25th ABCM International Congress of Mechanical Engineering
October 20-25, 2019, Uberlândia, MG, Brazil

COB-2019-1932
INFLUENCE OF TORREFACTION PROCESS ON CUPIUBA SAMPLES BY THERMOGRAVIMETRIC ANALYSIS

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Abstract. *Developing energy conversion technologies from renewable sources has been an important topic for recent researches. As a material distributed around the world in different species and forms, biomass can contribute with the global energy demand as a renewable source. However, it can present some negative points like high moisture content, low heating value, low bulk density and others aspects that difficult its direct conversion by combustion. Based in this context, this work presents a study about biomass pretreatment process by torrefaction, which favor the conversion of lignocellulosic biomass into energy. The torrefaction process aims to improve some biomass characteristics, making it hydrophobic, increasing its heating value, among others, like increased friability after processing. In this work, the effect of torrefaction process on cupiuba samples (Goupia glabra* Aubl.*) is evaluated through characterization and thermogravimetric analysis. Three temperatures were used. With the thermogravimetric analysis were identified two pyrolysis regions: region 1, between 200°C and 400°C, were the reactions of hemicellulose and cellulose are more intense, and region 2, between 400°C and 800°C, where the reactions of lignin are more intense. An increase in reactivity was observed as the torrefaction temperature was elevated, identified by the rise of DTG values above 300°C, where cellulose and lignin reactions are more intense. The reactions of hemicellulose decrease with torrefaction temperature, what causes a delay in volatile matter releasing and activation energy elevation from 77.71 kJ/mol (raw sample), to 129.13 kJ/mol, (torrefied at 280°C). However was observed elevations of the pre-exponential factor with the torrefaction degree.*

Keywords: *Biomass, torrefaction, reactor, thermogravimetric, cupiuba.*

1. INTRODUCTION

The global energy demand is growing every year, as like as the concern about renewables sources and fossil fuels impacts on economy, society and environment. Brazil reached the end of 2018 with a renewable energy participation of 45.3% from its intern energy demand. The biomass contribution is currently the third most important for power generation, with 8.8% stake in Brazilian energy (MME, 2019). Studies on energy conversion and lignocellulosic fuels characterization are becoming every time most important due this context and the great diversity of biomass species, forms and origins as like as the possibilities of biomass wastes valorisation.

Biomass conversion into energy could occur by various means like combustion for heat and steam generation in furnaces and boilers, pyrolysis (charcoal), gasification (flammable gases), fermentation (ethanol), etc. Vegetable biomass utilization are growing constantly, but it have some characteristics that may reduce its attraction as a fuel when compared to fossil fuels. The problems many times lies on high moisture content, low calorific value, low bulk density and high mechanical resistance. The moisture is related directly with the calorific value once the water present in biomass structure demand heat to vaporize. The moisture may increase or decrease due the hygroscopic behaviour of vegetable biomass. This characteristic in association with calorific value, bulk density and mechanical resistance impacts directly on biomass properties homogenization, transportation, burning, crushing, etc. An alternative to improve the properties of the material is the torrefaction, a pre-treatment process that can overcome all the mentioned issues.

Torrefaction is defined as a thermochemical process that occurs in an inert or limited oxygen atmosphere, where the material is subjected to a certain temperature in a stipulated time (Basu, P., 2013). Torrefaction also can be defined as a pre-carbonization process, developed in the endothermic phase of pyrolysis, between 250° C and 300° C (Rendeiro, G., et al. 2008). The usual temperature range of the process is between 200°C and 300°C (Bergman, et al., 2005). For vegetable biomass, the heating causes the thermal degradation of its main chemical components, hemicellulose, cellulose and lignin. The process breaks chemical bonds and the release volatile matter, what will significantly change its properties. Hemicellulose is the lower thermal stable component and is degraded between 200° C and 260° C, being the most affected by the process.

2. MATERIALS AND METHODS

2.1 Sampling and characterization

Cupiuba (*Goupia glabra* Aubl.) samples were obtained from a lumber company and processed in a knife mill with a ½” sieve, into wood chips. In sequence, the wood chips were torrefied in a pilot scale reactor (the process will be better described in the following topic). The raw cupiuba sample (*in natura*) and torrefied cupiuba samples passed through a characterization process in order to verify changes on biomass energy properties, before and after the process. Proximate and ultimate analysis, heating value determination and thermogravimetric analysis were performed in this step and all samples were crushed, sieved and submitted to a drying process at 105°C during 24h.

