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NON-ISOTHERMAL KINETICS OF THE THERMAL DEGRADATION OF HEMICELLULOSE SHEET OBTAINED FROM CURAUÁ FIBERS BY ALKALI TREATMENT

Vilson Dalla Libera Junior
Mariana Roldi de Oliveira
Sandra Maria da Luz
Engineering Materials Integrity Program, Gama Campus, Universidade de Brasília, Brasília, Brazil
vilson-dalla@hotmail.com, mroldi.arq@gmail.com, sandraluz@unb.br

Abstract. *The biodegradability of plant fibers and their intrinsic characteristics contribute to a sustainability of the environment, especially when we used to produce new materials. Natural fibers are constituted by microfibrils cellulose rolled and joined by lignin and hemicellulose. Hemicelluloses can be extracted from natural fibers and as a biodegradable polymer, it can be employed for manufacturing biofuel, edible bio-surfactant, food additives, and biomedicine. Learning more about the thermal properties of this polymer, the main objective of this work is to determine the reaction kinetics for hemicellulose sheets obtained from curauá fibers through thermogravimetric analysis (TG) and its derivative (DTG). This characterization is necessary to define processing conditions and temperature application limitations. The hemicellulose was extracted from curauá through an alkaline solution of KOH and the sheets prepared using water casting process. The behavior of its thermal degradation was investigated from room temperature up to 600°C under nitrogen flow, using heating rates of 10, 15, 20, 40 and 60°C/ min. The hemicellulose sheet activation energy was determined by reaction kinetics equations for each heating rate. The velocity of 15°C/ min was the rate that presented the lowest hemicellulose activation energy.*

Keywords: *hemicellulose sheet; curauá fibers; kinetics; activation energy; thermal analysis.*

1. INTRODUCTION

The biodegradability of plant fibers and their intrinsic characteristics contribute to a healthier and renewable ecosystem, especially when used to produce new materials (Satyanarayana *et al*., 2005). The number of researchers involved in the study of the natural fibers prospective as load-bearing elements in composite materials has been growing over the last few years. The application of these materials in composites has increased because they have good mechanical proprieties regarding strength per weight of material, as well their ability to recycle and relatively low cost (John and Thomas, 2008).

In the plants, the vegetable fibers can be categorized according to the part from where they are extracted, such as fiber (flax, hemp, jute, ramie), leaf (cantala, curauá, palm tree, pineapple, sisal), grass (bagasse, bamboo), straw fibers (straw), seeds (cotton) and fruit (palm oil) (Kalia *et al*., 2009). Natural fibers are considered as naturally occurring compounds, and its microfibrils cellulose are rolled and joined by lignin and hemicellulose. Lignin preserves water in the fibers, acting as a biological and reinforcement protection. It is considered that the hemicellulose molecules are compatible between cellulose (bonded by hydrogen) and lignin, acting as a cement matrix among the cellulose microfibers (John and Thomas, 2008).

Hemicelluloses are a natural and amorphous polymer, they have a molar mass expressively lower than that of cellulose, and, because they contain many hydroxyl and acetyl groups in their structure, the hemicellulose is very hydrophilic, partially soluble in water and soluble in alkaline hydroxides (John and Thomas, 2008; Spinacé *et al*., 2009). The presence of hemicellulose can be observed in a vast and varied number of products, such as biosheets and biomasses. Hemicellulose also provides broad application in the food industry, biofuel, edible bio-surfactant, food additives, and biomedicine (Brienzo, 2009; Li *et al*., 2017).

Thermal degradation of biomasses and the decomposition of carbohydrates are complex processes and include many different and simultaneous reactions (Patwardhan *et al*., 2011). The thermogravimetry (TG) and its derivative (DTG) provide information about the nature and degree of degradation of the material. Particularly in the field of polymers, kinetics of polymer degradation reaction is a way to represent the chemical phenomena of the polymer and represents a great advantage to determine the characteristic kinetic of all processes (Joseph, 2003; Mathot and Pijpers, 1989).

For the activation energy, it was considered that the reaction is activated when a reagent particle reaches enough energy to overcome the potential energy barrier preventing the reaction (Hatakeyama, 1999). In applications related to thermal decomposition of polymers, the Arrhenius equation is used to determine reaction kinetics (Huang *et al*., 2011).

