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Potential of Mild Torrefaction for Upgrading the Wood Energy Value of Different *Eucalyptus* Species

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Abstract: Torrefaction is a promising pre-treatment for improving the fuel quality of biomass. This study examined the effect of a mild torrefaction (from 160 to 230 °C) on the heating value, elemental composition, and thermogravimetric analysis of wood from eight *Eucalyptus* species (*E. botryoides* Sm., *E. globulus* Labill., *E. grandis* W.Hill ex Maiden, *E. maculata* (Hook.) K.D. Hill & L.A.S.Johnson, *E. propinqua* Maiden Deane, *E. rufida* Endl., *E. saligna* Sm., and *E. viminalis* Labill.). The higher heating values (HHV) increased from the initial average of 19 MJ kg⁻¹ to 21 MJ kg⁻¹ in the torrefied samples. The carbon content increased from 48.2% to 53.3% and the C/O ratio from 1.08 to 1.35. The torrefied wood samples showed more thermal stability with a shift of the mass loss peaks to higher temperatures and a higher residual mass at 450 °C of 36%, in comparison to 30% of the untreated samples. Torrefaction concentrated the biomass samples in the more energetic and thermal resistant components and decreased their sulfur and chlorine content, leading to a better combustion performance. The wood of the eight *Eucalyptus* species had a similar behavior and showed quality improvement. Therefore, torrefaction showed potential as a pre-treatment for eucalyptus biomass fuel improvement.

Keywords: *Eucalyptus*; torrefaction; high heating value (HHV); thermogravimetric analysis (TGA); elemental composition

1. Introduction

Renewable energy plays a fundamental role in the reduction of fossil fuels consumption, and studies on alternative energy sources have increased exponentially [1]. The goal is to obtain cleaner energy sources of acceptable quality and with environmental, strategic, and socioeconomic benefits; e.g., reduction of pollutant emissions, higher energy security for countries depending on imported fossil fuels, poverty reduction, and access to energy in remote areas [2]. Biomass accounts for the largest fraction worldwide among the different renewable energy sources, although its use is still low compared with other sources [3]. Brazil is singled out in this context by International Energy Agency (IEA) [3], with approximately 16% of the world biomass use for power generation in the industry, followed by the US (9%) and Germany (7%).

Biomass may be used to meet a variety of energy needs, including electricity, home heating, vehicle fueling, and industrial process heating. The wood industries and homeowners are the major consumers of biomass energy, e.g., the timber and pulp and paper industries burn their own wood

wastes to supply approximately 60% of their energy needs [4]. The potential environmental benefits from using well-managed biomass energy feedstocks as opposed to fossil fuels include lower emissions of certain pollutants and greenhouse gas emissions and CO₂ neutrality. Biomass energy facilities can also help increase jobs in areas with resource-dependent economies, which are usually characterized by a slow economic growth [5,6].

However, the use of wood biomass to produce energy still has some limitations, mostly because of the physical properties of the wood itself. In general, raw biomass is characterized by a high moisture content, hygroscopic behavior, low energy density (the primary energy conversion technologies only reach 15% to 20% conversion efficiency), low density, and possible storage problems. Furthermore, transporting wood fuels over long distances is generally not economically feasible [5,7]. Some of the drawbacks of raw biomass can be mitigated by pretreatments. A number of conversion methods have been proposed, of which torrefaction has attracted more attention in recent research because of its increasing application potential [8].

Torrefaction is a thermochemical process that is carried out at relatively low temperatures between 200 °C and 300 °C. In this range, the thermochemical degradation of lignocellulosic materials is moderate, with hemicelluloses as the most easily degraded structural component. This thermal treatment ensures a more homogeneous material with higher energy density, maintaining in average 90% of the energy and 70% of the mass content in relation to the raw material [9].

