

Eucalyptus Bark Charcoal: the Influence of Carbonization Temperature in Thermal Behavior

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Eucalyptus bark is a waste generated in large volume and has been used as a source of energy. This study tries to use the *Eucalyptus* sp. bark as a source of raw material for the charcoal production and to study the influence of pyrolysis temperatures on charcoal properties. Charcoal was produced at different temperatures: 300, 400 and 500 °C, and their properties were determined by proximate analysis, higher heating value and thermogravimetric analysis. It was observed that higher pyrolysis temperature resulted in increase of the fixed carbon content and higher heating value. In the thermogravimetry and derivative thermogravimetry curves it was possible to determine the differences in the thermal stability of charcoal produced. It can be concluded that the eucalyptus bark charcoal is an alternative for the energy reutilization of this waste and also can be used as charcoal for heating.

Keywords: TGA, Biomass energy, Wood residue, Solid Biofuel.

1. Introduction

Fossil fuels are the source of pollutants and greenhouse gases. Energy from non-renewable fuels can be partially, if not totally, replaced by renewable sources. This matrix exchange is the objective of several industrial sectors, as it entails financial and ecological gains. For example, the use of charcoal instead of coal in the iron and steel industry. Also, the use of biomass instead of gas or oil in boilers¹.

Biomass is any organic matter that can be transformed into energy, either thermal, electrical or mechanical. The biomass origin can be urban, industrial, agricultural or forestry. All the forms in which biomass is obtained are seen as promising energy sources with potential for growth in the domestic and overseas market².

Forest waste is a promising energy source for Brazil due to the large amount of forest plantations (7.8 million hectares)³. Canopies, branches, and bark of trees are forest exploitation wastes⁴. The use of eucalyptus and its residues for charcoal production have been studied^{5,6}. Coal partial substitution by biomass is an attractive route to mitigate CO₂

emissions in the ironmaking process⁷. Compared to coal, biomass presents advantages, such as lower ash and Sulfur contents⁸. In addition, the thermal treatments like torrefaction and carbonization can adjust the biomass volatile matter yield varying the maximum process temperature⁹. Thus, biomass research has received growing interest.

The objective of this study was to analyze the pyrolysis influence on charcoal properties, produced from eucalyptus bark at different temperatures.

2. Material and Methods

2.1 Materials preparation and charcoal production

The material used was *Eucalyptus* sp. bark, collected at a wood panel industry in the city of Salto, SP. The material after collection was weighed and dried using a Marconi MA 35 air circulation oven. A 100 g sample of dry material was milled using Marconi MA-340 Willey Knife Mill and separated for proximate analysis.

On the other hand, the dry bark was cut manually in 1x4 cm sizes for the charcoal production (Figure 1B).

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Three pyrolysis temperatures were used: 300 °C, 400 °C and 500 °C. Approximately 20 g of the chopped bark was placed in a covered metal container. For the carbonization, a muffle furnace was used (Jung brand model 0212) at a heating rate of 20 °C.min⁻¹. The pyrolysis temperature was maintained for 3 hours under inert atmosphere (reduced oxygen atmosphere)¹⁰⁻¹¹.

2.2 Materials characterization.

2.2.1 Proximate analysis and higher heating value

All analyzes for bark and charcoal (volatile matter, ash content and fixed carbon) were performed in triplicate. Approximately 1 g of the milled bark samples were placed in calcined crucibles. Then, they were heated in a muffle furnace (Jung brand, model 0212) at 950 ± 25 °C for 7 minutes. After heating, the crucibles were cooled in a desiccator with silica gel for 1 h and weighed to determine the volatile matter. After weighing, the crucibles were taken back to the furnace for 6 h at 600 ± 25 °C, cooled again in the desiccator, and reweighed to determine the ash content.

The same analyses (volatile matter, ash content and fixed carbon) were performed for the produced charcoal. The crucibles with approximately 1 g of dry charcoal sample were used. It was positioned at the edge of the preheated muffle at 950 ± 25 °C, remaining in this position for 3 minutes (around 500 °C), and then placed inside the muffle for 6 minutes with the door closed. After that, the crucibles were cooled in desiccator with silica gel for 1 h and weighed to determine the volatile matter. The same crucibles used for the volatile matter determination (with sample) were placed in the muffle furnace at 750 °C for 6 h. The crucibles were cooled in a desiccator for 1 h and weighed to determine the ash content. Fixed carbon is a value resulting from the sum of the ash content and volatile matter percentages subtracted from 100%.

The higher heating value was determined for bark and charcoal sample in the bomb calorimeter brand IKA model C200.

All analyzes were conducted complying with the standards of the American Society for Testing and Materials¹²⁻¹⁶.

