Production of activated carbon from fast-pyrolysis biochar

Pedro Henrique Gonzalez de Cademartori: PhD, Universidade Federal do Paraná, Brazil, pedrocademartori@gmail.com
Bruno Dufau Mattos: PhD student, Universidade Federal do Paraná, Brazil, brunodufauMattos@gmail.com
Tainise Vergara Lourençon: PhD student, Universidade Federal do Paraná, Brazil, tainise@gmail.com
Andrey Nicolas Harres: Undergraduate student, Universidade Federal do Paraná, Brazil, andreyharres@gmail.com
Gino Capobianco: Professor, UNIGUAÇU, Brazil, gcapgi@yahoo.com.br
Mailson de Matos: PhD student, Universidade Federal do Paraná, Brazil, mailsondematos@gmail.com
Graciela Ines Bolzon de Muniz: Professor, Universidade Federal do Paraná, Brazil, gbmunize@ufpr.br
Washington Luiz Esteves Magalhães: Researcher, Embrapa Florestas, Brazil, washington.magalhaes@embrapa.br

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 m²/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
Activated carbon was produced using chemical and physical activations under different conditions. The chemical activation was performed with phosphoric acid (H₃PO₄). The mass ratio of H₃PO₄ to biochar was 2:1. The biochar was soaked and mixed for 15 minutes with 100 mL aqueous solution containing 40 g of H₃PO₄. Then, this mixture was oven-dried for 24 hours at 103°C followed by chemical activation in a muffle furnace at 450°C, 550°C and 650°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°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 (CO₂) at 850°C for 30 and 60 minutes with a heating rate of 15°C/min. The CO₂ flow was set in 200 mL/min.

Results and Discussion

The chemical activation with H₃PO₄ 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 CO₂ produced activated carbon with yield lower than 35%. The best yield was obtained for the chemical activation at 450°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°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 CO$_2$ 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 CO$_2$ [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 CO$_2$. 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 CO$_2$. 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.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Moisture (%)</th>
<th>Fixed carbon (%)</th>
<th>Volatile matter (%)</th>
<th>Ash content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated biochar</td>
<td>10.93</td>
<td>79.51</td>
<td>3.97</td>
<td>5.59</td>
</tr>
<tr>
<td>CO$_2$ / 800°C / 30min</td>
<td>7.53</td>
<td>91.78</td>
<td>0.54</td>
<td>0.17</td>
</tr>
<tr>
<td>CO$_2$ / 800°C / 60min</td>
<td>7.78</td>
<td>91.71</td>
<td>0.41</td>
<td>0.12</td>
</tr>
<tr>
<td>H$_3$PO$_4$ / 450°C</td>
<td>8.02</td>
<td>90.58</td>
<td>0.91</td>
<td>0.50</td>
</tr>
<tr>
<td>H$_3$PO$_4$ / 550°C</td>
<td>7.92</td>
<td>90.9</td>
<td>0.82</td>
<td>0.36</td>
</tr>
<tr>
<td>H$_3$PO$_4$ / 650°C</td>
<td>7.76</td>
<td>91.3</td>
<td>0.69</td>
<td>0.26</td>
</tr>
</tbody>
</table>

*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 H$_3$PO$_4$. 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 CO$_2$ 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 CO$_2$ 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 – CO$_2$ – 30min; (C) Activated carbon – CO$_2$ – 60min; (D) Activated carbon – H$_3$PO$_4$ – 450°C; (E) Activated carbon – H$_3$PO$_4$ – 550°C; (F) Activated carbon – H$_3$PO$_4$ – 650°C.

Conclusions

The CO$_2$ and H$_3$PO$_4$ 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 H$_3$PO$_4$ at 450°C presented the most interesting results. On the other hand, even with a higher surface area, the CO$_2$ 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.

References


Acknowledgements

The authors would like to thank the Conselho Nacional de Pesquisa e Desenvolvimento (CNPq, grant number 406897/2013-1) for the financial support.