Thermogravimetric analysis was performed on a vacuum-tight thermo-microbalance, TG 209 F1 Libra-Netzsch. The present work follows the parameters approached by Parthasarathy (2013). An inert atmosphere with nitrogen gas was used to prevent secondary reactions, a flow rate of 40 ml/min. The samples were heated from 25°C to 800°C at a rate of 10°C/min. For this procedure, the samples mass was approximately 10 mg with specified grain size between 106 mm/µm and 250 mm/µm.

2.2 Torrefaction process

The torrefaction process was performed in a Vibrating Electrical Elevator and Reactor (REVE), Fig. 1. The procedure follows the study approached by Doassans-Carrère, N., et al., (2014) and Silva, D. O., (2016). Three temperatures were used for biomass torrefaction, 220°C, 250°C and 280°C, maintained by 30 minutes. The procedure consists of two steps: drying and torrefaction. First 12 kg of raw cupiuba were processed in REVE reactor at 120°C until complete evaporation of the biomass moisture content. After this step, 10kg of dry cupiuba chips were inserted inside the REVE reactor for the torrefaction process. The temperatures were determined to cover the usual temperature range of torrefaction for wood, between 200°C and 300°C, obtaining, in a qualitative approach, tree degrees of torrefied biomass: light, moderate and severe. Figure 2 presents the raw and torrefied cupiuba wood chips.

Figure 1. Vibrating Electrical Elevator and Reactor (REVE).

Figure 2. Samples: (A) raw cupiuba, (B) cupiuba 220°C, (C) cupiuba 250°C e (D) cupiuba 280°C.

2.3 Thermogravimetric analysis and Arrhenius parameters

This work focus mainly on the observation of thermogravimetric analysis (TG) and the information that is possible to obtain from its data in association with others characterization analysis. From TG analysis is possible to obtain the variation of the mass in according to the temperature increase, the rate of the mass loss and other features like Arrhenius parameters. To obtain this information, it is necessary to use a method previously investigated. The equation used in this work follows the model approached by Parthasarathy, P and Narayanan, S. K., (2013).

The equation (1) represent the global kinetic equation, (2) the Arrhenius equation and (3) the conversion rate. The equation (4) represents a combination of the equation (1), (2) and (3). Such equation follows the format of (5), where "x", "y" and "z" represent the data obtained by the thermogravimetric analysis and "B", "C" and "D" are constants that represent the Arrhenius parameters.

$$-\frac{dX}{dt} = k * X^n \tag{1}$$

$$k = A * e^{-E/RT} \tag{2}$$

$$X = \frac{w - w_f}{w_o - w_f} \tag{3}$$

$$\ln\left(\frac{-1}{w_o - w_f}\frac{dw}{dt}\right) = Ln(A) - \frac{E}{R*T} + n * Ln(\frac{w - w_f}{w_o - w_f}) \tag{4}$$

$$y = B + C * x + D * z \tag{5}$$

Using the multilinear regression method, the Arrhenius parameters were obtained. In equation (4): “dw/dt” represents the values of DTG (%/min), “w_o” is the initial time mass value (mg), “w_f” is the final time mass value (mg), “w” is the mass value varying with time (mg), “T” is the temperature value in Kelvin (K). All these terms are experimental data obtained by thermogravimetric analysis.

2.4 Results

The results of proximate analysis on dry basis, is shown on Table 1. When the torrefaction degree rises there is a reduction of volatile matter, while the fixed carbon and ash content are increased. The raw sample presents a volatile content of 83.12%, while the torrefied 280°C sample present 73.49%. Such reduction is one of the characteristics of the torrefaction process, where the heating of the material in an inert atmosphere or with low oxygen content will cause the volatilization of the fuel. The fixed carbon content is increased with the rise of the torrefaction degree. Such increase occurs due to mass concentration, torrefied samples lose volatile matter preserving most of their fixed carbon. The increased of the fixed carbon content influences directly on the energy content of the fuel. Higher concentration of carbon in the structure means higher energy content. The ash content of the raw sample is very low, around 0.37%.