2.2.2 Thermogravimetric analysis (TGA)

Thermogravimetry (TG) and derivative thermogravimetry (DTG) were performed in the Perkin Elmer equipment, Pyris TGA 1 model. Approximately 21 mg of the sample were used in a platinum pan under a high purity (99.999%) nitrogen atmosphere with a flow rate of 20 ml.min⁻¹. The heating rate was 20 °C.min⁻¹, temperature from 50 to 700 °C.

2.3 Statistical analyses

The effects of experimental treatments were analyzed using software R version 2.11.1, by analysis of variance (ANOVA) and Tukey's multiple range tests (5% of probability).

3. Results and Discussion

3.1 Proximate analysis and higher heating value

Figure 1 shows the physical aspects of the eucalyptus bark samples and the respective charcoal. The samples were chopped and dried to make it possible the charcoal production in laboratory scale.

Table 1 shows the results of the proximate analysis and higher heating value (HHV) of eucalyptus bark and produced charcoal. Using biomass for energy purpose has some disadvantages such as high volatile matter and low fixed carbon content which were identified in the results of this study. The burning speed of pulverized biomass fuels is considerably higher than that of charcoal, and this behavior can be explained because the biomass has higher volatile matter compared to charcoal¹⁷.

The ash content of a charcoal and biomass fuels is also important. Generally, it varies from 0.5% to more than 5% depending on the species, the amount of bark and the presence of soil and sand in the sample. High levels of ash represent a decrease in energy potential and can cause corrosion in metal equipment. A good quality charcoal must have an ash content of less than 3%¹⁸.

It can be seen in Table 1, that the ash content in the produced charcoal was higher than 3%. This can be explained by a possible contamination of the bark (soil adhered) during harvesting¹⁹.



Figure 1. Investigated sample (A) eucalyptus bark (B) chopped bark (C) charcoal bark samples EB300.

Table 1. Proximate analysis and HHV (dry basis).

Material	Volatile matter (%)	Ash (%)	Fixed carbon (%)	HHV (MJ/kg)
eucalyptus Bark	72.07 ± 1.76 a	5.44 ± 0,52 a	22.49 ± 1.77 a	18.23 ± 0.13 a
EB300	44.79 ± 0.79 b	11.27 ± 0,24 b	43.94 ± 1.03 b	20.88 ± 0.02 b
EB400	34.83 ± 0.77 c	17.76 ± 0,26 c	47.41 ± 0.63 c	20.22 ± 0.09 c
EB500	24.07 ± 0.21 d	17.68 ± 0,04 c	58.25 ± 0.22 d	22.94 ± 0.11 d

Means followed by the same letter in the column are not statistically different by the test of Tukey at 5% level of probability

The optimum volatile matter of a “good-quality” charcoal depends on its use. For example, metallurgical grade charcoal should have a fixed-carbon content of 85-90%, whereas charcoal intended for domestic cooking should have a minimum volatile matter content of 20-30%, and a maximum of 40%²⁰. Although the charcoal produced in the three treatments (300, 400 and 500 °C) did not meet the qualities of charcoal for metallurgy, they presented the necessary characteristics for domestic use.

The eucalyptus charcoal produced in the Sao Paulo state can be considered of good quality, with volatile matter, ash content, fixed carbon and HHV of 16.9%; 1.20%; 81.9% and 32.65 MJ/kg, respectively²¹. The HHV of EB500 (22.94 MJ/kg) represents 72.2% when compared to the HHV of commercial eucalyptus charcoal (32.65 MJ/kg). Thus, bark charcoal (EB500) produced at a temperature of 500 °C exhibits potential for residential use.

3.2 Thermogravimetric analysis (TGA)

Biomass is composed mostly of cellulose, a polymer of glucose; hemicellulose, a complex polymer of which the main chain consists primarily of xylans or glucomannans; and lignin, a complex phenolic polymer, in addition to the main constituents, other non-structural (extractive) materials are present in fewer amounts²²⁻²⁴. Pyrolysis causes thermal degradation of these compounds and as a result, the biomass properties change significantly. Thermal degradation occurs in the order of hemicellulose > cellulose > lignin²³. Figure 2 presents the TG curves in (wt %) for the materials.

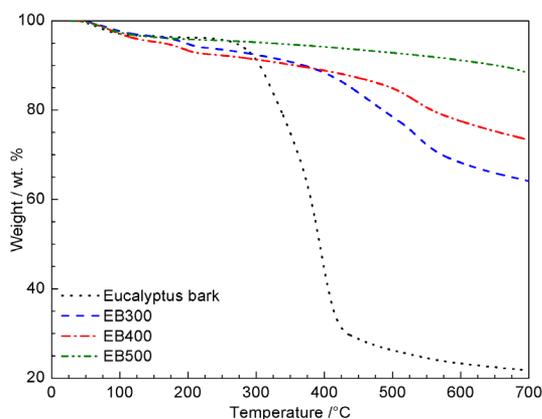


Figure 2. TG curves for eucalyptus bark and charcoal produced in nitrogen atmosphere and heating rate of 20 °C.min⁻¹.

