Morphological and elementary evaluation of wooden carbonaceous materials from activated carbon industry

Everson do Prado BANCZEK1, Aline Barbieri BRUGNERA1, André Luís CHRISTOFORO2, 
Gilmara de Oliveira MACHADO2

1Departamento de Química, Universidade Estadual do Centro-Oeste, Guarapuava, PR, Brasil. 
2Departamento de Engenharia Florestal, Universidade Estadual do Centro-Oeste, Guarapuava, PR, Brasil. 
*E-mail: edopradobanczek@yahoo.com.br

ABSTRACT: The worldwide concern of reducing greenhouse gases into the atmosphere combined with more stringent environmental laws has led to an increase in studies of renewable energy. This research aimed to characterize wood chips and activated charcoal by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The chips came from an energy forest of Pinus elliottii and were burned in the furnace of a boiler for steam generation. This steam generated by the boiler in appropriate furnaces is used in the activation of wood charcoal from small regional producers. SEM showed an increase in the porosity of the charcoal with the activation process, and EDS analysis indicated both chips and charcoals, with and without activation, have no contaminants, such as heavy metals. This study revealed a low toxicity of lignocellulosic materials based on Pinus elliottii. The burning of wooden chips in the boiler as well as the activation process of wood charcoal did not present apparent environmental risks.

Keywords: forestry energy, carbonization, activated carbon, metals, porosity.

Avaliação morfológica e elementar de materiais carbonáceos de madeira da indústria de carbono ativada

RESUMO: A preocupação mundial na redução dos gases de efeito estufa para a atmosfera, combinada com leis ambientais mais rigorosas, tem levado a um aumento dos estudos sobre a energia renovável. Esta pesquisa teve como objetivo caracterizar lascas de madeira e carvão ativado por microscopia eletrônica de varredura (MEV) e espectroscopia de energia dispersiva (EDS). Os cavacos são oriundos de uma floresta de Pinus elliottii e foram queimados em uma fornalha de uma caldeira de geração de vapor. Esse vapor gerado pela caldeira em fornalhas apropriadas é utilizado na ativação do carvão vegetal por pequenos produtores regionais. MEV indicou um aumento na porosidade do carvão vegetal com o processo de ativação, e a análise EDS indicou que tanto os cavacos quanto os carvões, com e sem ativação, não apresentaram contaminantes, como os metais pesados. Este estudo revelou uma baixa toxicidade dos materiais lignocelulósicos à base de Pinus elliottii. A queima de cavacos de madeira na caldeira e o processo de ativação de carvão vegetal não apresentaram riscos ambientais.

Palavras-chave: energia florestal, carbonização, carvão ativado, metais, porosidade.

1. INTRODUCTION

Many countries have tried to increase the share of renewable sources in their energy matrices, seeking to develop new modern technologies, which enable the increase of the mass production of food and industrialized products, while also reducing the emission of greenhouse gases. Forest biomass is an easily available resource in Brazil at competitive costs, which it has been a focus for several studies. The forest biomass presents potential for new energy generation and benefits for the reduction of greenhouse effect gases (MACHADO et al., 2013). But, to establish the mass production of activated carbon from biomass, it is important to secure the resources from the viewpoint of supply chain costs (XIA et al., 2012). For this, woody waste materials from reforestation and other agricultural waste materials emerge as an important way to supply this demand.

Low-cost and renewable agricultural wastes are efficiently being converted into activated carbon (YAHIA et al., 2015). Activated carbons derived from agricultural wastes have been investigated as a replacement for expensive methods of removing heavy metals from wastewater (MOHAN; SINGH, 2002).

Researchers have developed alternatives for biomass from agricultural waste such as flax shives (MARSHALL et al., 2007), rice stalk (AI et al., 2013), rice straw (HU; HSIEH, 2014), orange peel (KÖSEOĞLU; AKMIL-BAŞAR, 2015), cotton stalk (NAHIL; WILLIAMS, 2012), cocoa shell (AHMAD et al., 2013), grape stalk (DEIANA et al., 2009), apple peel (HESAS et al., 2013), and tea fruit peel (GAO et al., 2013).