The torrefied samples of 220°C, 250°C and 280°C, contain low amounts of ashes, getting in general below 1%, a reasonable value for Amazon region samples. There is an increase in ash content with the elevation of the torrefaction degree, however this increase is not very meaningful to assign torrefaction, because the process directly affects the volatile matter and fixed carbon.

Table 1. Proximate analysis of the samples of cupiuba.

Sample	Proximate analysis. Dry basis.		
	Volatile (%)	Fixed carbon (%)	Ash (%)
Raw	83.12	16.51	0.37
220°C 30 min	82.27	17.29	0.44
250°C 30 min	78.01	21.58	0.41
280°C 30 min	73.49	25.91	0.60

The torrefaction process reduces the volatile matter and raises the fixed carbon. When analyzed the elementary content, as presented in table 2, is observed the carbon content present in raw sample is 49.27% and for the torrefied 280°C sample is 55.71%, while the oxygen content decreases from 42.68% (raw sample) to 38.52% (torrefied 280°C sample). It is also observed a decrease of hydrogen content from 7.86% (raw sample) to 5.55% (torrefied 280ºC sample). The concentrations of those elementary contents influence on the energy potential. The calorific potential is directly proportional to the concentration of carbon and hydrogen and inversely proportional the concentration of oxygen. The higher heating value increases from 19.37 MJ/kg (raw sample) to 21.84 MJ/kg (torrefied 280ºC sample) as noted in table 2, where the increase of the higher heating value follows the increased of carbon content and decreased the oxygen content.

Table 2.Ultimate analysis and higher heating value for the samples of cupiuba.

Sample	Ultimate analysis. Dry and ash free basis.				Higher heating value. Dry basis (MJ/kg)
	C (%)	H (%)	N (%)	O (%)	
Raw	49.27	7.86	0.19	42.68	19.37
220°C 30 min	51.40	6.83	0.17	41.59	19.75
250°C 30 min	54.31	5.75	0.20	39.73	20.57
280°C 30 min	55.71	5.55	0.21	38.52	21.84

Fig. 3 shows the graphic of derivative thermogravimetric (DTG) for raw and torrefied samples. The graphic allows observing the thermal degradation of the main components of wood: hemicellulose, cellulose and lignin, simultaneously. In the work of Parthasarathy, P and Narayanan, S. K. (2013), they identified two regions of pyrolysis: region 1 where the reactions of hemicellulose and cellulose are more intense, and region 2 where the lignin reactions are more intense.

Eseltine, D., et al., (2013), also defines regions of reactions during pyrolysis of his samples. Between 200°C and 375°C there is the volatile release with low molecular weight and the breakdown of hemicellulose, cellulose and lignin, between 375°C and 500°C there is a greater release of volatiles and conversion of lignin in a slow process. The region 1 has a temperature range between 200°C and 400°C, and the region 2 between 400°C and 800°C. Hemicellulose has a temperature range of thermal degradation between 220°C and 315°C, while the cellulose between 315°C and 400°C (Yang, D. et al., 2007). Within the range of temperature used for torrefaction process, between 200° C and 300° C, the changes in their composition affect significantly hemicellulose and cellulose, components with less thermal stability.

Fig. 4 allows observing the beginning of the volatilization process, when the thermal degradation of hemicellulose starts. Was observed when the torrefaction degree rises, the curve tends to move itself to the right. This occurs by reduction of the hemicellulose content of the material by torrefaction process. The peak characteristic of hemicellulose reaction becomes less visible by thermogravimetric analysis, as approached in the work of Eseltine, D. et al., (2013) and Silva, A. G. et al., (2017). This implies a delay of volatile matter release, which in consequence will have effect in the formation of the flame, important step in the pyrolysis process.

The raw and torrefied 220°C samples have a temperature of volatilization around 200°C, while the torrefied 250°C and 280°C samples the temperature of volatilization is above 250°C. In this way, with the rise of torrefaction degree, hemicellulose reactions become less visible, only being observed the reactions characteristics of cellulose and lignin, as discussed in the work of Silva, A. G. et al. (2017), suggesting a lower content of hemicellulose on the samples with the torrefaction degree.

