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STUDY OF INFLUENCE OF ATMOSPHERE ON THERMAL DECOMPOSITION REACTION OF GUARANA SEED RESIDUE AIMING THE TORREFACTION PROCESS

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Abstract. *The objective of this work is to study the thermal decomposition of guarana seed residue under inert and non-inert atmosphere aiming the torrefaction process. The experiments were performed non-isothermally (25-900 °C) in thermogravimetric balance, while isothermally were done in muffle furnace varying temperature (195-280 °C) and residence time (15-45 min). The results showed that for non-isothermal process, both atmospheres, presented five stages of the thermal behavior (including the drying process), and they were similar up to 400 °C without changing the mass loss. The results from isothermal process indicated that the suitable products were obtained between 225 and 255 ˚C (mass losses below 30 wt. %) applying 45 and 15 min, respectively. The oxidized atmosphere resulted in higher mass loss with the higher temperature (280 ºC).*

Keywords: *Paullinia cupana, thermogravimetry, thermal decomposition*

1. INTRODUCTION

With the growing concern about energy supply, several new alternative energy sources have been studied in order to replace the current energy matrix. Among the possible alternatives, the use of biomasses is largely studied. Biomasses are mainly considered lignocellulosic materials, composed of three main components: cellulose, hemicellulose and lignin. Cellulose is the most abundant organic compound in the world, and it is a long chain polymer, with crystalline structure and high molecular weight. Hemicellulose is an amorphous polymer, with highly ramified chains, and resistant to hydrolysis. And finally, the lignin is also a highly ramified polymer, formed by phenylpropanoids, and it acts to maintain the plant structure (Basu, 2010).

One example for obtaining energy from biomasses is the so called “thermochemical route” consisting on the conversion of the solid material through the use of large range of temperatures presenting a number of advantages, such as renewability and sustainability as a function of their lower content of sulfur and lower ash content produced (Saxena *et al.*, 2009). Each one of the biomass components has a specific role in their own thermal decomposition. Yang *et al.* (2007) studied the thermal decomposition of these main components individually under nitrogen atmosphere and concluded that hemicellulose decomposes in the temperature range between 220 °C and 315 °C, and cellulose between 315 °C and 400 °C. Also, according to Stefanidis *et al.* (2014) and Yang *et al.* (2007) lignin decomposes in a broad temperature range (about 140 – 900 °C).

Despite biomasses being such an interesting energy source, some characteristics (physical, physicochemical, and thermal properties) difficult their direct use in the thermo-chemical conversion. Consequently, in order to apply the biomasses in an efficient way, the literature recommends applying some form of pretreatment step, such as pelletizing, grinding, or even torrefaction (Zwart *et al*. 2006, van der Stelt *et al.* 2011; Chew and Doshi, 2011). Torrefaction process occurs between 200 and 300 ˚C, and usually it is carried out in inert atmosphere. Under these conditions, the moisture is removed, facilitating the handling and storage of the material (Chen and Kuo, 2011), and also, mainly the hemicellulose is partially decomposed, releasing components with lower heating value (Luengo *et al*., 2008). Then, the solid material produced corresponds to 70 % of the initial mass containing around 90% of the initial energy related to the heating value (van der Stelt *et al.*, 2011). Bridgeman *et al.* (2010) also point out that torrefaction has the potential to lower the energy consumption necessary to grind the material.

Even though torrefaction process is usually performed under inert atmosphere, some studies have been made with non-inert gases in order to verify the influence on the yield and formed products. The possibility of using other gases (e.g., burners) for this process can present economical and environmental benefits. Eseltine *et al.* (2013) and Uemura *et al*. (2015) verified that the influence of a non-inert atmosphere (O_2 and CO_2) on torrefaction can be minimized by using lower temperatures (230 ˚C for wood, and 250 ˚C for oil palm kernel shell). The use of high temperatures (>250 °C) in non-inert atmosphere increases the mass and energy losses, and also influences on other properties such as the heating

value. Thus, as long as the temperature is kept low, it should possible to perform the torrefaction under non-inert atmosphere without greatly influencing the products.

