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Thermogravimetric Evaluation of Torrefaction Parameters on Thermal Properties of a Colombian Woody Biomass

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Torrefaction is a thermal pretreatment of biomass whose aim is to eliminate technical barriers of the biomass as an energy source. In this process, the raw biomass is heated in an inert atmosphere at temperatures of 200–300 °C and a low heating rate. Its purpose is converting the biomass into a carbonaceous material with improved physicochemical properties. The aim of this study was to assess the effect of torrefaction conditions on the thermal properties of a Colombian woody biomass.The results show that temperature and residence time torrefaction conditions presented a statistically significant effect on the thermal degradation of the biomass cellulose component and weight loss. In both responses, the temperature effect was higher than residence time. Besides, the residence time effect on the chemical transformation of the biomass increased when the torrefaction was more severe. TGA oxygen reactivity was measured and it was found considerable changes as the conversion of the biomass increase: high reactivity at the beginning of the oxidation reaction and diminution during the final stage of char oxidation.

1. Introduction

Renewable energy use will increase during the coming years because of the need to satisfy the energy global demand and minimize carbon emissions. Solar, wind and biomass energies are some of the alternatives currently used to try to meet those requirements (Bertrand, 2013). In the case of biomass, it is one of the world's largest primary energy sources and refers to any organic materials that are derived from plants and animals (e.g., including algae, trees, crops or manure) (Tumuluru et al., 2011). It has been an alternative option that could partially or totally replace coal in some engineering processes such as heat and electrical generation (Kumar et al., 2017). For example, the European Union is driving a program whose target is to reduce greenhouse gas emissions by 40% by 2030 using biomass or coal-biomass combustion (Hof et al., 2012). In spite of its relevance, biomass as an alternative to coal presents many disadvantages in storage, handling and transportation due to low material density, high moisture content and macromolecular heterogeneity, among others (Zulfiqar et al., 2006). Moreover, during thermal treatments as combustion or gasification, several logistical problems appear due to the biomass lower heating value and energy density than coal which causes high volumetric flow rates to obtain a comparable amount of energy (Sami et al., 2001). On the other hand, biomass fibrous structure makes difficult its pulverization and the hygroscopic nature may cause degradation of the labile macromolecular constituents. Therefore, to use the existing infrastructure based on coal energy it becomes necessary to make substantial modifications on coal-based devices and/or improve the physicochemical characteristics of the biomass.

Different alternatives that could improve the characteristics of biomass, allowing it to be used on combustion or gasification processes are drying, pelletization, co-firing and torrefaction (Batidzirai et al., 2013). Among these, torrefaction is currently being considered to produce a hydrophobic solid product with increased energy density and grindability. It consists of an energy process, where the biomass is heated in an inert atmosphere at low temperatures (typically between 200-300 °C) with the aim to increase the value of biomass as a fuel source (Brachi et al. 2018, Sommersacher et al. 2018). Problems due to biomass low heating value was investigated by (Shang et al., 2012) using Scots pine pellets. In this work, using a torrefaction temperature of 250 °C and 1 hour under N_2 atmosphere, it was found that the high heating value (HHV) increase from 18.37