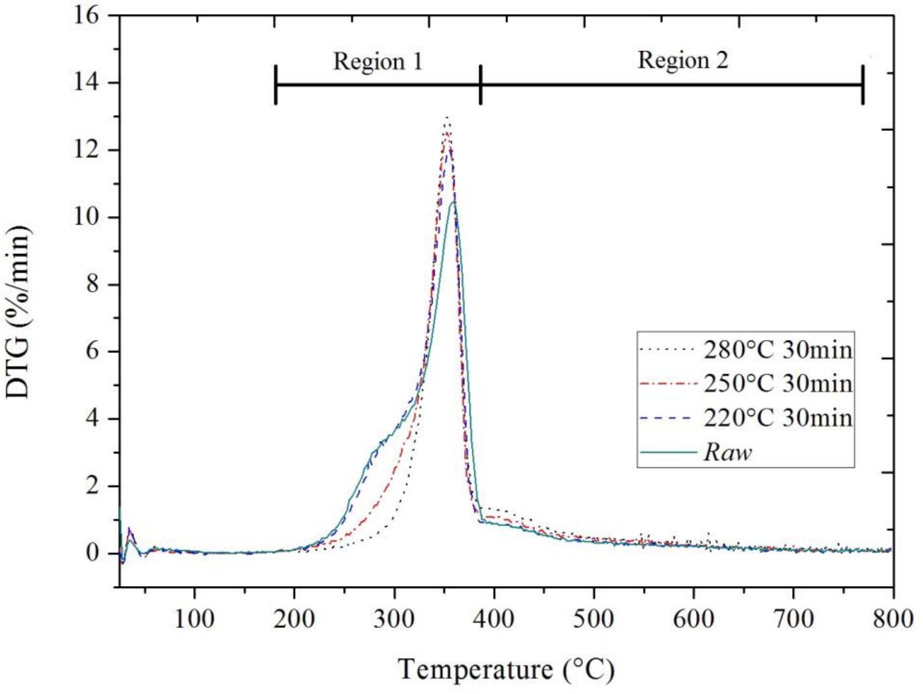

Figure 3. Derivative thermogravimetric graph (DTG).

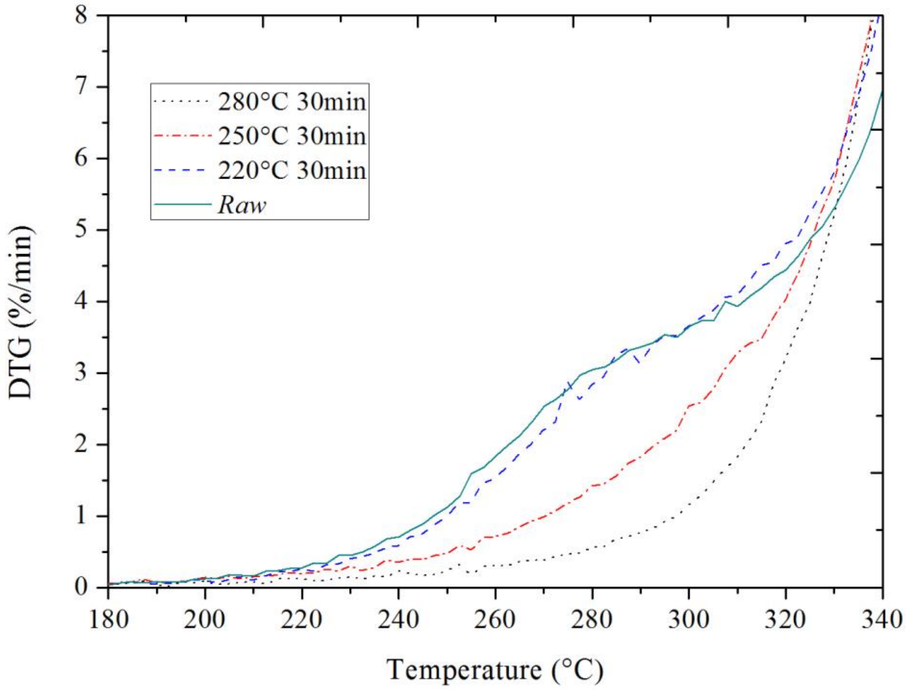

Figure 4. Region of volatilization.