Considering the changes on the biomass due to a thermo-chemical process, the Thermogravimetric Analysis (TGA) is a useful tool to characterize the material and verify its behavior and reactivity to increasing temperature under inert and non-inert atmospheres. Several researchers (Chen and Kuo, 2010; Chang *et al*., 2012; Wang *et al*., 2011) have been using this method to study the torrefaction applying different biomasses, verifying changes on mass loss rates and variations on the range of decomposition temperature. It is also possible to utilize TGA data to obtain the kinetics of the torrefaction process (Prins *et al.*, 2006) and for the combustion and pyrolysis of the torrified biomass (Arias *et al.*, 2008), useful to model the thermal-conversion of the materials.

Guarana plant, also called "guaranazeiro", is related to the *Sapindacea* family, *Paullinia cupana* Kunth species, which contain two varieties: *Paullinia cupana* var. *typical* found on Venezuela and Colombia, and *Paullinia cupana* var. *sorbilis* found on Brazil (Veiga, 2013). It is a native species and presents medical, energetic and stimulant properties. Their Brazilian production reaches up to 3 ton/year being the biggest soft and energy drink producers. Besides that, 15 % of their production is commercialized in different size of pellets, while the rest of the plant is sold directly as powder, extract or syrup (Ribeiro *et al.*, 2012). However, the processing of the feedstock has increased the generation of residues from seed, which is incorporated to the soil as a fertilizer rather than being available for energy generation.

Since the guarana seed residue is a biomass with little information about its characteristics, an exploratory research is required to insert this biomass in the Brazilian energy matrix. Therefore, this work aimed to study the thermal decomposition of guarana seed residue on inert and non-inert atmospheres through non-isothermal and isothermal torrefaction processes. For the latest process, temperature and residence time were evaluated for obtaining the scenario with efficiency process (lower mass loss).

2. MATERIAL AND METHOD

2.1 Biomass preparation and characterization

The biomass chosen for this study was an agroindustrial raw material from the production of guarana extract from Amazonas state (Brazil), and it was provided by *Agropecuaria Jayoro* (-1° 59' 21"S x -60° 8' 33"W). Physical, chemical, and thermal properties were determined using mean particle diameter of 256 µm: moisture content (10.84 ± 0.04 % w/w, wet basis) obtained by ASTM 871-82; true density (1444.0 ± 2.0 $kg.m^{-3}$, d_p = 4050 µm) by helium pycnometry method; apparent density (1354.0 $kg.m^{-3}$, d_p=4050 µm) by mercury porosimetry; proximate analysis (dry basis) with 82.84 ± 0.30 % of volatile material content (ASTM E 872-82), 1.39 ± 0.04 % of ash content (ASTM E 1755-01), and fixed carbon content 15.76 ± 0.26 (by difference); ultimate analysis with 41.55 ± 0.07 % of carbon, 6.44 ± 0.03 % of hydrogen, 1.51 ± 0.18 of nitrogen, and 49.11 % of oxygen (by difference minus ash content) by elemental analyzer; and the higher heating value (17.79 ± 0.27 MJ/kg) and the lower heating value (16.80 ± 0.003 $MJ.kg^{-1}$) applying the ASTM D-240-09, and Mendeleev equation (1949), respectively.

2.2 Thermogravimetric analysis

The thermal decomposition experiments were carried out with samples of about 10 mg (d_p = 256 µm) in a thermogravimetric analyzer (Shimadzu, TGA-50M, Japan) using high purity nitrogen (99.996 %) and synthetic air atmospheres (O_2 20.00 ± 0.05 % and N_2 80.00 ± 0.05 %). The raw samples were heated from 25 °C to 900.0 ± 2.0 °C at a heating rate of 15 $°C.min^{-1}$ and gas flow rate of 50 $mL.min^{-1}$. A blank experiment was done under the same conditions in order to exclude the effect of system error on the experiment result.

2.2.1 Kinetic parameters

For this work, a preliminary kinetic modeling was carried out in order to understand the biomass reactions in a non-isothermal analysis concerning torrefaction process. Independent parallel reactions scheme was applied to analyze the biomass thermal decomposition, in which activation energies were evaluated individually for each main component (Órfão *et al.*, 1999; Rueda-Ordoñez *et al*., 2014).