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MJ/kg (raw) to 21.35 MJ/kg; meanwhile, the total weight loss was 21.3%, which is an acceptable value due to the biomass does not lose much of its initial energy. On the other hand, a torrefaction temperature of 270 °C caused an increase of HHV from 18.37 MJ/kg to 24.34 MJ/kg, but the total weight loss was 41.9 %, which is very high representing a critical loss of biomass energy potential. Other research (Larsson et al., 2013) investigated several quality parameters to improve handling problems in a Norway spruce biomass. In terms of bulk density, it was increased from 630 kg/m^3 at operating conditions of 270 °C and 16.5 min, to 713 kg/m^3 at 300 °C and 16.5 min; the mass yield (daf) were 93 and 75% respectively. With regard to mill energy consumption, in (Strandberg et al., 2015) researched the relations between temperature and residence time in stem wood from Norway spruce. The findings were that the milling energy was reduced from 123 ± 17 kWh$_e$/ton (raw) to values as 69 ± 14 kWh$_e$/ton at torrefaction conditions of 260 °C for 8 min, and values as low as 8.9 ± 0.5 kWh$_e$/ton at 310 °C for 25 min. The mass yields were 97% at 260°C and 46% in the most severe temperature case: 310°C. This severe condition was able to produce a material with HHV comparable to lignite; however, the weight loss is very high and makes this torrefaction condition not suitable for valorizing the initial material.Torrefaction could change the hygroscopic properties of biomass from hydrophilic to hydrophobic, therefore, the saturated moisture content is significantly reduced (Tumuluru et al., 2011). For example, (Chen et al., 2015) made several tests and it was found that the moisture content of the studied softwoods and hardwoods samples was reduced from 6-30 to 1-5 wt.% at the range of 220-270 °C using residence times of 30 or 60 min. The hydrophobic behavior when biomass undergoes torrefaction was associated with the partial removal of hydroxyl groups through dehydration and the diminution of hydrogen bonding formation between water molecules and the biomass. On the other hand, (Kymäläinen et al., 2014) reported that increasing torrefaction temperature, it decreases fungal growth and moisture contents of a spruce tree and birch samples, but, a considerable loss of mass and carbon was noted.

From the above information, it is evident that exists a big variation on the torrefaction operating conditions to obtain a profit on the biomass key characteristics (e.g., heating value, bulk density, milling energy or hygroscopic behavior). Thus, the need to study the effect of the torrefaction parameters is critical on each biomass, due to its heterogeneous nature. The aim of this study was to evaluate the effect of temperature and residence time on torrefaction process of a Colombian biomass (*Cypress Pine*) based mainly on weight loss and macromolecular components degradation temperature. The process was carried out at five temperatures (200, 225, 250, 275 and 300 °C) and two residence times (30 and 60 min). Finally, the potential of the studied biomasses in the combustion process is discussed based on torrefaction results.

2. Materials and Methods

Selection process and sample preparation

For this study *cypress pine* sawdust was chosen on account of their wide availability in Colombia and their potential to be used as an energy source in combustion or co-combustion processes. *Cypress pine* residue was obtained from local sawmill residue (Southwest Antioquia, Colombia). The sample was powdered and sieved by a 70 mesh to obtain particles with sizes smaller than 212 μm whose aim is to reduce the variability in their physical and chemical properties during the torrefaction experiments. The proximate, ultimate and calorific analyses are indicated in Table 1.

Table 1. Proximate and ultimate analyses of the Cypress pine biomass

Sample	**Proximate analysis (wt. % dry basis)**[a]			**Ultimate analysis (wt. % dry basis)**[b]				**Gross calorific value**[c] **(MJ/kg)**
	Volatile matter	**Fixed carbon**	**Ash**	**N**	**C**	**H**	**O**	
Cypress pine	75.84	23.24	0.92	0.4	47.2	5.6	47.0	20.2

[a]Determined by a TGA using the standard method D7582-15. [b]Determined by an elemental analyzer using the standard method D5373-08. [c]Determined by an oxygen bomb calorimeter using the standard method ASTM D5865-13.

Evaluation of torrefaction conditions

Torrefaction experiments of the woody biomass were carried out using a thermogravimetry analyzer TA Instruments SDT Q600. In each run, 10 mg of raw sample was put into the alumina crucible, located inside the TGA. N_2 was used as the torrefaction atmosphere with a flow rate of 100 ml/min and the heating rate was kept constant, at a value of 20 °C/min. The sample was heated from room temperature to 120 °C and maintained for 15 min to remove the moisture content. Then, the sample was heated until it reaches the torrefaction temperature and the material was held during a specific residence time. Finally, an evaluation of the pyrolysis behavior of the biomasses was done through the heating of the torrefied biomass until a temperature of 800

