CELLULOSE CHEMISTRY AND TECHNOLOGY

THERMAL DECOMPOSITION OF WOOD FIBERS: THERMAL SIMULATION USING THE F-TEST STATISTICAL TOOL

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Received June 15, 2020

Wood biomass is an alternative for fossil fuels to produce bioenergy, due to its low cost, renewability and environmental friendliness. In order to use biomass as an energy source, understanding its thermal degradation behavior is highly recommended. This work focuses on the thermal degradation of wood fibers belonging to different species (*Pinus elliotti* (PIE), *Eucalyptus grandis* (EUG) and *Mezilaurus itauba* (ITA)), commonly used by the Brazilian lumber industry. The prediction of their degradation kinetics and overall thermal behavior was performed based on the most common theoretical data using the *F*-test statistical tool. The most probable degradation mechanism was found to be autocatalytic for all the wood fibers tested, with three different degradation steps. The results obtained were in accordance with the findings recently reported in the literature using other fitting methods. It was found that cellulose is the major contributor to Arrhenius parameters, while hemicelluloses – to reaction order.

Keywords: modelling and simulation, wood fiber, thermal decomposition, pyrolysis, model-fitting

INTRODUCTION

According to the policies of the European Union-28 (EU-28), it is expected that bioenergy (including bioheat, biofuels for transport and bioelectricity) would contribute to half of the renewable energy target for 2021. In comparison, in 2015, the bioenergy consumption more than doubled the oil consumption of 2000.[1] The primary energy supply of forest biomass used worldwide is estimated at about 56 EJ, which means that woody biomass is the source of over 10% of all energy supplied annually according to the World Energy Council,[2] and about 90% of the primary energy annually sourced from all forms of biomass.[3] Thus, wood biomass and wood processing residues are essential for meeting future energy needs, considering the inherent renewability of wood, although sustainable management of forest resources is imperative.

The use of wood biomass as a substitute for fossil fuel for energy generation (the main source of worldwide carbon dioxide emissions), along with its other applications, such as for reinforcing thermoplastic/thermoset composite materials,[4-10] has the advantage of not only reducing the CO_2 emission into the atmosphere (avoiding fossil fuel combustion on the one hand, and due to photosynthesis through intensive plantation for such purposes, on the other), but also of saving non-renewable resources.[7,9] Considerations of such aspects make pyrolysis studies on wood biomass very attractive.

Lignocellulosic materials, including wood fibers, are mainly composed of cellulose, hemicelluloses and lignin, which form a complex structure with anisotropic properties. Their chemical and physical properties, involving moisture content, chemical composition, density and crystallinity, are factors that directly affect their mechanical properties and thermal decomposition behavior.[10-14] Since chemical composition varies as a function of plant age, environmental conditions *etc.*, a wide range of properties are expected for the same type of fiber. In spite of this, the decomposition of the main components follows certain reaction rules.[15]

Thermal decomposition of wood occurs through the pyrolysis of its components. Pyrolysis turns biomass into an energy source or feedstock of chemical products, and occurs when the biomass is heated at a fast heating rate and the vapor produced is rapidly condensed, as reported by Mohan *et al.*[16] Therefore, it seems essential to obtain deep knowledge of biomass pyrolysis in order to gain further understanding of the combustion and gasification processes. The prediction of the kinetic and thermal behavior of biomass is useful for understanding its thermal degradation process, providing useful information about the pyrolysis process, besides saving costs and time.

Reliable knowledge of kinetic parameters (activation energy, pre-exponential factor and reaction order) is necessary to estimate the lifetime prediction and the thermal decomposition kinetics,[17,18] as well as to optimize model-fitting procedures.[19,20] As far as we know, there is no report in the literature presenting a simulation of wood fiber degradation from thermogravimetric data using the *F*-statistic tool, in which the most common theoretical degradation mechanisms are simultaneously fitted with experimental ones. Some of the studies found are very recent and concern different materials, such as thermoplastic nanocomposites,[21] chemically modified microcrystalline cellulose,[22] polyurethane[23] and poly(ethylene oxide).[17] The research works related to model-fitting in biomass determine a single degradation mechanism, and, from it, the curves are fitted and the results discussed. Cabeza *et al.*[19] studied a kinetic model considering Waterloo's degradation model and the autocatalytic degradation mechanism in biomass using a non-Arrhenius's dependence on temperature. The authors found an average absolute deviation between the theoretical and the experimental data lower than 7%. Ali *et al.*[20] realized an integral model-fitting procedure, aiming to determine the degradation mechanism present in the pyrolysis of coconut shell waste. The authors stated that the kinetic process can be described by four independent parallel reactions (water, hemicelluloses, cellulose and lignin) and the degradation mechanisms that control the pyrolysis were order-based nucleation and growth mechanism (F- and A-types, respectively). Sunphorka *et al.*[24] used ANN (artificial neural network) models to predict biomass pyrolysis using the data of 150 different plant fibers. The authors found that Arrhenius parameters strongly influence the activation energy, while hemicelluloses play a major role in reaction order.

