Quality of Wood and Charcoal from Eucalyptus Clones for Metallurgical Use

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ABSTRACT
The objectives of the present work were to determine the properties of wood and charcoal from Eucalyptus clones and assess impacts of charcoal features on the CO₂ gasification reactivity and to compare with coke reactivity. Gasification reactivity was performed using charcoal particles in a furnace setup at 820 °C, under CO₂ atmosphere. The results show that there is wood variability among evaluated clones and strong correlations between wood and charcoal properties. All charcoals had higher reactivity in comparison to coke. The decrease in porosity and increase in apparent density in Eucalyptus wood led to a slight decrease of CO₂ gasification reactivity. In addition, strong positive correlation between charcoal reactivity and potassium concentration (K) was found.

Keywords: CO₂ gasification, reductant materials, biocarbon.
1. INTRODUCTION

Brazil is the world’s leading producer of charcoal for industrial purposes, mainly used in the production of pig iron and steel, followed by ferrous alloys and silicon. It is noteworthy that the production of metal silicon by the metallurgical industry in Brazil is exclusively made with the use of charcoal, while in other countries, the use of coal is predominant.

Charcoal in the metallurgical industry acts as a bio-reducing agent and its use presents some advantages compared to fossil reductants, such as coal and coke. Charcoal has high reactivity, high porosity, high resistivity and low percentage of ashes, e.g. sulphur and phosphorus (Wang et al., 2016; Babich et al., 2010). Additionally, compared to the use of fossil reductants, the use of charcoal radically reduces SO\textsubscript{2} emissions, and helps reduce the environmental impact of CO\textsubscript{2}. On the other hand, charcoal has much lower mechanical strength compared to coal and coke, which might be challenging for some metal production processes. However, charcoals can be produced from different raw materials and under various process conditions, and have different properties influencing further applications (Kan et al., 2016; Oliveira et al., 2010).

Reactivity towards CO\textsubscript{2} is one of the most important properties of carbon materials used as reductants during metallurgical production processes (Wang et al., 2016). Reactivity should be appropriate for specific metallurgical processes to ensure optimum reduction process. In this study, the main objective was to assess the CO\textsubscript{2} reactivity of charcoal from Eucalyptus clones and to compare with coke reactivity.

2. MATERIALS AND METHODS

2.1. Raw material: sampling and characterization

Three short-rotation forestry species, Eucalyptus urophylla vs grandis hybrid clones, named as CL-1, CL-2 and CL-3, were used for this study. Samples of 7-year-old wood were collected from a Brazilian forestry company. These materials were selected due to the density variations. Six logs, representative of diameter variations, were sawn into 50-mm thick (discs), then divided in four to be used in chemical and physical analyses.

The wood basic density was determined according to NBR 11941 (ABNT, 2003). To determine macromolecular composition (lignin, extractives and holocellulose content) and ash content, samples were crushed and sieved between 250 and 400 µm. Wood extractive content was determined according to TAPPI 204 om-88 (TAPPI, 2001), using the total extractive method but substituting ethanol/benzene by ethanol/toluene. Lignin content was obtained by the sum of soluble and insoluble lignin. Insoluble lignin was determined using Klason method, which was modified according to procedure proposed by Gomide & Demuner (1986). Holocellulose content was determined by difference, based on extractive-free wood.

From each clone, logs with diameters from 60 to 140 mm were selected and sawn into pieces of approximately 1.0 m in height for carbonization. Charcoal was produced using a laboratory kiln built of refractory bricks, with diameter of 1.2 m and height of 1.1 m, with 1.04 m\textsuperscript{3} of usable volume. About 0.6 m\textsuperscript{3} of logs were loaded into the kiln for pyrolysis. Internal heating was used to initiate pyrolysis and maintain temperatures during the process. Temperature was monitored by five thermocouples, one inserted at the dome of the kiln and the others on the wall. The temperature of the carbonization process was controlled according to a pre-set theoretical model. The peak carbonization temperature was about 380 °C and the total carbonization time was approximately 50 hours. After carbonization, six 20-L bags of charcoal were randomly collected, homogenized and quartered. Samples were collected to determine charcoal properties.

