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Torrefied *Eucalyptus Grandis* Characterization as a Biomass to Using in Industrial Scale

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Biomass has been studied as an alternative for production of fuels. However, biomass presents some difficulties to overcome, such as its high moisture content, hygroscopic nature, low energy density, which causes high costs during transportation, handling, and storage. These difficulties could be overcome if the biomass is thermally treated. The solution is a torrefaction process, a thermal treatment to upgrade biomass to a higher quality and more attractive biofuel. The present work aimed to study the benefits of torrefaction process for the energetic properties of wood *Eucalyptus* chips. The raw and torrefied samples were characterized to compare the results. All analysis was performed according to the Standard Test Method (ASTM). The characteristics of the wood chips were determined by physic-chemical analysis as elemental analysis; determination of immediate analysis and Higher Heating Value (HHV). Temperatures degradation of lignin, cellulose and hemicellulose were determined by TGA/DTG (Thermogravimetric Analysis). According to the results, it was found that the roasting process has improved significantly the energy properties of biomass studied. The HHV has increased (around 30%) and the moisture (70%) and volatiles (around 60%) contents decreased. This demonstrates that torrefaction process is a viable procedure for energy conditioning of *Eucalyptus* biomass. Thermogravimetric analysis was conducted to show the dynamic weight of the eucalyptus biomass to understand the effects of temperature on torrefaction process. The trends of the TGA curves for the raw sample and torrefied sample at 250 °C are similar, were the samples that decreased a major biomass weight percent. This is due to the high amount of hemicelluloses was lost in these samples. In the stage from 260 to 300 °C, cellulose and lignin are the main energy components. TGA experiments have indicated that the torrefied samples presented different volatile release and burning profiles. This treatment causes significant changes in their properties and benefits for its transportation. Viable logistics and favorable changes of the torrefied biomass properties have different purposes for its application in the generation of thermal or electric energy.

1. Introduction

Considering the current environmental situation and all the consequences that the planet has been suffering, especially because of the use of fossil fuels as the main energy source, the search for alternative energy sources in the energy mix has been constant. So in such ways it is possible to ensure economic development with social inclusion without further environmental aggression occurs. An alternative researched is biomass, a primary and renewable energy source.
However, biomass presents some difficulties to overcome, which complicates their direct use as fuel. One of the main problem of biomass as an energy source is its low energy density, which increases the cost of transportation and logistics unfeasible. One way to alleviate that constrain is to convert biomass into a biofuel high potential energy by a thermal conversion method. The torrefaction process is a thermal treatment that improves the energy characteristics of biomass, enabling the production of energy and biofuels from biomass.

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Torrefaction is a thermal conversion method of biomass and it can be defined as a pre-carbonization process, which develops in the pyrolysis endothermic phase, between 200 and 300 °C.
The roasting process aims to concentrate the energy from biomass in a short time and obtain high yields, operating with low heating rates and moderate temperatures to allow that volatiles with higher heating value (HHV) are retained. This process results in an intermediate material between the raw biomass and coal (Doat J.,1985). The thermal treatment not only destroys the fibrous structure and tenacity of biomass, but it also increases the calorific value. Torrefaction process also improves grindability, increases hydrophobicity, reduces thermal degradation and prolongs durability, what makes storage and transportation of wood more attractive than non-torrefied wood (Anca-Couse et al., 2014).
The biomass treated, produces a high quality fuel that can be used for combustion and gasification processes. Woody materials are preferred over food crops because they are more energetic, and the amount of fertilizers and pesticides needed for wood is very low. (Van der Stelt et al., 2011). In this context, the main purpose of this paper was study the benefits of torrefaction process for the energetic properties of wood *Eucalyptus* chips. The raw and torrefied samples were characterized by thermal analysis.

2. Experimental

2.1 Material

The raw material used was *Eucalyptus grandis* chips with approximately 30 % moisture content and size of 2x10x12 mm.

