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Thermal analysis of the combustion of charcoals from *Eucalyptus dunnii* obtained at different pyrolysis temperatures

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Abstract DSC and TG/DTA were used to study charcoals obtained from eucalyptus wood at different pyrolysis temperatures, as well as the exchanged energy, and the transformations involved during the pyrolysis process. Charcoals DSC curves showed two exothermic peaks, at ~610 and ~750 K. The first peak was squashed for those charcoals obtained at higher final pyrolysis temperatures, and it disappeared in the charcoals obtained at 873 and 923 K. The second peak intensity increased and its location changed at the higher temperatures. Charcoal characterization showed a rise of heat values with the pyrolysis temperature.

Keywords Biomass · Charcoal · Combustion · DSC · TG/DTA

Introduction

Brazil is the major producer of charcoal in the World, and profits about 106 ton in 2005, meaning 25% of world-wide production, being siderurgy its major application [1, 2]. Charcoal production from forests and wood industry residues, and its use as fuel is being studied in Uruguay, taking into account the strong dependence on foreign sources of energy of this country and the National policies regarding the support of forestry activities [3].

Charcoal production from wood and its later use as fuel has many advantages regarding the direct use of forestry biomass, such as resistance to microbial and plagues action, lower humidity and higher net heat value.

The pyrolysis step is determinant in charcoal production. High yields must be obtained in order to make the entire process profitable and pyrolysis conditions regulated for obtaining the higher quality [4–7].

Variables as pyrolysis temperature and time, and the initial rate of heating have influence on charcoal physical and chemical properties [6, 8, 9]. Therefore, the study of the influence of these variables on charcoal properties at a laboratory level allows the prediction of the best operative conditions for industrial carbonization.

Several references have been found regarding TG and DTA studies of biomass, wood or charcoal combustion, as combustion involves mass changes and energy exchanges [10–20], and to a lesser extent, DSC studies on these subjects were also found [21–28].

In this work, DSC and TG/DTA were used to study the combustion of charcoals obtained from eucalyptus wood at different pyrolysis temperatures, as well as the exchanged energy, and the transformations involved during the pyrolysis. Charcoal samples were obtained in a laboratory tubular furnace with programmable temperature, in N_2 atmosphere. The maximum pyrolysis temperatures were in the range 573–923 K. *Eucalyptus dunnii* wood was chosen as raw material, taking into account its regional future potential as a wood resource. Wood and produced

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Table 1 *E. Dunnii* wood analyses (weight percentage, dry basis)

Elemental analysis[a]				
H/%	N/%	C/%	S/%	O/%[b]
6.6	0.0	46.7	0.0	46.7
Proximate analysis				
Moisture/%	Volatiles/%	Ash/%	Fixed carbon/%	
12.4	75.7	0.6	11.3	
Heating value				
HHV/kJ kg^{-1} (±200)		LHV/kJ kg^{-1} (±200)		
18,400		16,800		

[a] Ash free

[b] Determined by difference

charcoals were characterized by proximate and elemental analysis and heat value determination. DSC and TG/DTA analyses were performed in dynamic air atmosphere. The overall results were compared in order to find relationships among them.

Experimental

Charcoal production

Wood was ground in a mill (Retsch) until obtaining a particle size of about 1 mm^3. 25–30 g of the ground and dry wood (48 h in stove at 378 K) were placed in a ceramics tray, inside a tubular horizontal laboratory furnace (Carbolite CTF 12/75). All the experiences were made in inert atmosphere (N_2 99.995%, 100 cm^3 min^{-1} flow) and at a heating rate up to the maximum temperature of 4 K min^{-1}. Different experiments were performed changing the maximum pyrolysis temperature (573, 623, 723, 873 and 923 K). After 2 h at the maximum pyrolysis temperature the furnace was left to cool down until reaching the set temperature.

Charcoal and wood characterization

Wood and charcoals were characterized by means of proximate analysis (moisture, ash and volatiles), and elemental analysis (Carlo Erba); the high and low heating power were also determined. Moisture analysis was performed by drying a sample in stove at 378 K up to constant mass. Ash and volatiles contents were determined in agreement to ASTM D 2866-70 and ISO 562-1981 norms, respectively. To determine the high heating value (HHV) the calorimetric bomb method was used (Parr 1341 Oxygen Bomb Calorimeter), in agreement with Parr Company, instructions sheet 204 M. The low heating value (LHV) was determined from the HHV and the elemental analysis of the samples.

