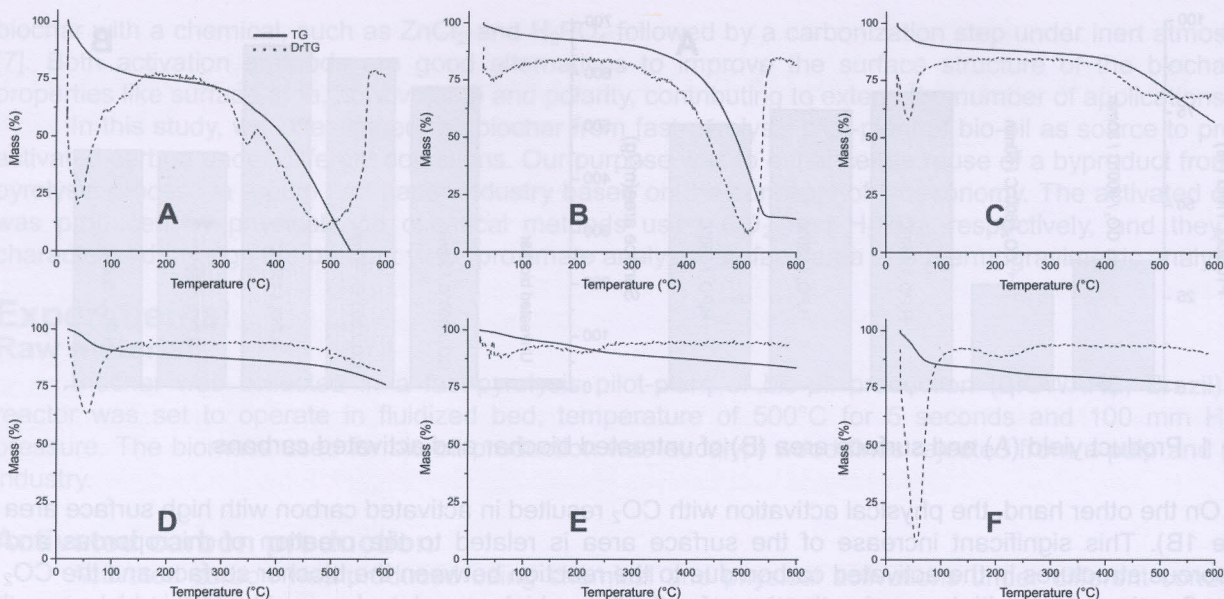


Figure 2. Thermogravimetric curves and their derivatives of the untreated biochar and activated carbons. (A) untreated biochar; (B) Activated carbon – CO₂ – 30min; (C) Activated carbon – CO₂ – 60min; (D) Activated carbon – H₃PO₄ – 450°C; (E) Activated carbon – H₃PO₄ – 550°C; (F) Activated carbon – H₃PO₄ – 650°C.

Conclusions

The CO₂ and H₃PO₄ activations changed the physical and chemical structure, and improved the properties of the biochar. The activated carbons presented higher surface area and thermal stability than the untreated biochar. The chemical activation with H₃PO₄ at 450°C presented the most interesting results. On the other hand, even with a higher surface area, the CO₂ activation presented the lowest product yields and thermal stabilities, which are not desirable from a biorefinery point of view. The biochar from fast-pyrolysis can be a profitable and environmentally friendly alternative to produce activated carbons with good properties. Future studies should investigate the adsorption capacity of these activated carbons for environmental applications.

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