2.2 Elemental analysis

Elemental analysis was performed using the CHNS/O elemental analyser - Perkin Elmer 2400 series II, at the Analytical Center of the Chemistry Institute of the University of São Paulo (USP). It was applied Pregl-Dumas methodin which the samples are subjected to combustion in an atmosphere of pure oxygen and the gases arising from that combustion are measured in a detector TCD (thermal conductivity detector). The oxygen content was obtained by difference, it is adding together the percentage of carbon, hydrogen, nitrogen and subtracting 100%.

2.3 Immediate analysis

Before completed the immediate analysis, the raw and torrefied samples, were dried at 105 °C for 24 hours followed ASTM E 871-82. These reference samples were used for all experiments.
After drying, the samples were ground in fractions. Drying process reduces moisture biomass besides facilitating the grinding. All analysis was performed according to the Standard Test Method (ASTM): D1102-84 – ash (AS), D 5832 - 98 – volatile matter (VM), E 1756-08 – moisture content (MC). The fixed carbon was obtained through an indirect measurement.

2.4 Higher heating value

The higher heating value was determined according to ASTM D 2015 (Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter). Dried samples were initially conducted to a bomb calorimeter, IKA (Basic C2000), to obtain the gross calorific value.

2.5 Themogravimetric analysis

Temperature degradation of the macro-constituents of biomass were analysed by thermogravimetric analysis (TGA) (TGA-50 Shimadzu). Around 10 mg of sample was measured at a heating rate of 10 °C/min from 25 to 1000 °C under a dry nitrogen flux. Both percentage weight change and derivative weight was reported.

3. Results

3.1 Elemental analysis

During the torrefaction process changes occur in macroconstituents of biomass. The main changes occur on the hemicellulose, followed by cellulose and lignin. The increase in temperature of the process has strong influence on degradation of the constituents.
Table 1 shows the results of elemental analysis. It is observed that increasing temperature of the torrefaction process, the oxygen and hydrogen content in the samples decreases. In contrast, the carbon content had a decreasing trend. The reduction of the hydrogen and carbon content is due to the water formation, CO and CO_2 during degradation of hemicellulose and cellulose. The results indicate that the torrefaction process increases the higher heating value by increasing carbon and removing oxygen.

Table 1: Elemental analysis of raw sample and torrefied samples in different temperature

Elemental Analysis	Raw Sample	Torrefied 250 °C	Torrefied 290 °C	Torrefied 310 °C
C (%)	46.81	47.35	63.76	69.64
H (%)	6.11	6.08	4.24	4.30
O (%)	46.76	46.28	31.68	25.80
N (%)	0.12	0.11	0.13	0.07
Ratio O/C	1.00	0.98	0.50	0.37
Ratio H/C	0.13	0.13	0.07	0.06

It can be observed that increasing torrefaction temperature the elemental carbon fraction also rises, suggesting a decrease in the molecular H/C and O/C ratios. This decrease in the O/C ratio during torrefaction process is attributed to the degradation of the macroconstituents of biomass which during its degradation generate volatiles rich in oxygen, such as CO, CO_2 and H_2O (Prins, 2006). This guarantees a greater amount of energy retained in the final solid product.

3.2 Immediate analysis

Analysing Table 2, it is observed the influence of temperature in the thermal treatment on the measured parameters. It is observed a trend in moisture reduction with increasing temperature of the torrefaction process. As the temperature increases, the torrefied biomass produced has higher hydrophobic character. This is due to the hemicelluloses degradation, which has hydroxyl groups in its structure which favour interactions with water molecules. It was observed that the moisture content was relatively low for the biomass.

The results presented below were obtained in order to evaluate the potential of torrefied eucalyptus biomass for its use as a solid biofuel.

Table 2: Immediate analysis of raw sample and torrefied samples in different temperature

Analysis	**Crude Raw Sample**	**Torrefied 250 °C**	**Torrefied 290 °C**	**Torrefeid 310 °C**
Moisture (%)	9.40	3.52	3.30	2.93
Volatile matter (%)	83.23	82.13	48.13	40.51
Ash (%)	0.50	0.34	0.84	1.26
Fixed carbon (%)	16.42	17.36	51.02	58.22

The volatile content also decreased with increasing temperature. During the degradation of biomass constituents is the release of volatiles with low HHV, such as CH_4, H_2, CO_2, CO. Just the volatiles with higher HHV are retained.