Figure 5 shows the region of highest rate of mass loss. On this region the cellulose reactions are prevalent. With the torrefaction degree the peak moves to the left and the value of DTG rise. Comparing the torrefied samples with the raw sample, the peak is great for the torrefied samples. This implies that the torrefaction process raises the reactivity of solid biofuel. Bach, et al. (2015) observes the same behavior for his samples, an increase in the DTG peak. Table 3 displays the values of the DTG peak in Figure 5. There is a slight decrease in peak temperature with the torrefaction degree. The peak is between 300°C and 400°C, where the thermal degradation reaction of cellulose is more intense.

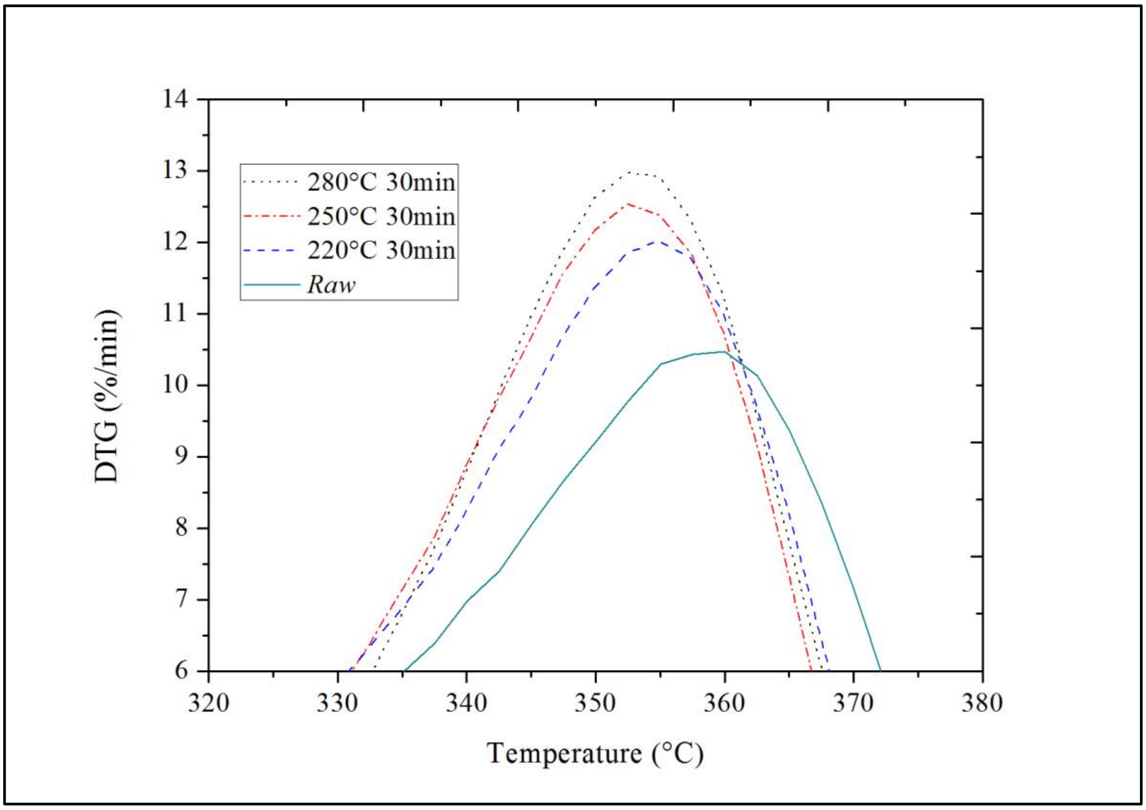

Figure 5. Region of greatest mass loss rate

Table 3. Values of DTG and temperature of greatest mass loss rate.