°C in N_2 atmosphere. Five different torrefaction temperatures were selected to represent the range of torrefaction dominion, such as 200, 225, 250, 275 and 300 °C along with two residence times, 30 and 60 min, (counted from the sample temperature reached the torrefaction temperature). These experiments were carried out by duplicated and analysis of variance (ANOVA) was performed.
The weight loss during torrefaction was calculated using the next equation:

$$W_L = \left(\frac{M_o - M_t}{M_o}\right) * 100 \tag{1}$$

Where W_L is the weight loss (%), Mo is the initial mass of the biomass before torrefaction and M_t is the value of mass after the torrefaction process. Biomass reactivity in oxidation experiments was evaluated using thermogravimetric analysis (TGA), specific reactivity versus conversion profiles are presented (Alvarado et al. 2016). Carbon conversion was calculated as follows: $(m_0 - m_t)/(m_0 - m_f)$, where m_0 refers to the coal char initial mass and m_f is the mass of the residue after the reaction, m_t is the mass in each time in the TGA data. The specific reactivity is expressed as $1/m_0 \times (dm_t/dt)$.

3. Results

Figure 1a shows the effect of torrefaction temperature on the weight loss of *Cypress* pine, using a residence time of 1 hour. The complete process has the following thermal events: the samples begin to dry during the first minutes in the N_2 atmosphere; then the weight reaches a constant value, which means the moisture has been removed from the biomasses. Later on, it starts the volatile matter release of the samples. This process is divided into two well differenced events: torrefaction or slight devolatilization (200-300°C) and devolatilization in the range of temperatures 300°C-800°C. As the torrefaction temperature increases the torrefaction weight loss for the biomass, becomes higher. In Cypress pine, there is little weight loss at temperatures of 200 °C or 225 °C, but the weight loss significantly increases at higher temperatures. The main decomposition affects mainly hemicellulose. However, the other macromolecular components lignin and cellulose also decompose in the range of torrefaction temperatures, but to a lesser degree.

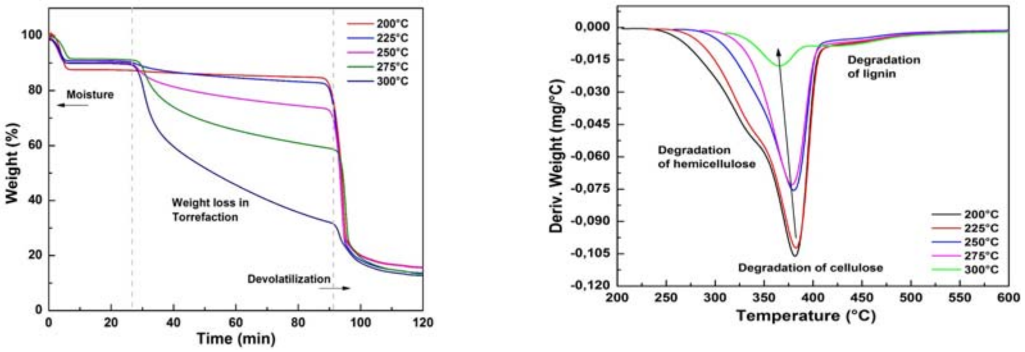

Figure 1: Effects of torrefaction temperature on (a, left) weight loss and (b, right) temperature of celullose degradation

During torrefaction, a partial removal of volatile matter is reached. Thus, it is important to study the thermal stability of each one biomass macromolecular constituent (Kihedu, 2015). Fig 1b shows the derivative weight as a function of temperature (DTG) on torrefied samples. Basically, it consists of two zones: the first one is associated with the relative decomposition of weak constituents (typically hemicellulose components) and the second one decomposition or rearrangement of cellulose at higher temperatures. As the torrefaction temperature increases, the maximum peak of cellulose decomposition occurs at a lower temperature, which implies that cellulose is being affected by heat treatment, mainly at higher temperatures. It is also observed that the macromolecular component associated with hemicellulose (first shoulder inside figure 1b) disappears at process temperatures greater than 250 ° C, this is explained due to this is the most labile volatile material of the analyzed biomass. On the other hand, there are no considerable changes with the lignin component of the sample materials when the temperature increases. Residence time is another relevant parameter to be studied with the aim to choose adequate torrefaction conditions. The results after the torrefaction in *Cypress* pine sawdust shows that weight loss depends more on temperature than residence time (Figure 2).