DSC and TG/DTA

Wood and charcoals combustion was studied by DSC and TG/DTA. DSC measurements were carried out using a Shimadzu DSC-50 in dynamic air atmosphere at 10 K min^{-1} using about 1.0–1.5 mg of samples in aluminium pans. The samples were heated from room temperature up to 373 K and maintained in isothermal conditions for 10 min, and then heated to 773 K. TG/DTA measurements were carried out using a Netzsch STA 409EP equipment in dynamic air atmosphere, in the temperature range from 303 to 1023 K using 10 K min^{-1} heating rate, with sample masses between 6.0 and 7.0 mg in alumina crucible.

Results and discussion

Table 1 shows the results of wood analyses, and Tables 2 and 3 show the analyses of the charcoals obtained in the different pyrolysis conditions. Charcoals moisture (Table 2) corresponds with that absorbed by the samples in the container where they were stored; this value is then related to the hygroscopic property of the obtained charcoal. An increase is observed in the hygroscopic property

Table 2 Effect of maximum pyrolysis temperature on charcoal properties: elemental and proximate analysis (weight percentage, dry basis)

Temp/K (±1)	Elemental analysis[a]					Proximate analysis			
	H/%	N/%	C/%	S/%	O/%[b]	Moisture/%	Volatiles/%	Ash/%	Fixed carbon/%
573	3.5	0.0	66.2	0.0	30.3	2.4	48.0	1.3	48.3
623	2.7	0.0	73.4	0.0	23.9	4.9	32.0	1.7	61.4
723	1.7	0.0	79.0	0.0	19.3	5.6	17.8	2.1	74.5
873	0.6	0.0	88.6	0.0	10.8	6.4	3.5	2.0	88.1
923	1.5	0.0	88.3	0.0	11.1	7.4	1.6	2.1	88.9

[a] Ash free

[b] Determined by difference

Table 3 Effect of maximum pyrolysis temperature on charcoal properties: yield and heating values (weight percentage, dry basis)

Temp/K (±1)	Charcoal yield/%	HHV/kJ kg^{-1} (±200)	LHV/kJ kg^{-1} (±200)
573	44.3	29,200	28,200
623	35.5	26,700	28,000
723	28.8	30,700	30,000
873	25.8	33,300	32,700
923	24.2	34,900	34,700

of the charcoals obtained for higher pyrolysis temperatures, which can be produced by a higher development of the porosity at higher temperatures. With regard to charcoal fixed carbon and ash content, an increase is observed in the values of these properties as it increases the maximum pyrolysis temperature. A progressive decrease of the carbonization yield with the maximum pyrolysis temperature increase, as expected, is observed (Table 3). An increase of the charcoals heating value when the pyrolysis temperature increased from 623 to 873 K was observed. This is a result of the loss of volatiles at higher temperatures.

In DSC curves (Fig. 1) two exothermic peaks are observed, at 610 and 750 K, approximately. The first peak could be due to volatile matter combustion coming from hemicellulose (lower temperatures), cellulose (medium-high temperatures) and lignin decomposition, whereas the second one could be due to charcoal combustion. Co-combustion of volatile matter and charcoal would be possible in the temperature range between the first and the second peak. These processes have been already reported in the literature [29–33] and they would agree with the disappearance of the first peak with increasing pyrolysis temperature and the increase of the second peak intensity, in addition with the tendency of this peak to move along to

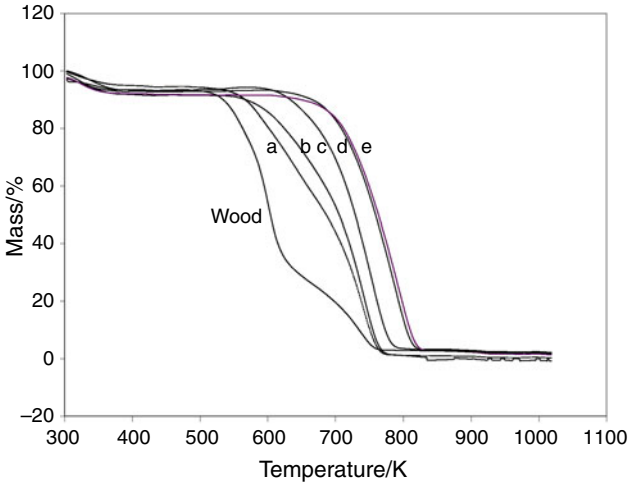

Fig. 2 TG curves in air of *E. dunnii* wood and charcoals prepared at maximum temperatures of (*a*) 573 K, (*b*) 623 K, (*c*) 723 K, (*d*) 873 K and (*e*) 923 K

high temperatures, as charcoal volatiles content and charcoal reactivity with oxygen decrease.