Sample	Temperature (°C)	DTG (%/min)
Raw	360.04	10.47
220°C 30 min	354.86	12.03
250°C 30 min	352.45	12.54
280°C 30 min	352.42	12.97

The region 2 the lignin reactions are prevalent. Figure 6 shows that the torrefied samples presents values of DTG high than raw sample. The temperature of lignin thermal degradation is between 160° C and 900° C (Yang. et al., 2007), being the most thermal stable component. Torrefied 220°C sample presents a behavior around the raw sample, since in such a torrefaction temperature, lignin is unaffected by the process (Chen, w. h. and Kuo, p. c. 2011), different from the torrefied samples on 250°C and 280°C, which show that the reactions of lignin degradation suffer influence of torrefaction process. Such observations of the DTG regions are important in relation to the Arrhenius parameters, because the concentration of these components as function of the torrefaction process effect will define the thermal behavior of the samples.

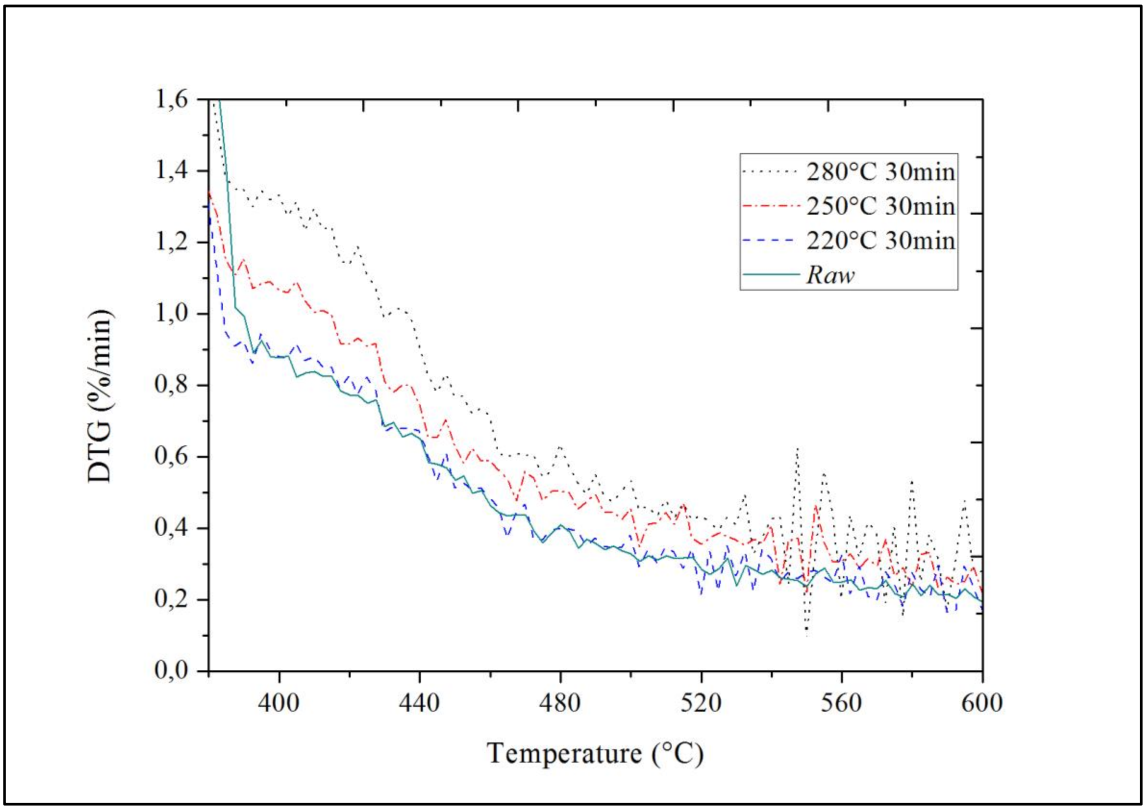

Figure 6. Region of lignin thermal degradation

Table 4 displays the Arrhenius parameters values for regions 1 and 2. For region 1, the activation energy presents an increase from 77.71 kJ/mol (raw sample) to 129.13 kJ/mol (torrefied 280°C sample) and the pre-exponential factor an increase from 1.39E+04 s^{-1} (raw sample) to 3.21E+08 s^{-1} (torrefied 280°C sample), with the rise of the torrefaction degree. The region 1 represents the thermal degradation of hemicellulose and cellulose and simultaneously, as presented in Fig. 4.where observed a decrease of hemicellulose content. In the work of Quang Vu Bach et al. (2015), the authors shown that with the rise of torrefaction degree there is a decreases of the activation energy, and the pre-exponential factor for hemicellulose increases of the values for cellulose.

