DETERMINATION OF THE GIANT-BAMBOO PYROLYSIS KINETIC PARAMETERS

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ABSTRACT – The kinetics involved in giant bamboo thermal degradation under N_2 atmosphere was investigated through non-isothermal thermogravimetric analyses (TGA) and derivative thermogravimetry (DTG) applying three isoconversional methods: Coats and Redfern (CR), MacCallum and Tanner (MT), and van Krevelen (VK). Besides that, samples characterization was conducted by van Soest's method and by proximate analysis. The TGA experiments were performed with a N_2 rate of 50 mL/min and five different heating rates were used: 5, 10, 15, 25 and 50 °C/min, for a samples aged 5.5 years. The van Soest's test indicated that the giant bamboo is composed of up to 73% of cellulose and the proximate analysis showed up to 84% of volatile matter. The highest weight loss region evaluated by the DTG was between 200-450°C, corresponding to a weight loss range of 10-85% in mass. The Coats-Redfern's fitting-model indicated that two-dimensional diffusion was the mechanism which best describes the pyrolysis process in the highest weight loss region. The kinetic parameters determined by CR's, MT's, and MT's methods, respectively, varied between 136 and 150 kJ/mol for the activation energy and between 2.75×10^{10} and 3.6×10^{11} s^{-1} for the pre-exponential factor. Comparing the calculated and experimental weight loss, was verified that the CR's and MT's average deviations were lower than the evaluated by VK's method, indicating that the CR's and MT's describe better the giant bamboo pyrolysis.

1. INTRODUCTION

The world necessity for clean energy and the continuous Earth's warming due to the high pollutant gases emissions, provokes an increase in research for new environmentally friendly energy sources. Lignocellulosic biomasses are an interesting option to obtain biofuels [Basu, 2010], being mainly composed of cellulose, hemicellulose, and lignin, compounds which present high heating value due to the high carbon contents in their molecules [Glasser, 1985; McKendry, 2002]. Giant bamboo, scientifically known as *Dendrocalamus giganteus*

Munro, is a potential material to be transformed into biofuels due to the high cellulose amount in its composition (Raveendran and Ganesh, 1996; Aparicio, 2005), and also, by presenting a high growth rate, growing up to 30% times faster than the trees species of rapid growth. As verified by Azzini et al (1989), giant bamboo presents a growth rate that lies between 2.00-7.88 cm/day, and as verified by some previous works, it grows up to 40 meters and can reaches up to 20 cm diameter (Keng and Wang, 1996; Pereira and Beraldo, 2007).

Pyrolysis is a thermochemical process which transforms biomass into biofuels through material degradation at different heating rates and in total oxygen absence (Maschio *et al.*, 1992; Yaman, 2004). Among the different types of pyrolysis, conventional pyrolysis is performed with a heating rate which varies from 10 to 50°C. According to Demirbas 2009, by varying the upper temperature process and the residence time, the conventional pyrolysis products can range from 25-91%$_{wt}$ of bio-char, 7-33%$_{wt}$ of bio-oil and 2-54%$_{wt}$ of bio-gas. In order to design an efficient and sustainable pyrolysis reactor, the reaction kinetic parameters, activation energy (E) and pre-exponential factor (A), must be determined (Varhegyi, 1997). Isoconversional methods which determine the kinetic parameters, such as Coats-Redfern (1964), MacCallum-Tanner (1970), and van Krevelend (1951), use thermogravimetric data to adjust the parameters to attain the best fit to the data experimentally generated. These methods were applied by previous works which studied the thermal degradation of materials, especially for polymeric materials as biomasses, resins, and some selected organic matter, and were related with thermogravimetric data (White *et al.*, 2011; Perondi, 2012).

This research aimed to obtain the kinetic parameters at five different heating rates of conventional pyrolysis of the giant bamboo from specie *Dendrocalamus giganteus* Munro aged 5,5 years. To attain this purpose, thermogravimetric and derivative thermogravimetry data were obtained and the experimental data was modelled using the isoconversional methods of Coats-Redfern, MacCallum-Tanner, and van Krevelen.

2. MATERIALS AND METHODS

2.1 Materials

Dendrocalamus giganteus Munro was the giant bamboo specie used in the pyrolysis kinetic parameters determination. The age of the sample studied in this work was 5.5 years, and the material was naturally air-dried previously under ambient conditions and crushed in a knife mill and sieved with Tyler's sieve to obtain particles with a size lower of 0.84 mm (20 mesh).