2.2. Charcoal preparation

Charcoals from the three different clones were used in this study. In addition, one type of metallurgical coke was investigated as a reference material. Charcoals were produced in a laboratory kiln built of refractory bricks, with diameter of 1.2 m and height of 1.1 m, with 1.04 m\textsuperscript{3} usable volume. About 0.6 m\textsuperscript{3} of logs were loaded into the kiln for pyrolysis. Internal heating was used to initiate pyrolysis and maintain temperatures during the process. Temperature was monitored by five thermocouples, one inserted at the dome of the kiln and the others on the wall. The temperature of the carbonization process was controlled according to a pre-set theoretical model. The peak carbonization temperature was about 380 °C. This temperature was used for maximizing charcoal yield.
2.3. Charcoal properties

Proximate analysis of produced charcoals was performed according to procedures described in D1762-84 ASTM standard (ASTM, 2013). The ultimate analysis was determined by using an elemental Eurovector EA 3000 CHNS-O Elemental Analyzer. Concentrations of inorganic elements in the produced charcoal were measured by means of an inductively coupled plasma optical emission spectrometry (ICP-OES). Silicon content was determined by X-ray fluorescence technique (XRF).

Apparent density (AD) was determined by the hydrostatic method, in which samples were immersed in mercury. Therefore, it was possible to obtain the fixed carbon stock (FCS), expressed in (kg m$^{-3}$), by the product of charcoal apparent density and fixed carbon content.

Absolute density was determined using an AccuPyc 1330 Helium Pycnometer. The material porosity was evaluated according to the equation 1 below:

$$\text{Porosity} = \left[1 - \left(\frac{\text{apparent density}}{\text{absolute density}}\right)\right] \times 100\%$$

Friability (denoted $F$, expressed in %) also named “impact strength” gives an idea of the extent of breakage that will occur during charcoal loading, transportation and screening. In this work, the drum test was used to determine the charcoal friability index or degree. The procedure was performed according to Noumia et al. (2016).

Charcoal morphology was investigated by field-emission scanning electron microscopy (LVFESEM, Zeiss Supra 55VP).

2.4. CO$_2$ reactivity apparatus and procedures

Charcoal samples were calcined in an induction furnace to remove volatile matter, prior to CO$_2$ reactivity tests. Thereafter, samples were crushed and screened to the fraction +2-4.5 mm mesh to be used in the reactivity test. The CO$_2$ reactivity test was performed in an electric tube vertical furnace (Figure 1).

In the electric tube vertical furnace experiments, nitrogen flow of 0.8 l.min$^{-1}$ was used to sweep char sample during the heating up period from the room temperature to the desired gasification temperature of 820 °C. Heating up was carried out at a nominal heating rate of 35 °C min$^{-1}$. As temperature reached 820 °C, the purge gas was shifted from $N_2$ to CO$_2$. The sample

![Figure 1. Apparatus used for the CO$_2$ reactivity experiment.](image)
was kept at final temperature in the presence of CO$_2$ for 60 min. The experiment was then cooled down under N$_2$ atmosphere to room temperature. Reactivity (Rn) was evaluated according to the equation 2 below:

$$ Rn = \frac{(m_2 - m_1)}{(t_2 - t_1) \cdot m_1} $$  

Where:
- Rn = reactivity at time t
- $t_1$ = time of start of the weight measurement
- $t_2$ = time of end of the weight measurement
- $m_1$ = sample mass at $t_1$
- $m_2$ = sample mass at $t_2$

2.5. Statistical analysis

The experiment was performed according to a randomized design with four treatments (carbon reductants) and two replicates (two-sample), totaling 8 sampling units. Data normality was verified by Lilliefors test and homogeneity of variance by Cochran. Thereafter, data were subjected to analysis of variance, and, when significant differences were established, treatments were compared through the Tukey test at 5% probability. The accuracy of measurements was assessed with the sample standard deviation, which represents the mean deviation observed of values from their mean.

3. RESULTS AND DISCUSSION

3.1. Wood characterization

Charcoal quality, among other factors, is a function of its parental wood. Thus, assessment of wood properties is also necessary for better understanding of charcoal properties. Additionally, information on wood properties are necessary to achieve efficient pyrolysis, good quality of charcoal and low cost.

The chemical composition of *Eucalyptus* feedstock are listed in Table 1. The clone CL-3 had the highest levels of lignin (31.5%) and the lowest of holocellulose (64.5%), however, these components did not differ significantly among the clones. The lignin content is an important parameter to be evaluated in production and quality of charcoal, because within molecular chemicals elements of wood it is the one that presents greater resistance to thermal degradation (Pereira et al., 2013b; Yang et al., 2007; Raad et al., 2006) and, consequently, has positive influence in charcoal yield (Pereira et al., 2012; Trugilho et al., 2011). However, additionally, the quality of the lignin (syringyl/guaiacyl ratio) should also be considered (Soares et al., 2014; Santos et al., 2016). According to Pereira et al. (2013a), a minimum lignin content of 28% is required for profitable charcoal production for industrial purposes.