As a first step, thermogravimetry (TG) and derivative thermogravimetry (DTG) were normalized using Eq. (1) and Eq. (2):

$$W = m_t / m_i \quad (1)$$

$$dW/dt = 1/m_i \, (dm_t/dt) \quad (2)$$

where W is the normalized mass, m_t is the mass at any time obtained by TGA and m_i is the initial mass. The conversion (α) was found by Eq. (3):

$$\alpha = (m_i - m_t) / (m_i - m_f) \quad (3)$$

where m_f represents the final mass at the end of the decomposition process. Also, the conversion rate $(d\alpha/dt)_{exp}$ were calculated using Eq. (4):

$$(d\alpha/dt)_{exp} = - (dm/dt) [1/(m_i - m_f)] \quad (4)$$

The independent parallel reactions model (Órfão *et al.*, 1999; Rueda-Ordoñez *et al.*, 2014) assumes that each fraction of the main components of biomass (hemicellulose, cellulose and lignin) reacts independently. In this method, the individual conversion rate can be expressed using Arrhenius equation by Eq. (5):

$$(d\alpha_x/dt)_{calc} = A_x (1 - \alpha_x)^{nx} exp[-E_x/(RT)] \quad (5)$$

where A_x, α_x, n_x, E_x are the pre-exponential factor, conversion, reaction order and activation energy related for each main component (x), respectively. Also, in the Eq. (5), R is the ideal gas constant, and T is the temperature in Kelvin. The term α_x was calculated by Euler method with an integration step h equal to 5, given by Eq. (6) and Eq. (7):

$$\alpha_{x,i+1} = \alpha_{x,i} + h [A_x (1 - \alpha_{x,i})^{nx} exp[-E_x/(RT_i)] = \alpha_{x,i} + h (d\alpha_x/dt)_{calc,i} \quad (6)$$

where $i = 0, 1, 2, 3 \ldots N$, and $\alpha_{x,0} = 0$ is the initial condition. Combining the individual conversion rates of each main components and regarding their mass fraction, the calculated conversion rate and calculated conversion are given by Eq. (7) and (8), respectively:

$$(d\alpha/dt)_{calc} = HC (d\alpha_{HC}/dt) + C (d\alpha_C/dt) + L (d\alpha_L/dt) \quad (7)$$

$$\alpha_{calc} = HC (\alpha_{HC}) + C (\alpha_C) + L (\alpha_L) \quad (8)$$

In Eq. (7) and (8), *HC* is hemicellulose, *C* is cellulose, and *L* is lignin volatilized mass fractions. Also, in Eq. (8), α_{HC}, α_C, and α_L correspond to the conversion of hemicellulose, cellulose and lignin. In order to evaluate the calculated data, the least squares method (S) is given by Eq. (9) and the average deviation (D) by Eq. (10), where the subscript j refers to the data points used:

$$S = \Sigma^N_j [(d\alpha/dt)_{exp,j} - (d\alpha/dt)_{calc,j}]^2 \quad (9)$$

$$D = 100 [(S/N)^{0,5} / (d\alpha/dt)_{exp,max}] \quad (10)$$

In Eq. (9) and (10), N is the total number of analyzed points and $(d\alpha/dt)_{exp,max}$ is the maximum value of conversion rate from experimental results.

2.3 Torrefaction Experiments

The torrefaction experiments (isothermal analysis) were carried out in a muffle furnace (Forlabo Ltda, model 2231, Brazil) using mean particle of 2,850 µm with mass of 1-3 g in recipients made of tinning (7.7 cm x 3 cm x 4.6 cm) and covered with aluminum foils. Three parameters were evaluated regarding the influences of the temperature (195, 225, 255, 270, and 280 ºC), the residence time (15, 30, and 45 min), and the atmosphere (inert and oxidize). For the latest, it was applied closed and open recipient, respectively simulating the environment. After the process, the samples were placed into a desiccator for one hour to cool at room temperature, and the final mass was determined with an analytical balance.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric analysis

Figure 1 shows the results from thermogravimetric analysis (TG) and differential thermogravimetric (DTG) of the guarana seed residue obtained under nitrogen and synthetic air atmospheres. These results show five distinguished stages of the biomass thermal behavior for both atmospheres: the first stage (up to 200°C) was related to the drying process and the other four stages (200°C – 900°C) were related to the thermal decomposition of biomass and it can be seen in Tab. 1.