Therefore, torrefaction is a promising technique to improve the performance of biomass for energy utilization. However, the number of studies is still limited, specifically regarding the thermochemical behavior of different lignocellulosic materials and wood species. Among them, the *Eucalyptus* species are especially interesting because some are already important industrial raw materials; e.g., *E. globulus* Labill.—for the pulping industry, and many are potential pulp and timber species or biomass crops [10,11]. In this study, the torrefaction of eight eucalyptus species was studied.

2. Materials and Methods

2.1. Materials

Six-year-old trees from eight eucalyptus species (*Eucalyptus botryoides* Sm., *E. globulus* Labill., *E. grandis* W.Hill ex Maiden, *E. maculata* (Hook.) K.D. Hill & L.A.S.Johnson, *E. propinqua* Maiden Deane, *E. rufida* Endl., *E. saligna* Sm., and *E. viminalis* Labill.) were collected from an arboretum located in the fields of the School of Agriculture (ISA), University of Lisbon (ULisboa), at Tapada da Ajuda, Lisboa, Portugal (38°42' N; 09°10' W). The trees were harvested, and the lower stem log from the base to 1.3 m of height was taken and then sawn into boards, were cut with 60 × 7.5 × 2 cm³ (in axial, tangential, and radial directions). The boards were air dried to moisture content between 12% and 15%.

2.2. Methods

The wood boards were torrefied with gradual heating from 160 to 230 °C by the Portuguese company Santos & Santos Madeiras (S&S) under the registered trademark Atlanticwood, a thermo-modification process. Depending on the treatment temperature and wood, the conditioning phase takes 5–15 h. The specific characteristics of the process (reactor and temperature gradient) are under industrial secrecy.

The higher heating value (HHV) was determined (ABNT 1984) [12] using an Adiabatic Bomb Calorimeter (Model IKA300, IKA, Staufen, Germany). For this analysis the samples were oven-dried at 103 °C ± 2 °C until a constant mass was reached.

Ash content was determined by Technical Association of the Pulp and Paper Industry, TAPPI standard method T15 os-58. The elemental composition was determined using the ASTM D5373-08 (2008) [13] with a Perkin-Elmer II 2400 (Shelton, CT, USA) element analyzer. The composition regarding carbon, nitrogen, and hydrogen (CHN) was determined, as well as Ca, Mg, K, Cl, and S, while the oxygen percentage was calculated as (100 – (ash + carbon + hydrogen + sulphur + nitrogen)) difference.

Thermogravimetric analysis (TGA) and derivative thermogravimetry (DTG) measurements were carried out using a differential thermal analyzer DTG-60H (Shimadzu, Kyoto, Japan) in a dynamic nitrogen atmosphere (gas flow of 50 mL min⁻¹) with a temperature range of 10 to 900 °C using a 10 °C/min⁻¹ heating rate, using 2 mg ± 0.1 mg samples in a platinum container. The thermogravimetric curve (TG) and the curve of the first derivative of the mass loss (DTG) were recorded. From the TG curves, the mass loss was calculated in the following temperature ranges: 50 to 100 °C, 100 to 150 °C, 150 to 200 °C, 200 to 250 °C, 250 to 300 °C, 300 to 350 °C, 350 to 400 °C, and 400 to 450 °C. The residual mass at 450 °C was also calculated.

3. Results

The higher heating values of the untreated and torrefied wood samples of the different eucalyptus species are compiled in Table 1. Overall, the results show that there is an energy gain with the torrefaction process for all species, i.e., the mean calorific value of the torrefied wood was 21 MJ kg⁻¹, while that of the untreated wood was 19 MJ kg⁻¹. The increase in calorific value by torrefaction was on average 7.4% when compared with the untreated samples. The highest values were found for *E. botryoides*, *E. grandis*, and *E. rufida* (9.3%, 9.9%, and 10.8% respectively), while *E. maculata* presented the lowest value (2.2%).

Table 1. Higher Heating Value (HHV, MJ kg⁻¹) of Untreated and Torrefied Wood Samples from Eight *Eucalyptus* Species.