Another modern trend for biomass is related to the utilization of lignocellulosic materials and their wastes, such as tropical peat (KHADIRAN et al., 2015), bamboos (GONZÁLEZ et al., 2014), natural fibers (REED; WILLIAMS, 2004), and woods. The use of woods and their wastes as inputs (fuel) for biomass is an important and popular
alternative for energy generation. Clear examples are given in the numerous studies based on the wood species *Hevea brasiliensis* (SRINIVASAKANNAN; ABU BAKAR, 2004), *Ailanthus altissima* (BANGASH; ALAM, 2009), *Tamarindus indica* (ACHARYA et al., 2009), *Prosopis ruscifolia* (NABARLATZ et al., 2012), *Cunninghamia lanceolata* (LIU; ZHAO, 2012), *Neobalanocarpus heimi* (FOO; HAMEED, 2012), *Eucalyptus camaldulensis* (HEIDARI et al., 2014), *Populus euramericana* (ZHANG; ZHANG, 2014), and *Cassalpinia coriaria* (HERNÁNDEZ et al., 2014), as well as other constituents and or wastes, e.g., *Delonix regia* pods (VARGAS et al., 2011), *Albizia lebbeck* seeds (AHMED; THEYDAN, 2014), *Copernicia prunifera* leaves and *Acrocomia aculeata* seeds (LACERDA et al., 2015).

Among the sources of forest biomass, wood is highlighted because of its potential use in natural form (firewood), even in processed products in solid form (charcoal) or liquid form (pyrolysis oils), and in the use of forestry waste (pruning debris and branches) or industrial products (biquettes and pellets). These aforementioned authors emphasize the possibility of exploration or planting, without exclusive reliance on fossil fuels, is another advantage of wood as an energy source. In this aspect, woods from human planted forests, especially those of rapid growth such as *Pinus spp.* and *Eucalyptus spp.* and their industrial wastes, emerge as cheaper alternatives to produce activated carbon on a large scale. Pine is widely used as charcoal, especially in Brazil, and sawmills produce large amounts of residues of pine lumber, characterizing this waste as a relevant raw material for activated carbon. On the other hand, *Eucalyptus* forests are almost completely used for cellulose and paper.

Boilers are industrial machines which use the burning of fuels such as biomass from firewood, wood chips, and sawdust to produce steam. In the activation process of wood charcoal, a carbon-rich material, the steam released by the boiler, under specific conditions, acts as an activating agent in special ovens (CUNHA et al., 1989).

Wood charcoal is a result of carbonization, a thermal process which raises the carbon content of wood from approximately 50% to 80% in charcoal. Carbonization is a slow pyrolysis process which occurs in the temperature range from 300 to 400 °C, generating gases (CO, CO₂, H₂, CH₄), as well as a liquid fraction rich in organic acids (pyrolygineous acid) and a solid fraction (charcoal). Charcoal production in Brazil has significant economic importance, and is basically developed in two ways: traditional, which uses wood from native forests, usually harvested for the transformation of forest areas in agriculture; and modern, which uses wood from planted forests (KRONKA et al., 2005).

Activated charcoal is produced by wood carbonization and activation, as well as is also known through the nomenclature activated carbon. Ngernyen et al. (2006) state the activated carbon is a highly porous material which is widely used as an adsorbent for separation, purification and recovery processes. Kroschwitz; Howe-Grant (1992) indicates there are two processes for the preparation of activated carbons: physical and chemical.

Chemical activation is performed in a single step of combined carbonization and activation by using chemical activating agents – zinc chloride, potassium hydroxide, or phosphoric acid – at temperatures in the range from 400 to 800 °C (KROSCHWITZ; HOWE-GRANT, 1992). Physical activation involves the carbonization of a carbonaceous material in an inert atmosphere followed by the activation of the resulting char at higher temperatures from 800 to 1100 °C in the presence of activating agents, e.g., carbon dioxide, air, steam or a gas mixture (NGERNYEN et al., 2006).