Based on the aforementioned literature, the main contribution of the present study is to determine the degradation mechanism (and other Arrhenius parameters, *i.e.* activation energy and pre-exponential factor) of fibers belonging to three different wood species commonly used in the Brazilian lumber industry, using a statistical tool (F-test). The determination of the degradation steps is based on the degradation characteristics and chemical composition, relying on the aforementioned literature. This study provides some insights to help understand the thermal degradation for similar or more complex materials, establishing some initial predictions in the development of new kinetic approaches.

Theoretical background

According to ICTAC,[18] there are different methods for calculating the Arrhenius parameters. Since the methods are complementary and not competitive, it is recommended to use at least two different isoconversional methods. In this paper, the Kissinger-Akahira-Sunose (KAS (integral method)) and the Friedman (FR (derivative method)) models were applied, aiming to obtain the activation energy (E_a) and the pre-exponential (A) factor. The most probable degradation mechanism (autocatalytic or diffusion, for example) can be obtained by using master plot curves[25] or model-fitting methods.[17] The former does not account for any degradation model and visual similarities between experimental and theoretical curves are compared; the most similar curve format is considered the most probable degradation mechanism. The latter assumes a specific degradation model, prior to simulation of the curves. In this study, it was assumed that the reaction pathway followed Waterloo's degradation model (cellulose, hemicelluloses and lignin decompose into volatiles and charcoal, in which water and oil/extractives can also be present). The conversion degree considered varied from 0.10 to 0.80. It was considered that the degradation of the components generates oligomers that accelerate further depolymerization.[19,20,26]

Isoconversional methods

The fundamental equation for any kinetic study is usually described by Equation (1):

$$\frac{d\alpha}{dt} = k(T).f(\alpha) \tag{1}$$

The conversion rate (α) is calculated according to Equation (2):

$$\alpha = \frac{m_0 - m_T}{m_0 - m_\infty} \tag{2}$$

For dynamic TGA experiments, different heating rates are used (heating rate (β)) (Eq. (3)):

$$\frac{d\alpha}{dT} = \frac{A}{\beta}.\mathrm{e}^{(-\frac{E_a}{RT})}.f(\alpha) \tag{3}$$

where α: conversion rate; *A*: pre-exponential factor; E_a: activation energy; *R*: universal constant of gases (8.314 $\mathrm{J.Kmol^{-1}}$); *T*: absolute temperature; *β*: heating rate; *f*(α): dependence of the conversion extension on the reaction model; m_0: initial mass; m_T: total mass; m_∞: final mass.[8,18,27] Isoconversional methods estimate the activation energy considering the reaction mechanism as a function of temperature.

The KAS (Kissinger-Akahira-Sunose) method is an integral method that provides more accurate results in comparison with most others (FWO).[20,28-29] When $ln\left(\frac{\beta}{T^2}\right) vs \frac{1}{T}$ fit is plotted, the slope gives $\frac{-Ea}{R}$, generating Equation (4):

$$ln\left(\frac{\beta}{T^2}\right) = const - \frac{E_a}{RT} \tag{4}$$

where *β*: heating rate; *A*: pre-exponential factor; E_a: activation energy; *R*: universal constant of gases (8.314 $\mathrm{J.Kmol^{-1}}$); *T*: temperature (K).

Another isoconversional method considered was Friedman's.[30] In this derivative method, the values of $\frac{E_a}{RT}$ can be obtained with a fit of $ln\left(\frac{d\alpha}{dt}\right) vs \frac{1}{T}$, according to Equation (5):

$$ln\left(\frac{d\alpha}{dt}\right) = ln\big(Af(\alpha)\big) - \frac{E_a}{RT} \tag{5}$$

where $\left(\frac{d\alpha}{dt}\right)$: derivative of the conversion degree as a function of temperature; *A*: pre-exponential factor; E_a: activation energy; *R*: universal constant of gases (8.314 $\mathrm{J.Kmol^{-1}}$); *f*(α): dependence of the conversion extension by the reaction model; *T*: temperature (K).