Wood Species	Higher Heating Value (MJ kg ⁻¹)	
	Untreated	Torrefied
<i>E. botryoides</i> Sm.	19.2	21.0
<i>E. globulus</i> Labill.	19.0	20.1
<i>E. grandis</i> W.Hill ex Maiden	19.0	20.9
<i>E. maculata</i> (Hook.) K.D. Hill & L.A.S.Johnson	19.1	19.5
<i>E. propinqua</i> Maiden Deane	19.9	21.3
<i>E. rufida</i> Endl.	19.2	21.3
<i>E. saligna</i> Sm.	19.6	21.0
<i>E. viminalis</i> Labill.	19.4	20.8

The results of the elemental analysis are presented in Table 2. There was a clear effect of the torrefaction in the elemental analysis for the eight eucalyptus woods, which presented a similar trend of an increase in carbon and a decrease in oxygen along with a slight decrease in hydrogen with heating. The largest carbon increase between treated and untreated wood was for *E. rufida* (16%), *E. botryoides* (14%), *E. grandis*, and *E. maculata* (11%). In contrast, *E. globulus* (6%), *E. saligna* (8%), and *E. propinqua* (9%) had the lowest C increase. The oxygen content of the torrefied woods decreased in all of the samples by an average of 11% with *E. botryoides*, *E. grandis* and *E. rufida* achieving the more pronounced drops (above 12%) and *E. globulus* the lowest variation (5.3%). The hydrogen content was only slightly reduced; i.e., on average H corresponded to 6.0% of the untreated wood samples and 5.8% of the torrefied samples.

The N content of the eucalyptus woods was low, on average 0.22% and 0.26% for untreated and torrefied samples, respectively. The ash content was low and slightly increased in the torrefied samples: on average 0.60% in untreated and 0.85% in torrefied wood samples. The contents for Ca, K, Mg, and S were low in both the original wood and in the torrefied samples. The chlorine content dropped in nearly all of the samples with torrefaction. The largest decrease was measured for *E. rufida* (0.4% vs. 0.2%), while for the other species the decrease was about 0.25%. The chlorine content only increased in the *E. grandis* wood.

Table 2. Elemental Analysis of Untreated (U) and Torrefied (T) Wood Samples of Eight *Eucalyptus* Species.

Wood		Ash (%)	C (%)	H (%)	N (%)	Ca (%)	S (%)	K (%)	Mg (%)	O (%)	Cl (%)
<i>E. botryoides</i>	U	0.7	48.27	6.06	0.4	0.02	0.04	0.1	0.02	44.10	0.4
	T	1.0	55.33	5.88	0.4	0.05	0.03	0.2	0.04	37.11	0.3
<i>E. globulus</i>	U	0.6	48.74	6.12	0.2	0.07	0.01	0.1	0.06	43.72	0.3
	T	0.7	51.50	5.77	0.3	0.10	0.01	0.2	0.04	41.40	0.2
<i>E. grandis</i>	U	0.6	48.08	6.12	0.2	0.04	0.01	0.1	0.02	44.40	0.1
	T	0.6	53.72	5.83	0.2	0.06	0.01	0.1	0.02	39.06	0.3
<i>E. maculata</i>	U	1.1	47.55	6.15	0.2	0.28	0.03	0.1	0.02	44.78	0.2
	T	1.4	52.67	5.56	0.2	0.30	0.01	0.1	0.03	40.31	0.1
<i>E. propinqua</i>	U	0.5	49.17	6.07	0.2	0.02	0.01	0.1	0.04	43.38	0.3
	T	0.8	53.75	5.81	0.2	0.03	0.01	0.1	0.04	39.08	0.2
<i>E. rufida</i>	U	0.8	46.04	5.70	0.2	0.04	0.04	0.2	0.09	46.83	0.4
	T	1.0	53.51	5.74	0.4	0.09	0.05	0.2	0.09	39.02	0.2
<i>E. saligna</i>	U	0.4	49.57	6.15	0.2	0.05	0.01	0.1	0.02	42.80	0.3
	T	0.6	53.56	5.80	0.2	0.07	0.01	0.1	0.02	39.26	0.3
<i>E. viminalis</i>	U	0.7	47.95	6.01	0.2	0.06	0.01	0.2	0.03	44.59	0.3
	T	0.7	52.60	5.76	0.2	0.07	0.01	0.1	0.02	40.32	0.2