The ash content is an important parameter, which must be evaluated when using wood to energy purpose. If the ash content is high, it influences in a negative way the calorific value of biomass. Analysing the results it is noted that the ash content increased with increasing temperature. According to Browning (1963) and Barcellos et al. (2005) the ash content is generally less than 1 % on dry basis. The results are consistent with the authors except for torrefied sample at 310 °C, in which the ash content was 1.26 %. This value greater than 1% is because of all organic matter has been decomposed, leaving only the inorganic material. Based on the literature and the results obtained, the material under study may be considered fit for use as fuel compared to levels found.

The fixed carbon content has an inverse relationship with the volatile content. Due to the high volatile extractives content in chemical composition of wood, increasing the heat treatment temperature increases the fixed carbon content.

3.3 Higher heating value

Figure 1 shows the comportment of the higher heating value with torrefaction temperature. The lower average HHV obtained was 18.42 MJ at 250 °C. Already the highest average of HHV was 25.98 MJ at 310 °C. This results show that HHV increase with increasing temperature of the torrefaction process. The increasing of the higher heating value of the torrefied samples is due to the great loss of oxygen during the treatment, which occurs by removing the dehydrating of water of all the organic product of the reaction (acetic acid methanol, furfural) and gases, mainly CO and CO_2 (Bergman and Kiel, 2005)

Figure 1 shows the relation between HHV and moisture content. There is an inverse relationship between HHV and moisture content. As the temperature increases, the moisture content decreases and the higher heating value increases. This is due to modifications in the structure of the biomass macrocomponents. With the hemicellulose degradation and partial degradation of cellulose and lignin, its reduce amount of hydroxyl groups, lowering the moisture and volatile content, and increasing the fixed carbon. Consequently, HHV increases.

Pincelli (2011) concluded that not only moisture, but also the chemical composition of wood, influences the higher heating value of the biomass, and that the higher lignin and extractives, the greater is the HHV. Browning (1963) has reported that the reason for HHV be higher for wood with high lignin and extractives is because these constituents of their lower oxygen than the polysaccharides in the cellulose and hemicellulose.

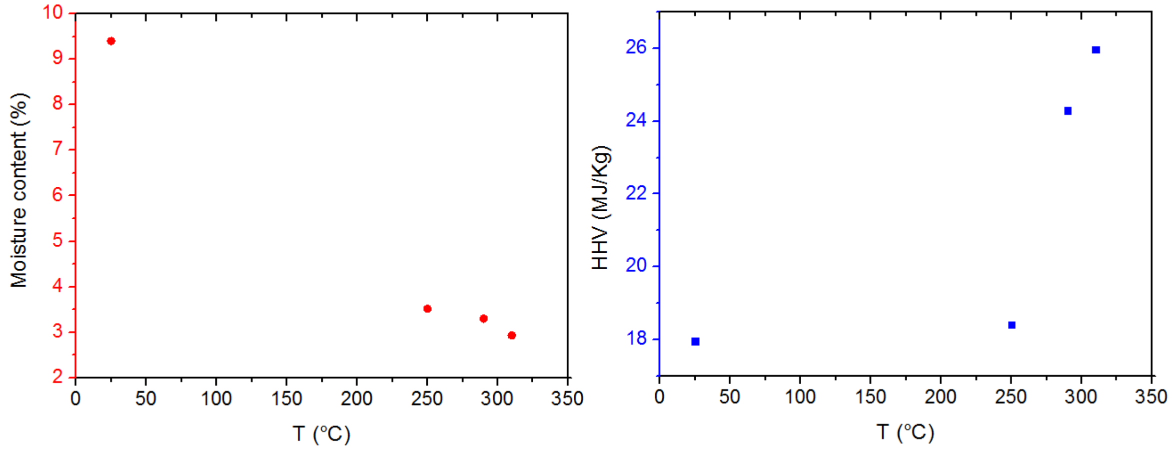

Figura 1: Relatio between HHV and moisture content.