In the Arrhenius equation, A is a pre-exponential factor (1/s), E_a is the activation energy of hemicellulose (J/mol), R is the ideal gas constant in the case (R = 8.314 J/ Kmol) and T is the temperature expressed in Kelvins (K) (Li *et al.*, 2014). The equation as a function of weight loss about time can be expressed as:

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E_a}{RT}\right)f(\alpha) \tag{1}$$

It can replace the term $d\alpha/dt$ with $d\alpha/dT$. As the heating rate is a constant of time, the equation 1 becomes:

$$\frac{\frac{d\alpha}{dT}}{f(\alpha)} = A\exp\left(-\frac{E_a}{RT}\right) \tag{2}$$

The biomass decomposition is of order 1, which $f(a)=(1-\alpha)$ can be expressed as the conversion function where an unreacted part of the sample is represented by $(1-\alpha)$. Transforming the equation 2 in a logarithmic function, we have:

$$\ln\left(\frac{d\alpha}{dT}\right)\Big/(1-\alpha) = \ln A - \frac{E_a}{RT} \tag{3}$$

The kinetic parameters of first-order reactions can be calculated by thermogravimetric data at the maximum reaction rate, and only the information such as reaction temperature and the reaction rate is needed (Huang *et al.*, 2011).

In the present work, we investigate by thermal analysis the hemicellulose properties at different heating rates. The primary objective is to perform a thermogravimetric analysis evaluating the reaction kinetics of the hemicellulose sheet obtained from curauá fibers by alkaline treatment.

2. EXPERIMENTAL

2.1 Materials

The hemicellulose sheets investigated was obtained from natural curauá fibers by an alkaline solution treatment of KOH based on the Oliveira and Luz (2016) methodology. In this process, the fibers were soaked in distilled water at the ratio of 5% w/v for 1h at room temperature, and then filtered. After that, the material was immersed in 10% (w/v) KOH solution using a mechanical stirring at 50 rpm on an orbital shaking at 150 rpm, simultaneously, for 3 h at room temperature. The pH was adjusted to 4.8 using acetic acid, and the liquor was centrifuged for 5 min at 4000 rpm. The liquor was precipitated with a solution 1:10 of acetic acid and ethanol at a ratio of 25% (w/v) and, after 24 hours, filtered and the hemicellulose sheets produced by casting. Finally, the hemicellulose polymeric sheets were dried at room conditions.

2.2 Thermal analysis

Five samples from hemicellulose sheets, with 10 mg each were analyzed by thermogravimetric analysis (TG) under heating rates of 10, 15, 20, 40 and 60°C/ min. The analyses were performed on a thermal analyzer SDT Q600 equipment (TA Instruments, USA) and its derivative thermogravimetric (DTG) were obtained from TG curves. The samples were put in an alumina pan, and then the analysis carried out at room temperature up to 600°C under an inert atmosphere of nitrogen with a flow rate of 50 mL/ min.

3. RESULTS AND DISCUSSION

3.1 Thermogravimetric analyses

The profiles of weight (TG) and their differential values (DTG) of the hemicellulose sheet varying with the temperature are illustrated in Fig. 1 and shows a typical result from TG–DTG test on non-isothermal thermogravimetric sample analyses.

The Fig 1. (a) shows the TG curves achieved by thermal analysis. The variation in the heating rates influenced the relation between weight loss and temperature (Peng and Wu, 2010). The thermal decomposition of lignocellulosic fibers results in complex reactions because they are composites of different parts, consisting of cellulose, hemicellulose, and lignin; some studies in the literature explain this behavior (Orfao *et al*., 1999). The Fig 1 (b) shows the DTG profiles; it can be noted that all curves present a three-stage of sample degradation.