Figure 1 shows the TG and DTG curves for the untreated and torrefied woods of the different eucalyptus species (for the 150 to 450 °C temperature range) and Table 3 reports the mass loss observed at different temperature ranges. The first step, which corresponded primarily to the loss of physically absorbed water and some low-molecular weight compounds, is evident in the range of 50 to 200 °C (Table 3).

Table 3. Mass Loss (%) of Untreated (U) and Torrefied (T) Wood of Eight *Eucalyptus* Species during Thermal Degradation (along Successive Temperature Ranges).

Wood	Temperature range (°C)									
	50 to 100	100 to 150	150 to 200	200 to 250	250 to 300	300 to 350	350 to 400	400 to 450	Residual Mass (450)	
<i>E. botryoides</i>	U	1	2	1	3	21	26	13	4	30
	T	2	0	0	2	18	24	13	5	37
<i>E. globulus</i>	U	0	2	1	2	20	29	15	4	28
	T	1	1	0	1	13	27	15	7	34
<i>E. grandis</i>	U	0	1	1	1	15	40	8	6	29
	T	1	0	0	1	20	26	9	7	35
<i>E. maculata</i>	U	0	1	1	3	17	27	19	4	29
	T	0	1	1	1	6	38	9	7	37
<i>E. propinqua</i>	U	1	2	1	3	21	26	13	4	31
	T	1	1	0	1	8	37	9	6	36
<i>E. rufida</i>	U	0	1	1	2	17	34	7	4	33
	T	1	0	0	1	12	32	10	7	37
<i>E. saligna</i>	U	0	2	1	1	19	27	16	6	30
	T	1	0	0	1	11	36	8	7	35
<i>E. viminalis</i>	U	0	1	1	2	22	27	14	3	29
	T	1	1	0	1	17	22	17	4	35