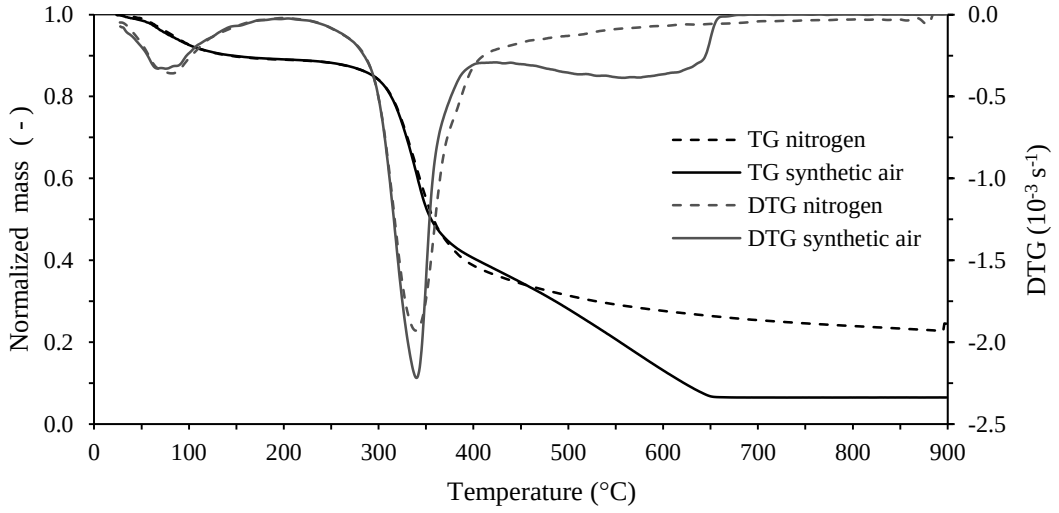

Figure 1. Thermogravimetric (TG) and differential thermogravimetric (DTG) curves of decomposition of guarana residue seed under nitrogen and synthetic air atmospheres.

Table 1. Distribution of mass loss (volatile matter contents) during biomass decomposition in TGA.

Atmosphere	I	Temperature ranges / Distribution of mass loss, wt.% (*dry basis*)				Total
	wt.% (*wet basis*)	II	III	IV	V	mass loss
	< 200 °C	200 – 300 °C	300 – 400 °C	400 – 700 °C	700 – 900 °C	wt. (%)
Nitrogen	10.97	5.47	51.02	14.97	0.95	72.42
Synthetic air	10.97	5.80	48.81	38.08	0.00	92.69

The region I is the drying stage associated with the moisture content loss and low-molecular weight compounds (García-Maraver *et al*., 2013; Lasode *et al*., 2014). As shown on Tab. 1, this stage corresponded to approximately 11 wt. % of the total mass. The temperature between 200 and 400 °C (regions II and III) corresponded to the highest mass released for both atmospheres (> 50 wt. % of the volatiles released). At this range, Raveendran *et al*. (1996), Yang *et al*. (2007) and Lasode *et al*. (2014) affirmed that low-molecular weight volatiles are released occurring the breakdown of hemicellulose and cellulose, and the partial decomposition of lignin.

Regarding the region II, it is possible to predict that the torrefaction process could be performed in any of the two atmospheres tested since it does not cause significant differences on the biomass thermal decomposition (less than 0.5 wt. %).

In the region III the mass loss presented slight differences between the two atmospheres from around 2 %. In the DTG curves there is one peak between 300-400 °C, corresponding to the overlap of the hemicellulose and cellulose decompositions. According to Órfão *et al*. (1999), for temperatures up to 300 °C only typical pyrolysis reaction occurs, mainly due to release of volatiles. Beyond that temperature, the presence of oxygen allows the simultaneous formation of volatiles and combustion of the formed residue, increasing the mass loss.

In regions IV and V, it is clear that the synthetic air atmosphere affected the thermal decomposition of the biomass. According to Luengo *et al*. (2008), at 400 °C under an inert atmosphere, there is mainly a slow conversion of lignin and formation of heavy tar and some hydrocarbons. However, under synthetic air atmosphere, the combustion of remaining char also occurred in this work. Shen *et al*. (2009) and García-Maraver *et al*. (2013) found similar results using oxidizing atmosphere. For Gani and Naruse (2007) the cellulose content would improve the ignition characteristics of lignin, since it is easily volatilized, and increase the particle porosity from carbonaceous material. As a result, the diffusion of oxygen also increases, which allows oxidative reactions within the biomass.