It can be observed that temperature plays an important role on the degradation of macromolecular compounds, mainly hemicellulose, which is responsible for the hydrophilic nature of biomass due to the content of hydrogen bonds that form OH groups (Ibrahim et al., 2013; Saleh et al., 2013). On the other hand, residence time has a lower impact than temperature in terms of weight loss in the sample; this finding is

similar to reported by (Gong et al., 2016; L. Wang et al., 2017). However, in Figure 2 it is interesting to note than the residence time effect is higher when the torrefaction becomes more severe.
An analysis of variance (ANOVA) was performed to evaluate the influence of each factor in the weight loss and the cellulose degradation temperature. Tables 2 and 3 show the experimental conditions with their respective experimental responses together with the analysis of variance.

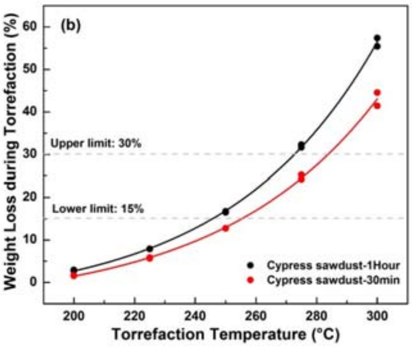

Figure 2: Residence time and temperature effect on weight loss during torrefaction

In Table 3 it can be seen that all p values are lower than 0.05, confirming the effect of the temperature and residence time, on both parameters. It is interesting to mention that a good correlation was obtained, between the temperature and residence time with the cellulose degradation temperature. As the temperature and residence time increase the cellulose degradation temperature decreases; and the effect is statistically significant. This behavior is not as simple in other biomass like agriculture residues.

Table 2. Variation of the weight loss and cellulose degradation temperature with the torrefaction temperature

Torrefaction temperature(°C)	Weight loss (%)	Cellulose degradation temperature (°C)	Weight loss (%)	Cellulose degradation temperature (°C)
	1 Hour		**30 minutes**	
200	2,75	382,00	1,65	381,96
200	2,93	382,00	1,54	381,61
225	7,90	382,73	5,66	382,87
225	7,88	382,73	5,86	382,87
250	16,50	380,56	12,72	381,62
250	16,73	380,20	12,75	381,27
275	32,32	378,81	25,25	380,39
275	31,65	378,81	24,19	380,22
300	57,78	366,60	44,52	373,37
300	67,15	371,10	41,43	374,24

Table 3. Analysis of variance (ANOVA)

			Weight loss ANOVA		
Source	**DF**	**Sum of squares**	**Mean square**	**F Value**	**Prob > F**
Temperature	4	7143,97	1785,99	115,04	0,000
Time	1	169,01	169,01	10,89	0,005
Error	14	217,36	15,53		
Total	19	7530,34			
			Cellulose degradation temperature ANOVA		
Temperature	4	340,79	85,198	43,18	0,000
Time	1	11,07	11,071	5,61	0,033
Error	14	27,62	1,973		
Total	19	379,49			

Residence time is a parameter used to study the commercial-scale reactor to carry out torrefaction; and the investment costs increase with longer residence time (Park et al., 2015; Strandberg et al., 2015). So, shorter times are recommended to obtain biochar with improved physicochemical properties (Ibrahim et al., 2013;

Rudolfsson et al., 2017). Figure 3 shows the effect of residence time on cellulose thermal degradation under three different torrefaction processes: light (225 °C), mild-severe (275 °C) and severe (300 °C). During the light torrefaction, weight loss and temperature of degradation of cellulose changes were a little noticeable. This is associated with cellulose is a more ordered and compact component than hemicellulose, so it requires more energy to be affected (Saleh et al., 2013; Wang et al., 2017). On the other hand, when the process was severe major changes with respect to the residence time were found: the maximum peak of cellulose degradation was lowered and the area under the DTG curve decreased significantly. So the cellulose is affected and undergoes structural rearrangement.