2.1.1 Material Characterization

The giant bamboo samples compositions were gravimetrically determined by van Soest's method (Soest, 1968), which evaluates the cellulose, hemicellulose and cellular, lignin, and ash contents. The volatile matter, fixed carbon, and moisture were determined by proximate analyses.

2.1.2   Thermogravimetric analyses

The thermogravimetric analyses were performed in a thermobalance (TG-50 Shimadzu) in an inert atmosphere with a N_2 flow of 50 mL/min in the absence oxygen. The initial mass used in the analyses was around 10 mg and were used five heating rates: 5, 10, 15, 25 and 50 °C/min, characterizing the process as conventional pyrolysis (Demirbas, 2009). The initial and final temperatures were 200 and 800 °C, respectively.

2.1.3   Kinetics Modeling

The TG data was used to obtain the ratio loss of samples masses, as shown in equation 1.

$$\alpha = \frac{(m_0 - m_t)}{(m_0 - m_f)} \tag{1}$$

where m_t is the sample weight in the time t; m_0 is the initial sample weight and m_f is the final sample weight. The degradation rate depends on the reaction rate (k), which is dependent on the analysis temperature, and depends on the unreacted material function $(f(\alpha))$, which depends on the sample weight, as shown in equation 2.

$$\frac{d\alpha}{dt} = k.f(\alpha) = A.e^{(-E/RT)}.f(\alpha) \tag{2}$$

In equation 2, the reaction rate (k) was related by Arrhenius' equation, presenting the dependence of this rate with the kinetic parameters, the activation energy (E) and pre-exponential factor (A). By variables separation of equation 2 and considering the heating rate (dT/dt) of the system (β), is obtained a dependence between the weight loss and the temperature related with the kinetic parameters, as shown in equation 3:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_0^T e^{(-E/RT)}.dT = \frac{A.E}{\beta R} p(x) = g(\alpha) \tag{3}$$

where:

$$p(x) = \int_\alpha^x \frac{e^{-x}}{x^2} dx$$

Resulting in equation 4:

$$g(\alpha) = \frac{A.E}{\beta R} p(x) \tag{4}$$

Dividing equation 4 by p(x) and by applying logarithm on both sides of the equation, one obtains an equation which can be related by linearization, as shown in equation 5.

$$\log g(\alpha) - \log p(x) = log \frac{A.E}{R.q} \tag{5}$$

The unreacted material functions f(α) and their integrated inverse forms g(α) for different mechanisms are reported in Table 1 (Fraga and Nunez, 2001).

Table 1 – Unreacted material functions f(α) and the inverse of its integrate form g(α).

Degradation mechanism	f(α)	g(α)
Chemical Reaction		
First order (F1)	$(1-\alpha)$	$-\ln(1-\alpha)$
Second order (F2)	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Order n (Fn)	$(1-\alpha)^n$	$\dfrac{[(1-\alpha)^{1-n}-1]}{n-1}$
Nucleation		
Bidimensional Avrami-Erofeev (A2)	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
Tridimensional Avrami-Erofeev (A3)	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
Prout-Tompkins (PT)	$(1-\alpha)\alpha^{0,5}$	$\ln\left[\dfrac{(1+\alpha)^{0,5}}{(1-\alpha)^{0,5}}\right]$
Diffusion		
Bidimensional (D2)	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$
Tridimensional (D3)	$\dfrac{(2/3)(1-\alpha)^{2/3}}{1-(1-\alpha)^{1/3}}$	$\left[1-(1-\alpha)^{1/3}\right]^2$
Zhuravlev (ZH)	$\dfrac{(2/3)(1-\alpha)^{5/3}}{1-(1-\alpha)^{1/3}}$	$\left[(1-\alpha)^{-1/3}-1\right]^2$
Ginstling-Brounshtein (G-B)	$\dfrac{(2/3)(1-\alpha)^{1/3}}{1-(1-\alpha)^{1/3}}$	$1-\dfrac{2\alpha}{3}-(1-\alpha)^{2/3}$
Phase Boundary Reaction		
Contracting Sphere (R2)	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Contracting Cylinder (R3)	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$

Several methods using different approaches have been developed aiming to solve the term log[p(x)] in equation 5. This work determined the kinetic parameters based on those approximations presented by Coats and Redfern, MacCallum-Tanner and van Krevelen.