In Figure 2, the difference in the thermal degradation between the eucalyptus bark and charcoal produced can be observed. Comparing the thermogravimetric curves it is observed that the pyrolysis process improves the thermal stability of the charcoal. As expected, the hemicelluloses were completely degraded in the charcoal, which can be proved by the absence of hemicelluloses peak in charcoal curves. According to Yang et al.²⁵, the hemicelluloses decompose in the range from 220 to 315 °C²⁵. Also, it is possible to observe that the higher pyrolysis temperature, the lower the percentage of mass loss in an inert atmosphere. For example, at 700 °C the curves of charcoal showed low percentage of mass loss 35.9%, 26.6% and 11.8% for charcoal produced EB300, EB400 and EB500 respectively, when compared to eucalyptus bark 78.1%. The curves showed that at 700 °C remained material are fixed carbon and ashes (same results of proximate analysis). Among the treatments (300, 400 and 500 °C), it was found that EB500 was thermally more stable charcoal.

In Figure 3 the DTG curves (wt. % /min) of the materials are shown. It is possible to observe the temperature with the peaks of the major mass losses and the maximum degradation rates of the materials. Table 2 presents the percentages of mass loss for the samples with the respective temperature and obtained residues (charcoal).

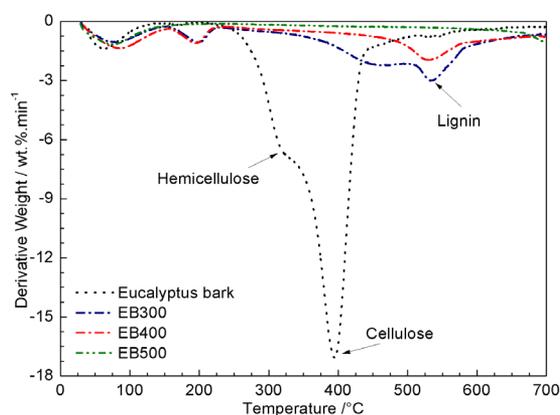


Figure 3. DTG curves for eucalyptus bark and charcoal produced.

In the DTG curves the initial mass loss at about 100°C was due to the water evaporation²⁶. It was observed for EB300 and EB400 treatments another mass loss peak at

Table 2. Data obtained from the TG/DTG curves for the produced eucalyptus bark and charcoals

		Material			
		eucalyptus bark	EB300	EB400	EB500
1 st step	T _{Peak} max	319	457	530	-
	DTG (%/min)	6.6	2.2	1.9	-
2 nd step	T _{Peak} max	395	533	-	-
	DTG (%/min)	16.9	2.9	-	-
3 rd step	T _{Peak} max	541	-	-	-
	DTG (%/min)	0.7	-	-	-
	Residue (%)	21.9	64.1	73.4	88.2

*No detected

197°C. It must be due to a dehydration process involving the splitting off of a hydroxyl group and of a hydrogen between two hydroxyl groups to form water²⁷.

The shoulder in the range from 230 to 360°C for eucalyptus bark DTG curves is due to the hemicellulose degradation. Another step was observed in the range from 360 to 430°C, with the maximum mass loss rate (16.9 %·min⁻¹) at 395 °C, attributed to the cellulose degradation and part of the lignin. Finally, a slight loss of mass occurred in the range from 430 to 570°C, with a maximum rate 0.7%/min⁻¹ at 541 °C. The eucalyptus bark degradation after maximum mass loss rate at 395 °C indicates gradual lignin degradation into a carbon-rich residual solid, until it reaches approximately 21.9% weight at 700 °C^{23, 27, 28}.

The pyrolysis temperature influenced the charcoal properties. DTG curves also showed that for charcoals the hemicellulose peaks disappeared, and the cellulose peak decreased dramatically, indicating thermal degradation of the hemicellulose and part of the cellulose during pyrolysis. When the pyrolysis temperature increased from 300 to 400°C, the cellulose peak disappeared, which indicates that the cellulose was also degraded in EB400. In the treatment EB500 all the peaks almost disappeared indicating that the pyrolysis temperature used (500°C) was sufficient to completely degrade the major biomass components.

The solid residues increased with the temperature charcoal production, for EB300, EB400 and EB500 treatments it was 64.1%, 73.4% and 88.2% respectively at 700 °C. Comparing to proximate analysis, it was observed that higher pyrolysis temperature also resulted in increase of the fixed carbon content and HHV. Therefore, the difference between charcoals produced in different temperatures could be due to thermal degradation biomass components during pyrolysis, resulting in carbon-rich residual solid.

4. Conclusion

It is concluded that the eucalyptus bark can be used as a source of raw material for the charcoal production. Charcoal obtained from eucalyptus bark has enough quality to be applied for heating or domestic use. The DTG curve showed

that pyrolysis temperature causes thermal degradation of the biomass components (hemicellulose, cellulose and lignin) resulting in properties changes as increase of the fixed carbon content and HHV.

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