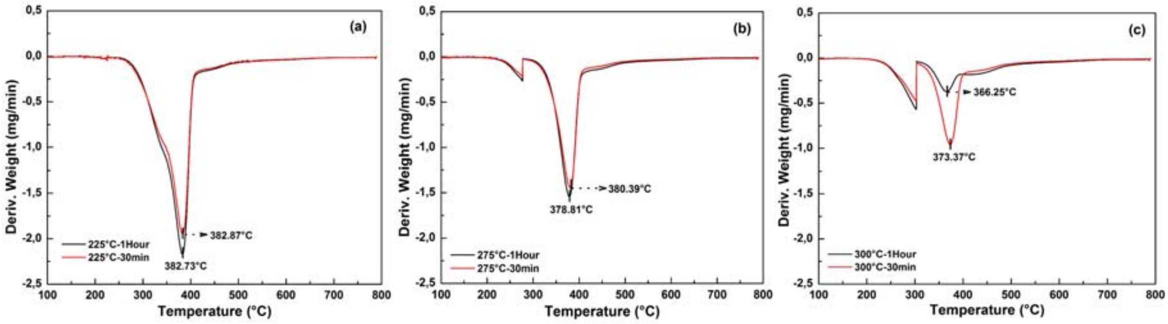

Figure 3: Effect of residence time at same torrefaction process: (a) 225°C, (b) 275°C and (c) 300°C.

Finally, Figure 4a shows the behavior of the *Cypress* pine samples during oxidation experiments. The mass loss of untreated material starts earlier than the other samples, as a consequence of its complex structure without partial removal of volatile matter. Before 350°C, the mass loss is lower at higher torrefaction temperatures, due to the decomposition of macromolecular components as hemicellulose and cellulose. As a result of the partial devolatilization, the specific reactivity decreases (Fig 4b) at the initial stage of the oxidation with a lower conversion level. This behavior is associated with an increase in the aromatization and ordered degree of char samples (Zhang et al. 2020). During the second stage of the oxidation of the remaining carbonaceous material the reactivity is considerably lower; as this stage corresponds to the oxidation of the char. The diminution of the reactivity at the end of the combustion can cause incomplete combustion in conventional combustion systems and must be taken into account during the device´s design.

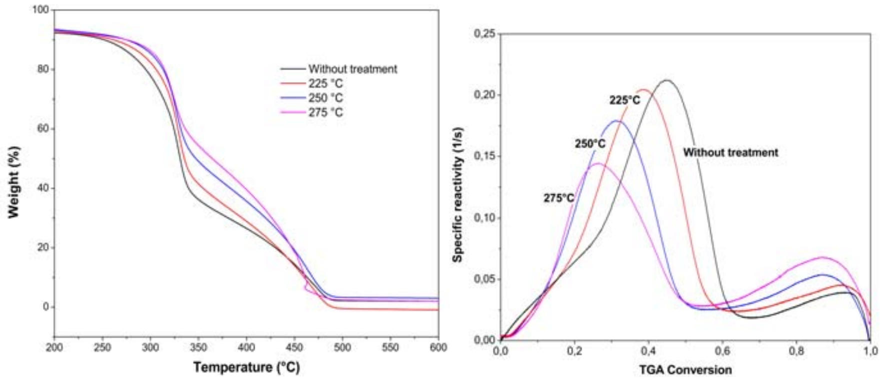

Figure 4: Oxidation of biomass under several temperature of torrefaction: 225, 250 and 275°C (a, left) thermograms, (b, right) reactivity of the sample as a function of the conversion

4. Conclusions

Torrefaction of *Cypress* pine biomass was evaluated in this study. Temperature and residence time torrefaction conditions presented a statistically significant effect on the thermal degradation of the cellulose component of the biomass and the weight loss. In this study the residence time had a lower impact on weight loss than torrefaction temperature, but its effect was considerable higher at high torrefaction temperatures. On the other hand, torrefaction severity decreases the biomass reactivity, during the initial stage of oxidation, because of volatiles deployed in the process and char formation from polymers. This shows that the solid product of torrefaction has good properties when being considered as a solid fuel because of the properties similar to those of coal, with great potential for the energy industry.

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