3.   RESULTS

3.1   Characterization of the giant bamboo samples

The composition obtained from the van Soest's method confirmed the high concentration of cellulose in giant bamboo, possessing 73% in mass of this compound. Hemicellulose and some proteins, fats and some fibers amounted 20.1%, while lignin and ash represented 5.3 and 1.6% in mass, respectively. Based on these results, the giant bamboo presents a high amount of

volatile matter. It was confirmed by the proximate analysis which indicates that the sample possess 83% of volatile matter, 9.2% of moisture and 2.6% of fixed carbon.

3.2 Pyrolysis degradation of the giant bamboo samples

The sample degradation for the five different heating rates is shown in Figure 2. As can be seen in Figure 2, giant bamboo degradation occurs at three different stages. The first weight loss, about 10% of matter, was due to the water content, being in agreement with proximate analyses results. The second step is noticed by the abrupt weight loss region, where sample decomposition occurred, indicating that approximately 70% of biomass was consumed. The third stage is verified on the region where a very low degradation rate occurs due to lignin residues and solids and liquids products degradations, like tar and char. As can be observed in Figure 2, the degradation curves presented the same behavior, differing only the reaction time.
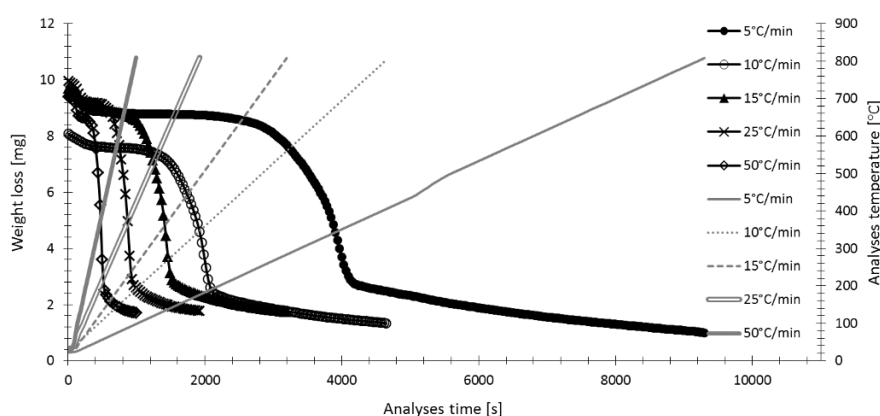

Figure 2 – Weight loss curves and heating rate of sample.

Figure 3 presents the DTG of the giant bamboo. The region covered by the peak in this figure represents the second stage.
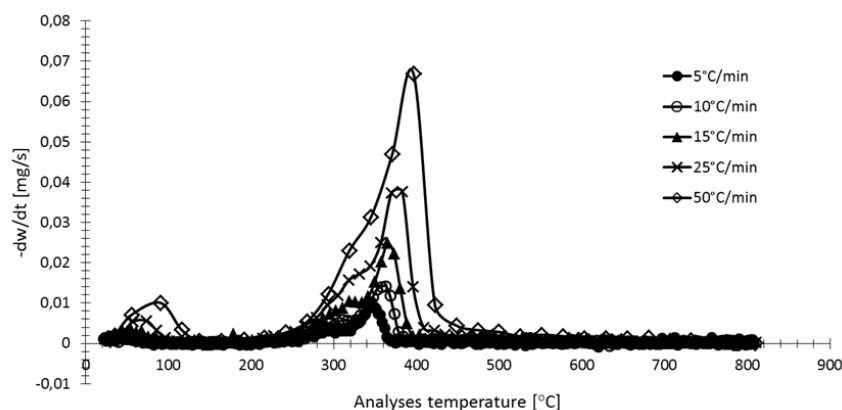

Figure 3 – DTG curves for giant bamboo.

It is possible to verify that the highest degradation rate occured at 347.9°C for the 5°C/min heating rate and at 391.2°C for the 50°C, varying between these values for the others heating rates. Furthermore, it is observed that the abrupt weight loss increase lies between 270-430 °C and the same behavior occurs for the five different heating rates. The temperature range of samples degradation agrees with those of cellulose, hemicellulose, and lignin estimated ranges (Ramiah, 1970).