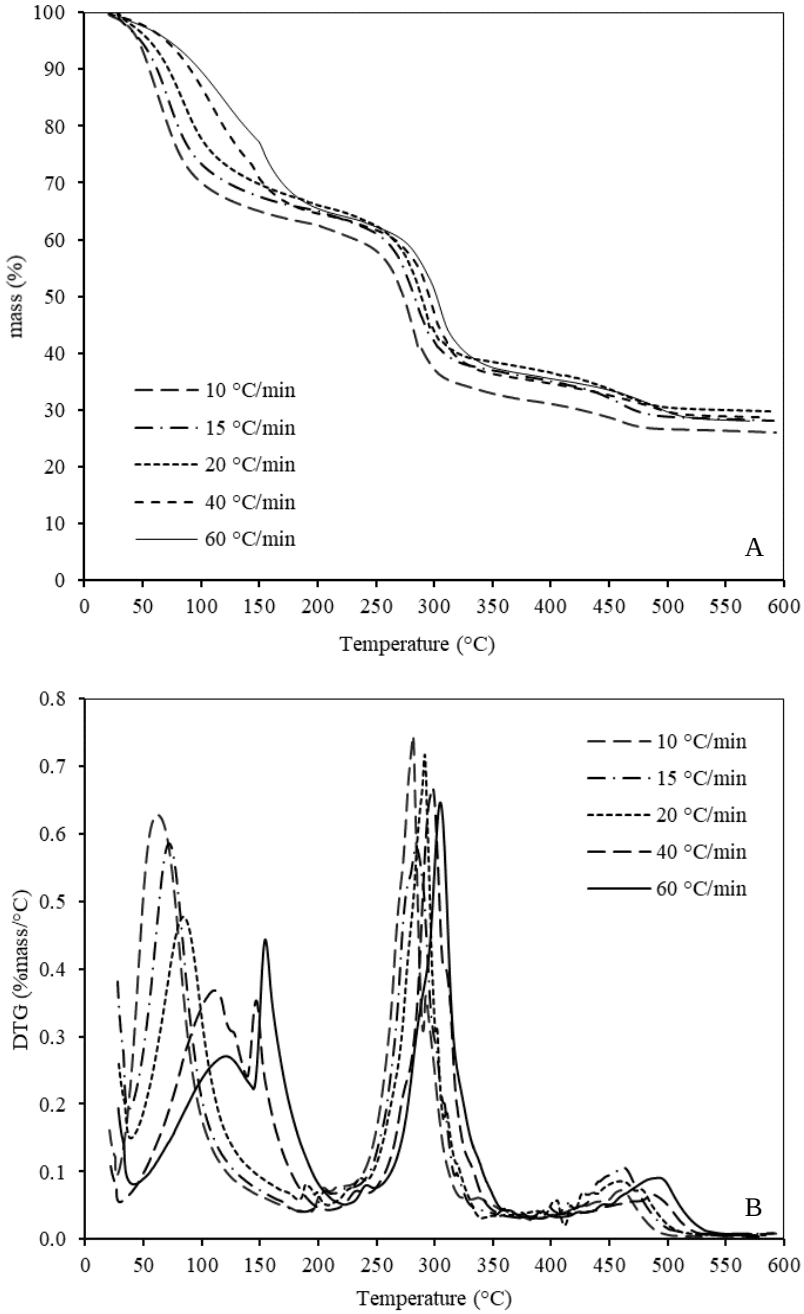

Figure 1. Profiles from thermal analysis of hemicellulose sheet at different heating rates (A) TG and (B) DTG.

Fig. 1 and Table 1 show that at the first stage (~200°C), the samples just lost humidity; the greatest weight loss occurs between 220 to 320°C, which was referred the degradation of hemicellulose, usually occurring from 200 to 300°C (Hoareaua *et al.*, 2004). From 350 to 500°C the third step of thermal degradation occurs, attributed to residual cellulose and lignin degradation (Leão *et al.*, 2017).

Table 1. Pyrolysis data of curauá fibers hemicellulose sheet at different heating rates.

Heating rate (°C/min)	$T_{on\ set}$ (°C)	Peak temperature (°C)	Residue yield at 600°C (wt.%)
10	258.2	281.1	26
15	260.7	284.0	28
20	270.1	291.6	30
40	279.0	298.0	29
60	285.5	305.3	28

The weight loss of hemicellulose amounted to 70–75%. These results agree with some previous studies carried out in similar conditions (Yang *et al.*, 2007). The first weight loss between 61 and 156 °C is linked to the volatilization of the water present in the sample, approximately 18% of its weight (Hoareaua *et al.*, 2004).