3.4 TGA

The deconvolution curves obtained by TGA have shown the decomposition tracks of the macro-constituents biomass. The fractions related with the decomposition of the macro constituents were called of: reaction 1 (hemicellulose), reaction 2 (cellulose), and reaction 3 (lignin). As can be seen in Figure 2, the thermal decomposition of the *eucalyptus* biomass started about 200 °C, followed by a high weight loss in a zone between 210 and 450 °C and a flat area up to 600 °C, which shows that the devolatilization is complete. The higher loss mass area correspond to hemicellulose decomposition (reaction 1), the cellulose peak (reaction 2), and the small area corresponding to lignin (reaction 3) (Figure 2).

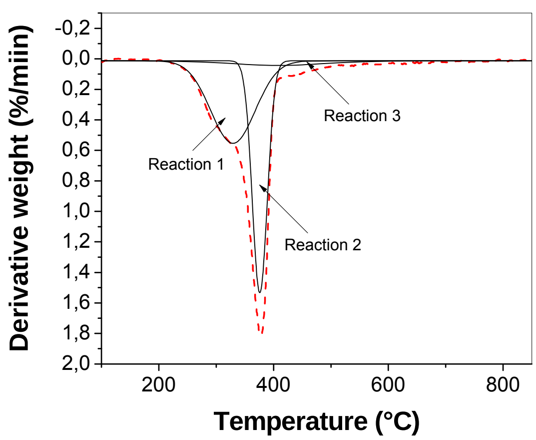

Figure 2: Deconvolution curve

The biomass macroconstituents have different thermal behavior and from TGA, it is possible to understand better the effects of temperature in the roasting process. The results of the TGA indicate that these macroconstituents degrade at different temperature ranges. Hemicellulose it is more sensitive to temperature effects, is the first polymer which decomposes between 200 and 300 °C. Then the cellulose, between 300 and 400 °C, and finally lignin, which decomposes more slowly in a wide temperature range between 250 and 500 °C (Macedo, 2012).
The TGA was conducted to show the dynamic weight of the *eucalyptus* biomass to understand the effects of temperature on torrefaction process (Figure 3). As the temperature of torrefaction process increased the biomass weight percentage decreased. The trends of the TGA curves for the raw sample and torrefied sample at 250 °C are similar, were the samples that decreased a major biomass weight percent. This is due to the high amount of hemicelluloses was lost in these samples. In the stage from 260 to 300 °C, cellulose and lignin are the main energy components. The partial loss of cellulose could be due to degradation of amorphous cellulose, which is more sensitive to heat reactions than crystalline cellulose. It is concluded that biomass structure as well as its characteristics change depending on torrefaction conditions.