3.3 Determination of the fit pyrolysis process mechanism

The degradation mechanism was determined using the Coats-Redfern's method. Figure 4 illustrates the relation between $\ln[g(\alpha)/T^2]$ and $1/T$, indicating the fitting mechanism by data linearization.
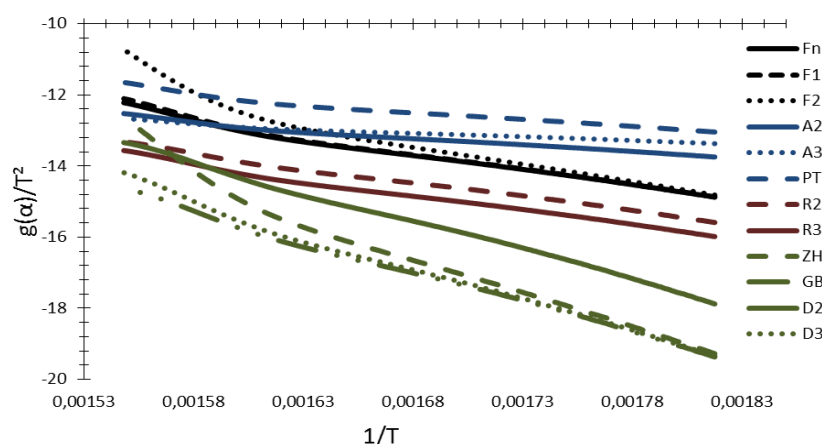

Figure 4 – Mechanism degradation of giant bamboo determined by Coats-Redfern's method.

Each of this curves were linearly related and the best coefficient of determination indicated the degradation mechanism for the giant bamboo. Among those calculated r^2, the higher was found for the two-dimensional diffusion mechanism, best describing the giant bamboo pyrolysis for the five different heating rates, indicating that the biopolymer material degrades by mass diffusion.

3.4 Giant bamboo kinetic parameters determination

The activation energy (E) and the pre-exponential factor (A) were calculated by Coats-Redfern's, MacCallum-Tanner's, and van Krevelen's methods. For the kinetic parameters determination, the $g(\alpha)$ function was consider to be equal to $\alpha+(1-\alpha)\ln(1-\alpha)$, as indicated in Table 1. The kinetic parameters were calculated by the relationship between the angular and linear coefficient from the straight lines obtained by the fitting of CR's, MT's, and VK's methods. The kinetic parameters calculated with these three methods are summarized in Table 2. As can be observed, the parameters determined from CR's and MT's methods presented close values, while the calculated by MT's method differs around 10%.

Table 2 – Sample kinetic parameters calculated by CR's, MT's, and VK's methods.

β	Coats-Redfern		MacCallum-Tanner		van Krevelen	
	E [J/mol]	A [s^{-1}]	E [J/mol]	A [s^{-1}]	E [J/mol]	A [s^{-1}]
5	137771	3,10E+10	139793	4,37E+10	150988	4,24E+11
10	134903	2,14E+10	137069	3,08E+10	147735	2,60E+11
15	135327	2,52E+10	137608	3,73E+10	149106	3,56E+11
25	134920	2,60E+10	137352	3,95E+10	148551	3,41E+11
50	135493	3,35E+10	138132	5,31E+10	149622	4,59E+11

The calculated data were determined by equation 5 using the kinetic parameters summarized in Table 2. When were compared with those calculated experimentally, it was observed that CR's and MT's methods determined better the calculated data than VK's method, presenting an average deviation between the experimental and calculated data of 4.39, 4.42 and 4.8% for CR's, MT's, and VK's methods.

4. CONCLUSION

The giant bamboo conventional pyrolysis kinetics was investigated by the CR's, MT's, and MT's isoconversional methods using thermogravimetric data. The CR's method showed that the giant bamboo degradation occurs by two-dimensional diffusion and the DTG presented that the temperature range which reaction occurred was between 200-450°C. The kinetic parameters obtained by CR's, MT's, and VK's methods varied between 135-137, 138-139 and 149 to 151 kJ/mol for the activation energy and between 2.14×10^{10}-3.35×10^{11}, 3.08×10^{10}-5.31×10^{10} and 2.6×10^{11}-4.59×10^{11} s^{-1} for the pre-exponential factor. With these values, it is possible to design a pyrolysis reactor to obtain bioenergy from giant bamboo. The relation between the experimental and calculated data showed that the kinetic parameters adjusted with weight loss data through CR's and MT's method described better the giant bamboo pyrolysis than the VK's method, which presented a higher calculated data average deviation.

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