3.2 Kinetic analysis of hemicellulose sheets pyrolysis

Pyrolysis kinetic analysis is an essential method for the considered investigation of the process of the thermal chemical conversion of biomass mechanisms (Ramiah, 1970). The second stage in the TG profile is the main reaction section of hemicellulose pyrolysis. Based on the thermal analysis at different heating rates, the kinetic parameters of hemicellulose sheet were obtained from a non-isothermal study.

The hemicellulose-pyrolysis process was investigated according to the resulting kinetic parameters, and a kinetic model was proposed for the main reaction section. Through model simulation of different pyrolysis processes, the behavior diversity of hemicellulose sheets degradation was analyzed, and pyrolysis mechanism discussed. The consequent results are beneficial for the development and optimization of hemicellulose biosheets thermal chemical conversion technology (Peng and Wu, 2010).

The activation energy (E_a) and the pre-exponential factor A of hemicellulose sheets were determined according to the Arrhenius equation. A linear curve and the pyrolysis information was achieved from each heating rate as shown in Fig. 2 and Table 2.

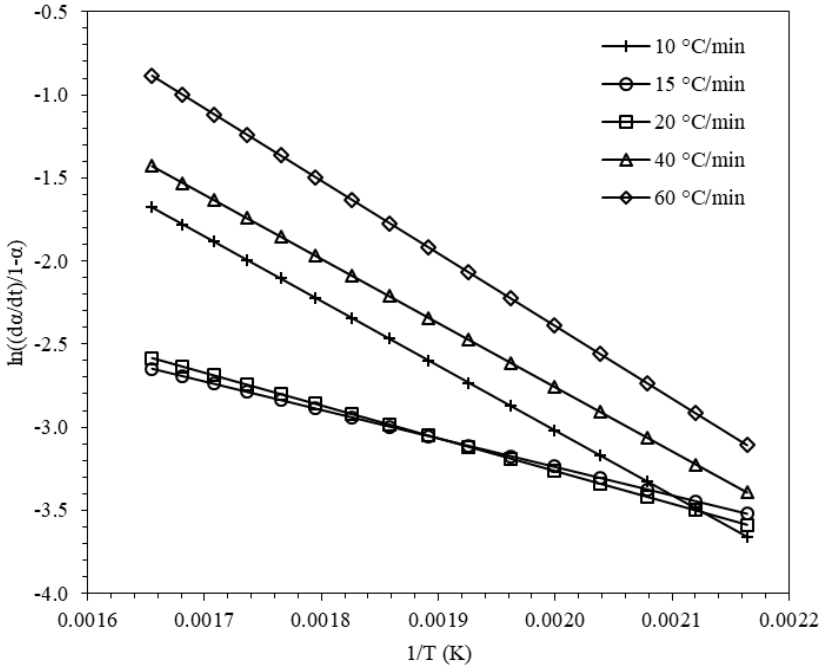

Figure 2. Linear curves of curauá fibers hemicellulose sheets at different heating rates.

The linear curves described in Figure 3 were obtained applying the Equation 3 for each TG profile. An interval of hemicellulose sheet degradation was established, and the temperature range occurs between 200 and 350°C. The kinetic analysis of hemicellulose sheet described in Table 2 shows that the heating rate of 60°C/ min presented the highest activation energy (36.31 kJ/mol) while the heating rate of 15°C/ min provided the lowest one (14.25 kJ/mol).

Table 2. Kinetic reaction parameters of hemicellulose sheet derived from TG-DTG measurements.

Heating rate (°C/min)	E_a (kJ/mol)	A(1/s)
10	32.36	$9.68x10^1$
15	14.25	1.11
20	16.38	1.79
40	32.06	$1.17x10^2$
60	36.31	$4.59x10^2$

4. CONCLUSIONS

A volatile thermal stability and the heating rate influences on hemicellulose degradation. The TG and DTG curves suggested the decomposition of hemicellulose mainly happened between 280 and 305°C and the residue at 600°C was found to be ~28%. A model using the Arrhenius equation was developed and applied to analyze the pyrolysis processes. The kinetics parameters of hemicellulose appear in the second stage and considering an interval of 200 to 350°C. The heating rate of 60°C/ min provided the highest activation energy and 15°C/ min the lowest one. The best characterization of this polymer is fundamental for future works, especially for its application as polymeric materials.

5. ACKNOWLEDGEMENTS

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7. RESPONSIBILITY NOTICE

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