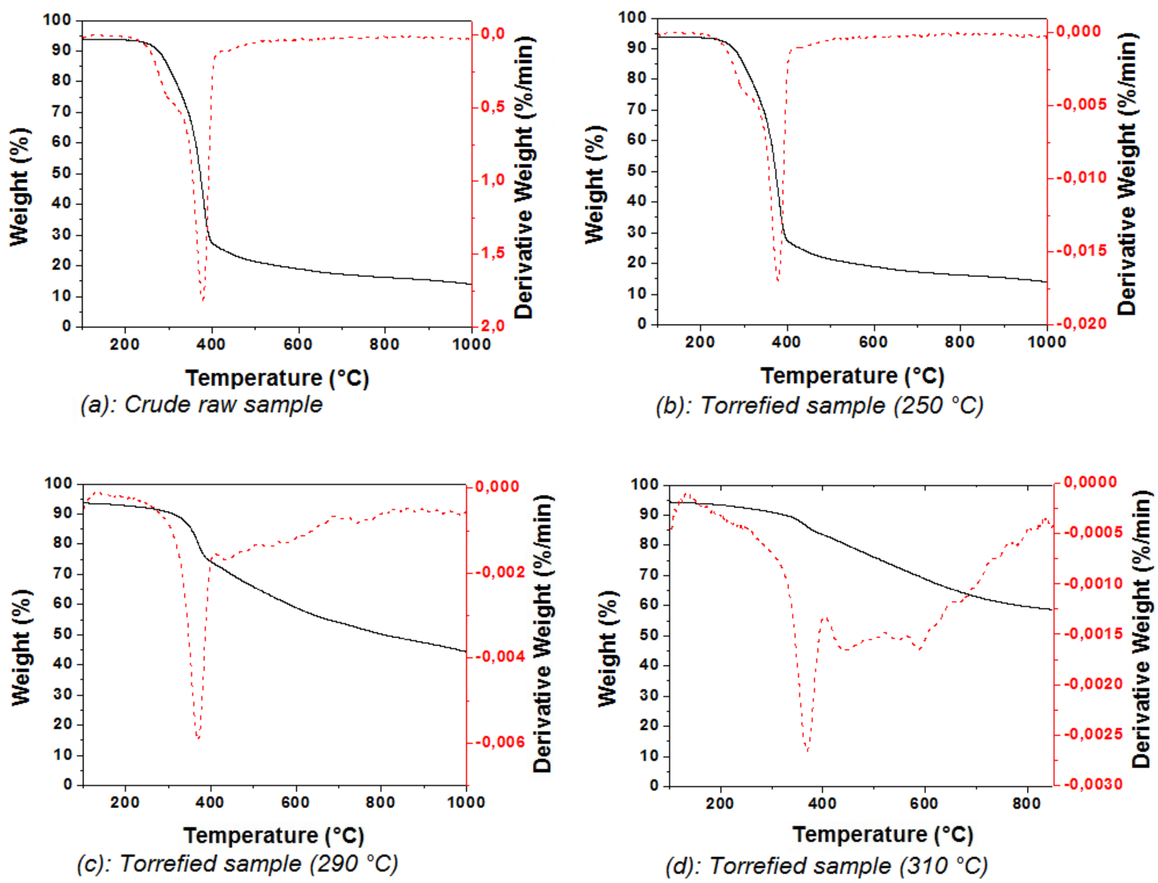

Figure 3: Thermal gravimetric and derivative gravimetric analysis of raw and torrefied eucalyptus samples.

The mass loss region to temperature below 100 °C is because of clogged present of the pores of biomass or loosely bound water. In Figures 3a and 3b can be better observed the curve that representing degradation of hemicellulose. Already in Figures 3c and 3d, this curve is no longer visible, which indicate that the hemicellulose was degraded completely during torrefaction process at 250 °C. The lignin is the macroconstituent more resistant to high temperatures and has a specific structure. Because of that is the component that has lower weight loss during the process. Its degradation increases progressively with increasing temperature of the torrefaction process.

4. Conclusions

According to the results, it was observed that the torrefaction process is a viable thermal treatment for the energy conditioning of *Eucalyptus* biomass, improves the biomass to a higher quality biofuel. This pre-treatment causes significant changes in their properties and benefits for its storage and transportation. It was found that the torrefaction process improved significantly the energy properties of biomass studied. The moisture content decreased 70 % and the volatile content also decreased (around 60 %). With less volatiles consequently increases the fixed carbon content, indicating their best use. The higher heating value has increased around 30 %. The thermogravimetric analysis showed the influence of temperature on mass loss of the samples according to the increase of torrefaction temperature. It was possible to identify the temperature range that macroconstituents biomass began to degrade. The torrefied samples at 290 and 310°C were who suffered less mass reduction due to the absence of hemicellulose in the composition, hence, these samples have higher quantity of concentrated energy. These samples are also those having a higher amount of energy concentrated. This treatment causes significant changes in their properties and benefits for its transportation with the reduction of water and increased energy density the logistical aspects are improved.

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