Activated carbon has been used as all-purpose sorbent with extensive applications in the removal of organic and inorganic contaminants from solutions as well as in processes of gas purification (KIM et al., 2001). Activated carbons, with their high porosity, are extensively used in industrial purification and chemical recovery operations (TENG et al., 1998).

Analysis by Energy Dispersive Spectroscopy (EDS) is a very important tool associated with Scanning Electron Microscopy (SEM) for the characterization of metallic and semi-conductor materials because it allows the researchers to identify the elemental composition of samples in specific points of an image. In organic raw materials, EDS can identify the presence of heavy metals, which contributes to the evaluation of toxicity and of the possible environmental impact of the use of wood chips in the processes of combustion and of activated charcoal.

This study aimed to evaluate the surface morphology and the occurrence of heavy metals through SEM and EDS of *Pinus elliottii* chips used in the generation of thermal energy by a boiler and of the activated charcoal from the steam generated by this boiler.

2. MATERIALS AND METHODS

Samples of wooden chips of *Pinus elliottii*, activated carbon, and waste from the activation process were collected. Wooden chips were used as the boiler fuel for steam generation, which was used in the activation of charcoal in the activation furnaces. The wood charcoal went through an initial process of sieving to separate finer materials (waste). After this stage, thicker material was utilized in the activation process. These samples were collected from the Brazilian company named Brascarbo Agroindustrial Ltd.

The morphological characterization was performed by scanning electron microscopy (SEM) using a 2011 Tescan, Czech Republic, Vegas 3 model microscope. Three samples of wood chips were analyzed as follows: boiler fuel, with image magnification of 500x; sample of finer material (waste) which had not been activated and represented the original charcoal, with image magnification of 1500x; and activated carbon (final product) at 1500x. The samples were fixed using a double-sided conductive tape on a Quorum Q150R display. After this tape fixation in the device, the samples were dispersed in powder over the conductive tape and the excess was removed, with a double repetition of this step. The samples were metallized with gold and analyzed by a sputtering coater of Quorum Technologies Ltd., (model Q150 R, Ashford, Kent, England).

3. RESULTS

A micrograph of the wood chip sample is shown in Figure 1a, and the EDS spectrum for this respective sample is given by the Figure 2. Micrographs obtained by SEM of waste charcoal, representing the original wood charcoal and the activated charcoal, are shown in Figures 1b and 1c, respectively. The samples were also evaluated with respect to elemental chemical composition (Figures 3 and 4).

The EDS spectra present the elemental composition of the materials. Thus, we observed many elements are present, which were measured as percentages (Table 1).
Figure 1. Micrographs (magnification of 1500x): (a) micrograph obtained by MEV for wood chip sample, (b) charcoal waste, and (c) charcoal after the activation process.

Figura 1. Micrografias (ampliação de 1500x): (a) micrografia via MEV para a amostra de lascas de madeira, (b) resíduos de carvão e (c) carvão depois do processo de ativação.

Table 1. Elemental composition of wood chips and wood charcoals: non-activated and activated.

<table>
<thead>
<tr>
<th>Elements</th>
<th>wood chips (samples (%))</th>
<th>Non-activated charcoal (samples (%))</th>
<th>Activated charcoal (samples (%))</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>66.04</td>
<td>39.05</td>
<td>54.33</td>
</tr>
<tr>
<td>Mg</td>
<td>0.00</td>
<td>0.59</td>
<td>1.54</td>
</tr>
<tr>
<td>Al</td>
<td>3.68</td>
<td>1.23</td>
<td>0.79</td>
</tr>
<tr>
<td>Si</td>
<td>4.35</td>
<td>1.46</td>
<td>0.34</td>
</tr>
<tr>
<td>Cl</td>
<td>0.00</td>
<td></td>
<td>0.96</td>
</tr>
<tr>
<td>K</td>
<td>0.7</td>
<td>2.11</td>
<td>2.37</td>
</tr>
<tr>
<td>Ca</td>
<td>0.94</td>
<td>4.86</td>
<td>5.50</td>
</tr>
<tr>
<td>Mn</td>
<td>0.00</td>
<td>0.71</td>
<td>0.79</td>
</tr>
<tr>
<td>Cu</td>
<td>0.00</td>
<td>1.25</td>
<td>0.47</td>
</tr>
<tr>
<td>Mo</td>
<td>7.77</td>
<td>7.38</td>
<td>4.69</td>
</tr>
<tr>
<td>Sn</td>
<td>0.00</td>
<td>0.00</td>
<td>0.17</td>
</tr>
</tbody>
</table>