Finally, in region V, no significant differences happened on the mass loss for both atmospheres. Nevertheless, the residual solid (in dry basis) achieved 27.58 wt. % and 7.31 wt. % for inert and oxidizing atmosphere, respectively. The residual solids are composed by char and ash found in inert atmosphere, and only ash in synthetic air.

3.2 Decomposition kinetics

According to the results of TG-DTG for non-isothermal tests, no significant differences on the thermal decomposition process was found between 200-300 ˚C, recommended for the torrefaction process, when it was performed under inert and non-inert atmosphere. Thus, it was decided to study the kinetics of thermal decomposition in inert atmosphere using the three independent parallel reactions scheme, which provides a better understanding about the conversion of biomass

with temperature (Fig. 2). This conversion represents the volatilization of the main components, hemicellulose, cellulose and lignin (Eq. 3). The kinetic parameter results, activation energy (E_x), pre-exponential factor (A_x), and reaction order (n_x) can be seen on Tab. 2. The experimental and calculated data presented a good agreement concerning to 2.85 % of deviation. According to Órfão *et al*. (1999), this value represents a good fitting with the experimental data, since keeps lower than 5 %.

Table 2. Kinetic parameters obtained using three independent reactions under nitrogen atmosphere.

Event	Component	E_x (kJ.mol^{-1})	Log A_x (s^{-1})	n_x	Mass fraction	D (%)
1	Hemicellulose	140.11	10.02	1	0.57	2.85
2	Cellulose	200.00	14.21	1	0.13	
3	Lignin	48.98	1.01	2	0.30	

However, in this particular study, the hemicellulose is more relevant for the torrefaction process. In Fig. 2, the calculated conversion of hemicellulose occurred beyond 280 °C along with lignin. In this way, it can be assumed that torrefaction processes using guarana seed residue should not apply temperatures of processing higher than 280 °C in order to avoid the volatilization of other biomass components.

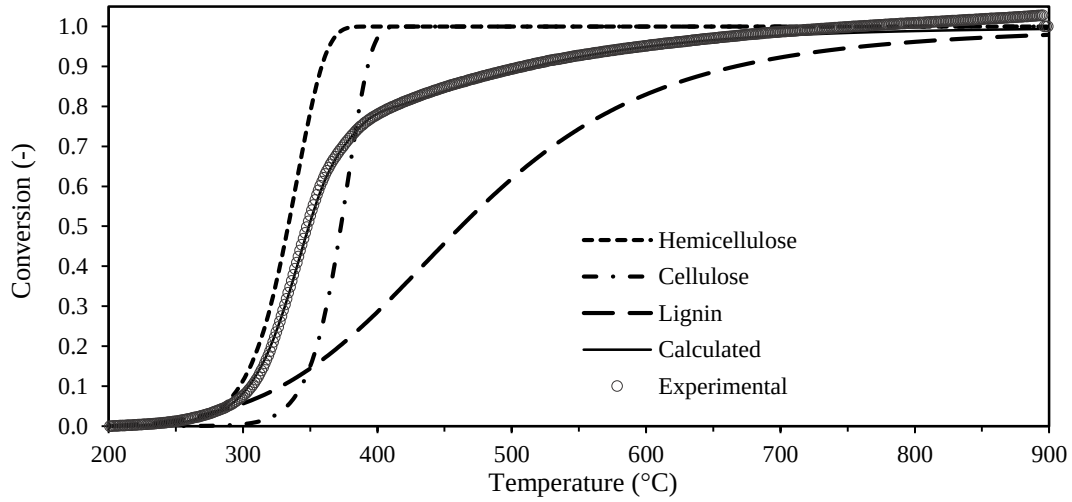

Figure 2.Conversion as a function of temperature using three independent reactions scheme.

For future studies, a comparative of independent parallel reaction scheme for raw and torrified guarana seed residue should be done in order to evaluate the effect of torrefaction process on the thermal behavior.