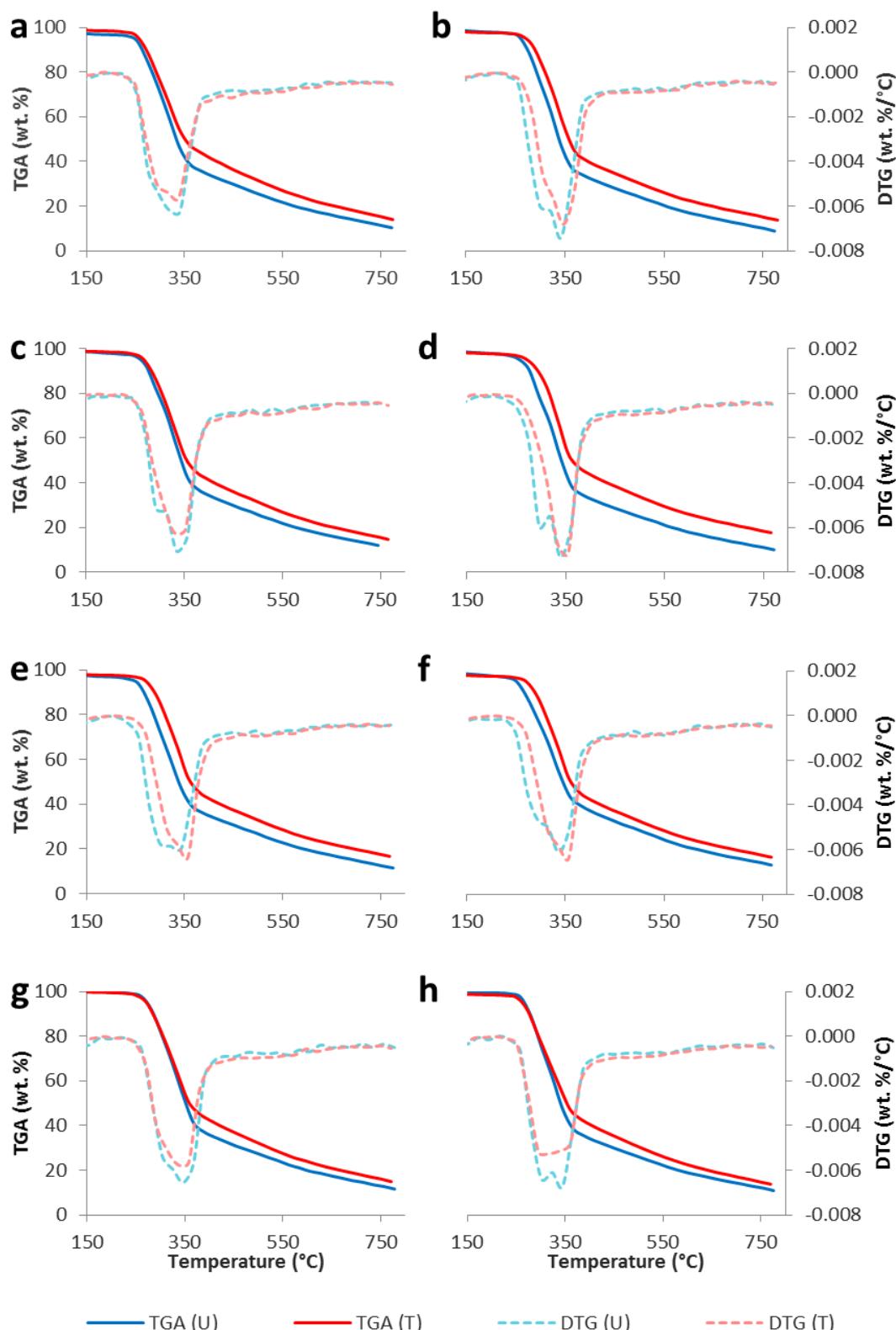


Figure 1. Thermogravimetric analysis (TGA) (left y-axis) and derivative thermogravimetry (DTG) (right y-axis) curves of untreated (U) and heat-treated (T) wood samples of *E. botryoides* Sm. (a), *E. globulus* Labill. (b), *E. grandis* W.Hill ex Maiden (c), *E. maculata* (Hook.) K.D. Hill & L.A.S.Johnson (d), *E. propinqua* Maiden Deane (e), *E. rufida* Endl. (f), *E. saligna* Sm. (g) and *E. viminalis* Labill. (h) under a nitrogen atmosphere and 10 °C/min heating rate.

The mass losses were overall negligible until 250 °C, and were slightly higher in the case of untreated wood samples. Degradation was substantial in the 250 to 300 °C range being lower for the torrefied wood samples with an average of 19% and 13% for untreated and torrefied samples, respectively. The same occurred in the 300 to 350 °C range when most of the thermochemical degradation occurred: on average 28% and 20% for the untreated and torrefied samples, respectively. Overall the mass losses in the range of 250 to 400 °C were 54% and 62% for the torrefied and untreated samples, respectively.

The TGA curves show that the untreated wood has a higher thermal degradation than the heat-treated wood; i.e., a lower thermal stability than the torrefied material. For the untreated samples, compared to treated ones, the mass loss began at lower temperatures and the bulk of the mass loss also occurred at a lower temperatures, with higher mass loss that resulted in a lower yield of the residual material. The residual mass at 450 °C was higher for the torrefied samples (36% vs. 30% for the untreated samples).