Soon the increase on activation energy occurs by concentration of cellulose content, which is a more thermally stable component than hemicellulose. The elevation of activation energy means a major energy will be necessary for the reaction occur, it implies a delay in the release of volatile matter to the torrefied samples. The pre exponential factor is linked to molecular collisions. Its elevation increases volatilization reactions, however as noted in Fig. 4, the reaction speed of the torrefied samples are less than raw sample at low temperatures, because under 300°C hemicellulose degradation reactions are more intense that the other components. However above 300° C, the speed of reaction is greater for the torrefied samples, as evidenced in Fig. 5, which occur because of the increase on the number of atomic collisions, by pre-exponential factor.

Table 4. Values of Arrhenius parameters.

Sample	Region 1				Region 2			
	A (s^{-1})	E (kJ/mol)	n	r2	A (s^{-1})	E (kJ/mol)	n	r2
Raw	1.39E+04	77.71	0.66	0.97	4.63E-07	-45.75	-0.10	0.98
220°C 30 min	5.53E+04	84.05	0.74	0.96	5.19E-07	-45.00	-0.10	0.92
250°C 30 min	3.35E+05	93.91	0.73	0.95	1.40E-06	-39.27	-0.05	0.94
280°C 30 min	3.21E+08	129.13	0.81	0.94	2.84E-07	-48.59	-0.11	0.80

The values of activation energy for the region 2 feature negative values, characteristic of exothermic reactions. It is possible to observe with the torrefaction degree an increase in activation energy from -45.74 kJ/mol (raw sample) to -39.27 kJ/mol (torrefied 250°C sample). Torrefied 280°C sample presents a decrease, -48.59 kJ/mol. Bach, Q. V., et al., (2015) comments on your work the change in reactivity of lignin is not very clear, because of the complexity of its structure. The pre-exponential factor increase from 4.63E-07s^{-1} (raw sample) to 1.40E-06s^{-1} (torrefied 250°C sample), then presents a decrease to 2.84E-07s^{-1} (torrefied 280°C sample).

2.5 Conclusion

The effect of torrefaction process on biomass energy properties and the thermal degradation behavior was evaluated through characterization and thermogravimetric analysis. The torrefaction process has improved the energy properties of cupiuba wood. The main point was the elevation of high heating value, from 19.37 MJ/kg (raw sample) to 21.84 MJ/kg (torrefied 280°C sample), an increase of 12.75%. The flame temperature and the energy released for torrefied biomass are higher than raw material. Such increase is directly linked to the carbon content and decreased of oxygen content of the samples. Associating with its hygroscopic propriety, make the torrefied material a better fuel than raw material.

The main change caused by the torrefaction process on the material is related to the structure of its main chemical components: hemicellulose, cellulose and lignin. The first point was the decrease of volatile matter, because of hemicellulose thermal degradation. It`s observed a delay on the releasing of volatile matter, due a reduction of the hemicellulose content and concentration of cellulose content. This causes an increase on the energy activation value, from 77.71 kJ/mol (raw sample) to 129.13 kJ/mol (torrefied 280°C sample), however, the reactions became more intense at high temperatures, above 300°C, when the torrefied samples presents highest values for DTG. The torrefaction speed rise because the increase of the pre-exponential factor, from 1.39E+04 s^{-1} (raw sample) to 3.21E+08 s^{-1} (torrefied 280°C sample). The second point is the rise of the greatest mass loss rate peak, due to the cellulose concentration, on this region the reaction are more intense. The torrefied material have an improvement on the pyrolysis process, increased the conversion of mass into energy. This means the torrefaction process change the pre-exponential factor values more than activation energy values, making the torrefied material more reactive during the pyrolysis process. The region 2, where the reactions of lignin are more intense, was observed an increase of the reactivity of the torrefied samples. On this region, the reactions are exothermic. The changes on the activation energy and the pre-exponential factor values are not very significant. This means that the torrefaction process doesn`t affect significantly the lignin component.