TG curves in air (Fig. 2) show the thermal stability of the charcoals and wood. As the pyrolysis temperatures increase, charcoal reactivity decreases, which is revealed by the higher initial ignition temperature.

Figure 3 shows the qualitative comparison of DTA curves in air for *E. dunnii* and the charcoals. As in DSC curves two peaks are found. For wood, these peaks have a similar intensity, the first one at a temperature of 620 K and the other one at 750 K. Both peaks can be interpreted in the same way that the corresponding DSC peaks. As the DTA results are expressed in μV mg^{-1}, from the area under the curves in Fig. 3 combustion enthalpies may be compared (*Note*: in Fig. 3 DTA curves are only displaced in order to enhance the figure clarity). Charcoal combustion

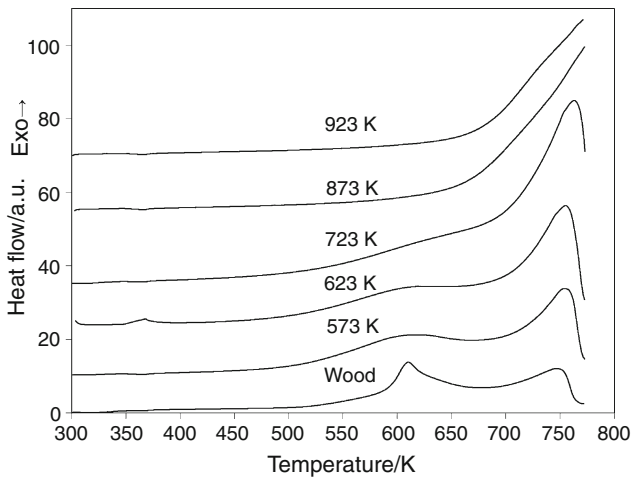

Fig. 1 DSC curves in air of *E. dunnii* and charcoals (carbonization temperature indicated on each curve); *a.u.* arbitrary units

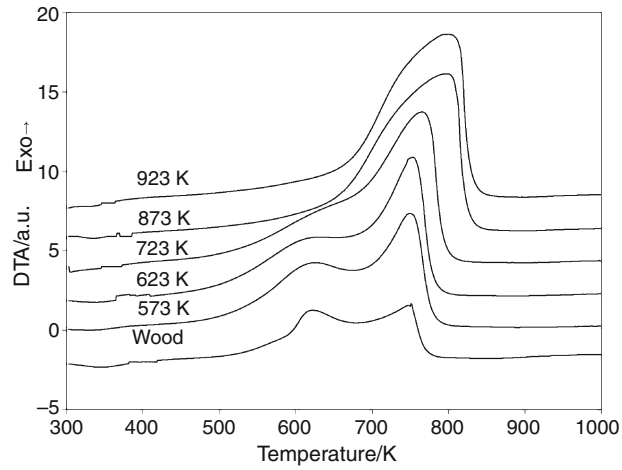

Fig. 3 DTA curves in air of *E. dunnii* and charcoals (carbonization temperature indicated on each curve); *a.u.* arbitrary units

enthalpy is clearly higher than that for wood, and shows a tendency to increase with the maximum pyrolysis temperature, in agreement with what was shown in Table 3.

Conclusions

DSC and DTA curves in air atmosphere of wood and charcoals obtained from *E. dunnii* showed two exothermic peaks, at ~610 and ~750 K. For those charcoals obtained at higher final pyrolysis temperatures, the first peak was squashed and in the charcoals obtained at 873 and 923 K this peak disappeared. For the second peak an increase of its intensity and dislocation was observed at higher temperatures. These facts are in agreement with the occurrence of at least two combustion stages: a flammable gas combustion at a lower temperature and a solid charcoal combustion at higher ones. The characterization showed a rise of the wood heating values with the pyrolysis temperature, also in agreement with the loss of volatile matter with increasing pyrolysis temperature.

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