The content of extractives of CL-1 clone was the highest, average extractives of 4.5%, followed by CL-3 (3.9%) and CL-1 (3.3%). The content of extractives differed statistically among clones. The variation of extractives content can be attributed to different proportions of heart and sapwood, as well as to losses of extractives due to timber storage time (Costa et al., 2017; Pereira et al., 2013c; Silverio et al. 2008).

As it can be seen from Figure 2, the wood basic density ranged from 459.8 to 559.2 kg m$^{-3}$ among evaluated clones. CL-1 clone presented the highest

![Figure 2. Mean wood basic density values kg cm$^{-3}$ from *Eucalyptus* clones. Standard deviation = 40.3; variation coefficient = 7.9%. Means followed by same letter do not differ at 5% probability by the Tukey test.](#)

<table>
<thead>
<tr>
<th>CLONE</th>
<th>Lignin* (%)</th>
<th>Holocellulose (%)</th>
<th>Extractives (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL-3</td>
<td>31.5 ± 1.9 a</td>
<td>64.5 ± 1.9 a</td>
<td>3.9 ± 0.02 b</td>
</tr>
<tr>
<td>CL-2</td>
<td>29.4 ± 0.9 a</td>
<td>67.2 ± 1.1 a</td>
<td>3.3 ± 0.07 a</td>
</tr>
<tr>
<td>CL-1</td>
<td>29.6 ± 0.4 a</td>
<td>65.8 ± 0.5 a</td>
<td>4.5 ± 0.03 c</td>
</tr>
</tbody>
</table>

*Extractive-free wood. Means in the column followed by the same letter do not differ at 5% of probability by the Tukey Test. (±) Standard deviation.
average basic density, 559.2 kg m\(^{-3}\), 18.2% higher than the mean value of the other clones.

Basic density should be considered one of the main criteria for selection of species and clones of *Eucalyptus* for charcoal production. High-density wood is usually preferred, because the use of denser woods results in higher charcoal production for a certain volume of wood placed in the kiln (Pereira et al., 2012; Neves et al., 2011). Moreover, wood density is positively correlated to charcoal apparent density. Denser wood produces denser charcoal, thus, it is expected to have higher mechanical strength (Assis et al., 2016; Couto et al., 2015).

### 3.2. Reductant material characterization

Parameters that characterize the chemical properties of charcoal and coke are shown in Table 2. Inorganic elements are listed in Table 3.

*FC* showed small variation among charcoals, which is explained by the homogeneous pyrolysis conditions. The coke sample exhibited the highest *FC* as expected. The ash content of charcoal was less than 1% in all charcoal samples, whereas it was 6.9% in coke. Compounds that can be found in ashes are mainly metal oxides. Metals are reduced by carbon and are transferred to the metal alloy contaminating them, and in addition to influencing the chemical composition of the melted alloy, minerals can influence the properties of reducing materials (Gładysz & Karbowniczek, 2008).

As it can be seen in Figure 3, there is significant variability of apparent density and fixed carbon stock among charcoals. CL-3 wood char presented the lowest apparent density and FCS values, followed by CL-2 and CL-1 respectively. These results can be attributed to the variability found in wood bulk density. The clone that stood out with the highest bulk density also presented the highest apparent density and fixed carbon stock values in charcoal. It is noteworthy that wood density and pyrolysis conditions are two factors that significantly affect the charcoal apparent density (Assis et al., 2016; Kan et al., 2016). Coke apparent density and fixed carbon values were 1024.5 and 911.8 kg m\(^{-3}\) respectively.

Table 2. Proximate and ultimate analysis of charcoal samples (dry basis, wt %).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ultimate analysis (wt %)</th>
<th>Proximate analysis (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>CL-1</td>
<td>75.2 a</td>
<td>3.5 b</td>
</tr>
<tr>
<td>CL-2</td>
<td>75.5 a</td>
<td>3.2 b</td>
</tr>
<tr>
<td>CL-3</td>
<td>76.4 a</td>
<td>3.4 b</td>
</tr>
<tr>
<td>COKE</td>
<td>95.0 b</td>
<td>1.7 a</td>
</tr>
</tbody>
</table>

C: carbon; H: hydrogen; S: sulfur; N: nitrogen; O: oxygen; O/C: Oxygen/Carbon Ratio; VM: volatile matter; FC: fixed carbon. Means followed by same letter do not differ at 5% probability by the Tukey test.