The torrefaction process changes the main properties of raw cupiuba: raising the higher heating value, concentrating the carbon content and decrease the oxygen content. However the most important change for the torrefied material its associated with its reactivity, were the decrease of hemicellulose content and concentration of cellulose content, by release of the volatile matter during the torrefaction process, ensures to the material higher values for reaction speed (DTG), improving its reactions during the pyrolysis process

3. ACKNOWLEDGEMENTS

The authors would like to thank FAPESPA-VALE and CNPq for finance the activities of the project Co-firing (ICAAF 071/2011), were we obtain the data of this work. Thanks the CAPES for the scholarship during the internship on the EBMA research group laboratory.

4. REFERENCES

Basu, P., 2013. *Biomass Gasification, Pyrolysis and Torrefaction: Pratical Design and Theory*. 2. ed. Elsevier. pp 548.

Bach, Q., Tran, K., Skreiberg, O. and Trinh, T., 2015. “Effects of wet torrefaction on pyrolysis of Woody biomass fuels”. *Energy*, No. 88. pp. 443-456.

Chen, W. H., Kuo, P. C., 2010. “A study on torrefaction of various biomass materials and its impact on lignocellulosic structure simulated by a thermogravimetry”. *Energy*, No. 35. pp. 2580-2586.

Chen, W. H., Kuo, P. C., 2011. “Isothermal torrefaction kinetics of hemicellulose, cellulose, lignin and xylan using thermogravimetric analysis”. *Energy*, No. 36. pp. 6451-6460.

Chen, W. H., Kuo, P. C., 2011. “Torrefaction and co-torrefaction characterization of hemicellulose, cellulose and lignin as well as torrefaction of some basic constituents in biomass”. *Energy*, No36, pp. 803-811.

Coelho, P.; et al., 2007. *Combustão*. 1. ed. Amadora, Portugal: Orion. pp 714.

Cortez, L. A., et al., 2008. *Biomassa para Energia*. 1. ed. UNICAMP. pp 736.

Doassans-Carrère, N., et al., 2014. “Reve-a new industrial technology for biomass torrefaction: pilot studies”. *Fuel Processing Technology, Elsevier*, v. 126. pp.155-162.

Eseltine, D., et al., 2013. “Torrefaction of wood biomass (Juniper and Mesquite) using inert and non-inert gases”. *Fuel Processing Technology, Elsevier*, v. 113. pp. 379-388.

MME, 2019. “Resenha Energética Brasileira” Ministério de Minas e Energia. 25 Jul. 2019 <http://www.mme.gov.br>.

Parthasarathy, P.; Narayanan, S. K., 2013. “Determination of kinetic parameters of biomass sambles using thermogravimétric analysis”. *Environmental progress & susainable energy,* v. 33, No. 1, pp. 256-266.

Rendero, G. et al., 2008. *Combustão e Gaseificação de Biomassa Sólida: Soluções Energéticas para a Amazônia*. 1. ed. Brasília: Ministério de Minas e Energia. pp 194.

Rousset, P. L.; Rodrigues, T. O., 2009. “Torrefação como pré-condicionamento da biomassa para uso energético: Estudo da Arte”. *Escola de Combustão II*, pp. 64-87.

Rousset, P. L.; Macedo, L. A., 2013. “Pré-tratamento da biomassa para uso energético: A torrefação”. *Escola de Combustão IV*, pp. 35-60.

Silva, D. O., 2016. “Metodologia para produção de biomassa torrada utilizando um reator elevador eletro vibrante”. Dissertação de mestrado, Universidade Federal do Pará, Belém, Brasil.

Silva, A. G. et al., 2017. “Estudo do processo de torrefação de resíduos de biomassa para fins energéticos”. *RBCIAMB*, No. 45. pp. 86-99.

Turns, S. R., 2013. *Introdução a Combustão: Conceitos e aplicações*. 3. ed. Porto Alegre: AMGH. pp 420.

Yang, H., et al., 2007. “Characteristics of hemicellulose, cellulose and lignin pyrolysis”. *Fuel*. No. 86, pp. 1781-1788.

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