When comparing the studied eucalyptus species', it is possible to verify that they all showed a similar behavior in the thermogravimetric analysis, with small visual differences in the TGA/DTG thermograms. In general, the highest peaks of thermal degradation occurred between 300 and 400 °C. In the untreated samples, a first peak occurred at approximately 300 °C and the maximum peak occurred at 340 to 350 °C; in the torrefied samples, the first peak decreased or disappeared.

4. Discussion

The calorific values found in this work for the untreated eucalyptus woods fall within previous literature's values, as reported for *E. globulus* (17.6 to 19.8 MJ kg⁻¹), *E. botryoides* (19.9 MJ kg⁻¹), *E. grandis* (18.8 to 19.9 MJ kg⁻¹), *E. maculata* (18.8 to 19.6 MJ kg⁻¹), and *E. saligna* (18 to 19.5 MJ kg⁻¹) [14,15].

The torrefaction increased the calorific values of the wood samples to 21 MJ kg⁻¹ (Table 1). This effect is in accordance with previous reports e.g., the heating value increased from 19 MJ kg⁻¹ to 21 or 23 MJ kg⁻¹ in torrefied woods [16]. In eucalyptus wood treated at 220 °C, 250 °C, and 280 °C, the increase was 4%, 10%, and 16%, respectively [9].

The higher energy content in the torrefied wood samples was related to the chemical changes that occurred during the heat treatment where the higher energetic components were concentrated [17]. In fact, the torrefied wood samples increased their C content and decreased their O content, resulting into C/O ratios of 1.35 in comparison with 1.08 for the untreated samples (Table 2). This was reported for several cases with a higher C content increase for the more severe torrefaction conditions [18–20]. For eucalyptus wood, 24% more C content and 26% less O content were found after torrefaction at 280 °C for 3 h [21].

The carbon increase was related mostly to the degradation of hemicelluloses during the torrefaction process, while lignin (the component with the highest carbon content) remained mostly unaltered [22]. Moreover, the thermal behavior of wood during heating (Figure 1) showed a first mass loss at the lower-temperature range (the first peak of the DTG curve), which corresponded to the decomposition of the hemicellulose fraction. As the temperature rose, the chemical reactions became more complex and cellulose degradation occurred near 350 °C (the second peak of the DTG curve). Similar results were obtained from the TGA analysis of other kinds of biomass [23–25].

The torrefied wood samples showed an overall higher thermal stability compared to the untreated samples (Table 3), with a shift of the mass loss to higher temperatures. The higher residual mass at 450 °C was also indicative of the thermal stability of the torrefied samples in comparison to the untreated woods. This was in accordance with the fact that the torrefied samples were concentrated in cellulose and lignin, which were more heat resistant [20,26,27].

Biomass fuels exhibit different rates of fouling depending on their ash content and composition, which may influence fouling and slagging [27]. For instance, the N content is important in the formation of pollutant emissions, while S and Cl may cause fouling and slagging [28]. The untreated

and the torrefied wood samples were at the same 0.01% level of S, and all were under the limits set in EN (European Norm) 15289 [29]. In general, the heat treatment reduced the S and Cl contents (Table 2), thereby decreasing the associated risks.

The mild torrefaction used in this study confirmed an improvement in the biofuel properties of all tested eucalyptus species, which showed no noticeable differences between them. Therefore, the torrefied woods of the different eucalyptus species may be considered a rather homogeneous biofuel. All of the heat-treated wood samples had calorific values higher than the minimum value required by ISO (International Organization for Standardization) 17225-1 [30].

5. Conclusions

A mild torrefaction process considerably improved the thermal properties of eucalyptus wood biomass by increasing their C/O ratio by 20% and their calorific value by 10%.

Torrefaction concentrated the biomass samples in more energetic and thermal resistant components and decreased their sulfur and chlorine contents, leading to a better combustion performance.

The wood of the eight *Eucalyptus* species had a similar behavior and quality improvement, which allows for their use as mixed feedstocks. Therefore, the torrefaction showed its potential as a pre-treatment for biomass fuel improvement.

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