Table 3. Ash composition of reductant materials.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>CaO</th>
<th>MgO</th>
<th>P(_2)O(_5)</th>
<th>MnO</th>
<th>K(_2)O</th>
<th>Na(_2)O</th>
<th>TiO(_2)</th>
<th>S</th>
<th>SiO(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CL-1</td>
<td>2.0</td>
<td>2.5</td>
<td>28.1</td>
<td>10.1</td>
<td>8.4</td>
<td>1.2</td>
<td>32.0</td>
<td>9.5</td>
<td>0.1</td>
<td>1.5</td>
<td>4.6</td>
</tr>
<tr>
<td>CL-2</td>
<td>0.4</td>
<td>0.7</td>
<td>22.7</td>
<td>11.3</td>
<td>7.9</td>
<td>1.2</td>
<td>47.8</td>
<td>4.9</td>
<td>0.0</td>
<td>1.1</td>
<td>2.0</td>
</tr>
<tr>
<td>CL-3</td>
<td>1.3</td>
<td>1.1</td>
<td>31.3</td>
<td>8.6</td>
<td>8.9</td>
<td>3.8</td>
<td>31.3</td>
<td>9.5</td>
<td>0.1</td>
<td>0.8</td>
<td>3.4</td>
</tr>
</tbody>
</table>
| COKE   | 17.4          | 15.9          | 14.5 | 8.7  | 0.1          | 0.6  | 0.9     | 2.3     | 0.7     | 4.3 | 34.5    

about 3 times higher than the average values of charcoal, which is mainly related to intrinsic characteristics of parental coal (Sakurovs & Burke, 2011).

Figure 4 shows the scanning electron microscopy (SEM) images of wood and charcoal. In general, anatomical characteristics of wood, such as shape, arrangement and organization showed little or no alteration due to carbonization, and the charcoal surface presented well defined structures. These results are similar to those cited by Pereira et al. (2016), who characterized the anatomical properties of *Eucalyptus* ssp. and the microstructure of produced charcoal.

The porosity values of charcoals and coke are shown in Figure 5, and porosity values ranged from 42.2% to 77.2%. Coke had the lowest porosity, 43% lower than the average values of charcoals. In addition, the high porosity and, hence, the low apparent density were related to higher charcoal friability. These results were similar to those found by several authors, among them Noumia et al. (2016) and Siebeneichler et al. (2017).

CO$_2$ gasification reactivity can be seen in Figure 6. All charcoals had significantly higher reactivity than coke. The charcoal characteristics, such as high porosity, low apparent density and reduced fiber wall fraction, which are indices connected to pore development in charcoal, should facilitate CO$_2$ diffusion into the carbon matrix when compared to coke. However, among *Eucalyptus* wood chars studied, the contribution of pore structure in changing activities seems to be relatively small. As it can be seen in Figure 4 and 5, although CL-2 charcoal presented intermediate porosity levels, it had the highest CO$_2$ gasification reactivity, 33% higher than the average of the other charcoals. By observing the ash chemical composition in Table 3, CL-2 charcoal presented the highest potassium concentration (K), 1.5 times higher than CL-3 and CL-1 charcoals. These indicate that the catalytic activity of potassium may have higher influence on charcoal gasification reactivity than porosity. It is known that the presence of K in charcoal improved its reactivity for CO$_2$ catalytically gasification (Mitsuoka et al., 2011; Kaczorowski et al., 2007). Additionally, it is worth noting that the CO$_2$ kinetic gasification of porous carbon at low temperature, where gaseous reactant molecules entering the porous
has high probability to diffusion deeply into the particle before reacting with the pore surface. The gaseous reactant concentration is necessarily uniform throughout the porous solid. Therefore, reactions are generally controlled by chemical reaction (Radovic et al., 1983).

4. CONCLUSION

There is wood variability among evaluated clones and strong correlations between wood and charcoal properties. The high apparent density and low porosity values of charcoal were mainly related with higher bulk wood density. In addition, the high charcoal porosity led to high friability.

Wood anatomical characteristics, such as shape, arrangement and organization showed little or no alteration due to slow pyrolysis and the charcoal surface presented well defined structures.

All charcoals from Eucalyptus clones had higher reactivity values when compared to coke. The decrease in porosity and increase apparent density values in Eucalyptus wood char led to a slightly decreased CO₂ gasification reactivity.

In this work, strong correlation between charcoal reactivity and K concentration was found.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support from the Brazilian Federal Government Agency (CAPES - scholarship) and Research Council of Norway and the partners of SFI Metal Production.

SUBMISSION STATUS

Received: 27 nov., 2018
Accepted: 13 dec., 2018

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