3.2 Torrefaction Process Analysis

Fig. 3 shows the influences of temperature, residence time and atmosphere regarding the mass loss on the torrefaction processes chosen for this work. At the temperature of 195 °C, it was released mainly the moisture content and low-molecular weight compounds with the residence time from 15 to 45 min, comparable results to the drying stage obtained from TG/DTG curves. Analyzing the torrefaction at 225 °C, the maximum mass loss obtained was 17.5 wt. % for a residence time of 45 minutes. However, at 255 °C, similar result (17.4 wt. %) at 15 minutes of residence time was found, while at 270 °C for 15 minutes, the mass loss achieved about 21 wt. %. Thus, for higher temperatures, shorter residence times are enough to avoid excessive mass losses. The behavior agrees with Chew and Doshi (2011) work, where the authors mention that the effect of residence time is less significant on the changes of biomass properties (woody and non-woody) than the temperature.

Considering the residence time equal or longer than 30 minutes, torrefaction performed at 255, 270 and 280 °C, presented mass losses between 35-57 wt. % for an inert atmosphere. When the torrefaction reached 280 ˚C under non-inert atmosphere, the mass loss was about 9 % higher than that with inert conditions (56.9 wt. %). This mass loss (over 30 wt. %) is not suitable for the thermal pretreatment, since it possibly involved an initial volatilization of the others main components besides the hemicellulose. However, that behavior was observed only for temperatures above 300 ˚C in the TG/DTG curves (Fig. 1). These results showed that an isothermal process anticipates some thermal decomposition reactions that would occur only at higher temperatures on a non-isothermal process. Therefore, TG/DTG experiments

could be used to understand the mechanism of decomposition which occurs on torrefaction process, albeit its use to predict the mass losses involved on an isothermal processes is limited.

In summary, the torrefaction experiments indicated that the solid product obtained between 225 and 255 ˚C were the most suitable for further analysis due to their acceptable mass losses, and further investigations should be done, aiming thermal and physical characterizations. Besides that, economical analysis could be implemented to investigate the ideal temperature and residence time for torrefaction process of guarana residue seed.

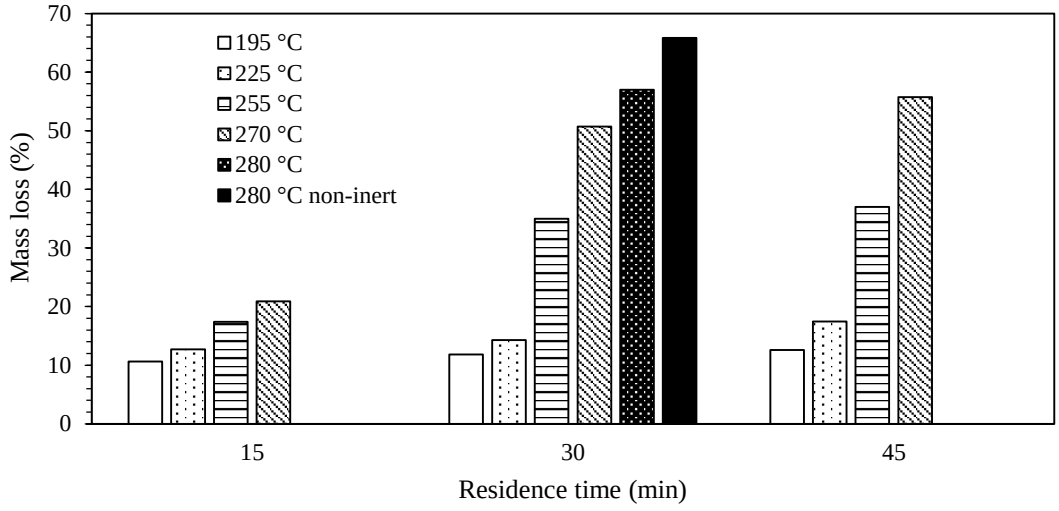

Figure 3. Comparison of mass losses of torrefaction as a function residence time related to temperature and atmosphere.

4. FINAL CONSIDERATIONS

The thermal decomposition experiments performed in thermogravimetric analysis under inert and non-inert atmospheres were not presented significant differences up to 400 °C. The torrefaction experiments (isothermal) demonstrated that mass losses were increased with the increasing of temperatures and residence time. Comparing the inert and non-inert torrefaction conditions, the temperature and residence times influenced on the mass losses, indicating that for higher temperatures, an oxidizing atmosphere resulted in higher mass loss in comparison with inert conditions. Further investigations should be done aiming to find out the best parameters to torrefaction processes related to techno-economical aspects.

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