O: oxygen; Mg: magnesium; Al: aluminium; Si: silicon; Cl: chlorine; K: potassium; Ca: calcium; Mn: manganese; Cu: copper; Mo: molybdenum; Sn: tin.

4. DISCUSSION

Wooden chip is a material with relative porosity and a heterogeneous surface. These chips were stored in a hangar at Brascarbo Agroindustrial Ltd., near the boiler and the furnace, ensuring drying before wood chip burning. While combustion is a heterogeneous chemical reaction between the fuel and oxygen, the porosity of chips will favor gas exchange and increase the contact surface between reactants, favoring a clean burning.
With the EDS spectrum it is possible to detect the quantities of metals present in the chip samples, such as oxygen, 66.04% (O); aluminum, 3.68% (Al); silicon, 4.35% (Si); calcium, 0.94% (Ca); potassium, 0.70% (K); titanium, 0.45% (Ti); molybdenum, 7.77% (Mo); iron, 3.05% (Fe); tin, 0.00% (Sn); and gold, 18.03% (Au) from sample treatment. Therefore, by EDS analysis is observed there is no presence of toxic heavy metals (e.g., cadmium, mercury, lead, and arsenic), characterizing the chip sample as very low toxicity material (Figure 4).

The activation was accomplished with steam generated by the boiler in activation furnaces at a temperature ranging from 800 to 1100 °C. Through a comparison between Figures 1b and 1c, we can perceive the activation promotes an increase in the material porosity, especially the internal porosity. This increasing porosity was also present in the study of BANGASH; ALAM (2009) for activated carbon of Ailanthus altissima wood species at 800 °C.

Differences in pore size can also be observed, where this different porosity is classified according to the size of macro-, meso-, and micro-porosity. The increase in porosity also causes an increase in the internal surface area, where the adsorption occurs; in larger surfaces, the adsorption efficiency will be greater. The size and shape of pores can also influence the selectivity of adsorption by the molecular sieve effect. The porous structure alteration is important for the development of the surface area of activated charcoal, where most of its superficial characteristic is attributed to the micropores, with some contribution of mesopores (LU et al., 1995). Activation increased the porosity of the charcoal residue, which suggests an increase in the adsorbent characteristics. According to the data obtained by EDS, we verified there was an increase in the amounts of oxygen (O), magnesium (Mg), tin (Sn), potassium (K), manganese (Mn), calcium (Ca), and chlorine (Cl), as well as a decrease in the contents of aluminum (Al), silicon (Si), copper (Cu), and molybdenum (Mo), for the non-activated sample compared with the activated carbon sample. The decrease in the amount of metallic elements shows that the process of activation of the charcoal promotes the leaching of these elements from the active sites of the charcoal. This behavior may be interesting if we consider that, after activation, if this charcoal is used to remove metals from residual waters, it can be reused after re-activation, since the adsorption of the metals is not irreversible.

However, as detected in the elemental composition of wood chips, we observed the non-occurrence of toxic heavy metals, which, if present, could make the use of charcoal for both activation and for the application of activated carbon unavailable because toxic metals promote environmental pollution and can accumulate, which is very dangerous for living beings.

5. CONCLUSIONS

The characterization by scanning electron microscopy (SEM) showed an increase in the porosity of the wood charcoal after the activation process.

The activation process increased the internal area of the charcoal, making the material more efficient when used for adsorption.

Through the analysis of energy dispersive spectroscopy (EDS) was revealed wood chips, charcoal and activated carbon had no toxic heavy metals in their compositions, which enables the use of Pine charcoal, both for activation and for applications of activated charcoal.

6. REFERENCES


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