Integral methods provide more accurate Arrhenius values, while differential methods are more sensitive to data noise, but the DTG gives more useful information about the degradation steps.[31]

Netzsch thermokinetics software

Netzsch–Thermokinetics[32] is multipurpose software used to save costs and time, and simplify kinetic calculations, which are based on previous knowledge of the degradation characteristics of materials, such as the degradation model, Arrhenius-based models and the composition of the material. The calculation usually involves multiple steps and can be very complex. The software allows a complete kinetic study by using thermal analysis, such as TGA, DTG and DSC. It works with isoconversional analysis methods, linear regression for single-step processes and non-linear regression for multi-step processes. In addition, it has an advanced statistical analysis,[17] allowing the comparison of results. The degradation mechanisms used are based on the most common models for the solid-state reaction.[8,18,21,27]

The curve fit for the chosen models is performed by minimizing the difference between the measured and the calculated data, using the least squares method, which ensures the quality of the statistical adjustment. The most probable kinetic method is the one with F_{test} lower than F_{crit}. Besides the mathematical values, the interpretation of the data has to be based on the physical/chemical structure and on the material degradation characteristics. It is highly recommended to use it in combination with other methods of calculation.[18,23,33-34]

EXPERIMENTAL

Wood flour of the following species: *Pinus elliotti* (PIE), *Eucalyptus grandis* (EUG) and *Mezilaurus itauba* (ITA), obtained as a residue from Brazilian lumber mills, was used. Chemical information about the fibers used in this study is summarized in Figure 1. More data about the fibers can be found in the authors' previous studies.[35-36]

Thermogravimetric analysis was performed using a Shimadzu TGA50, under inert N2 atmosphere at a flow rate of 50 $\mathrm{cm^{-3}.min^{-1}}$. Approximately 10 mg of each sample was used for the tests and the temperature range investigated was from 25 to 800 °C. The analysis was performed using four different heating rates (5, 10, 20 and 40 $\mathrm{°C.min^{-1}}$). The results obtained were calculated using Netzsch Thermokinetics software and based on Erceg's study.[17]

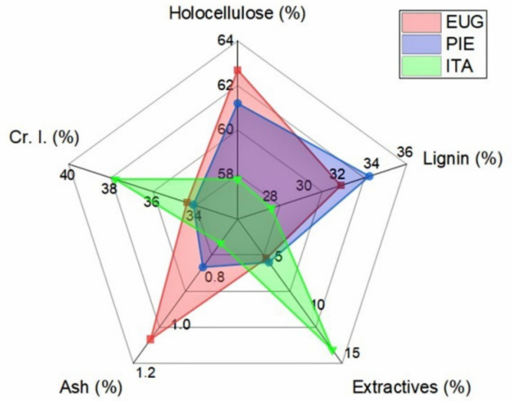


Figure 1: Properties of the fibers used in this study

RESULTS AND DISCUSSION

Thermal behavior

Representative TG and DTG curves for all the wood fibers, at a heating rate of 10 °C.min^{-1}, are shown in Figure 2. The main degradation events are similar for all the wood fibers studied. Three main mass losses are observed: (*i*) at 50-100 °C, there is evaporation of moisture, intrinsic water loss and elimination of low molecular weight components; (*ii*) a slight decrease after the plateau in the TG curves due to hemicellulose degradation (better visualized by the shoulder in the DTG curve at 200-300 °C); and (*iii*) the main degradation event due to cellulose degradation (the main peak of the DTG curve at 300-400 °C). Lignin degrades over almost the whole range of temperature (160-800 °C) and it is well observed as a slight decrease in mass loss after the main cellulose degradation event (from ~400 °C to 800 °C), without showing any degradation peak. Higher lignin content is represented by a “tail” in the final degradation stage.

According to F. Yao *et al.*,[15] the active zone for degradation takes place from 250 °C to 400 °C, which presents a mass conversion from 10% to 80% for all biomass. Hemicelluloses and mainly cellulose are the major contributors to this mass conversion. In this range, lignin also degrades. In addition, parallel degradation of the components can occur. The overlapping of reactions, as for example those for hemicelluloses and cellulose, seems to follow certain degradation rules. For example, cellulose degradation seems to be always governed by the Arrhenius law, independently of fiber composition. On the other hand, hemicelluloses play a major role in the reaction order and thermal stability (plateau).[19-22,24] Higher hemicellulose content should reflect in higher thermal stability, but it also increases moisture absorption, which can accelerate the degradation process.[13] Higher lignin and cellulose contents result in higher char formation and flammability, respectively.[15] Hence, the properties of the fibers are influenced by the combination of these main components and their interactions.

Dependence of activation energy on conversion

The relation between the activation energy and the conversion degree is an indicator of a single- or multiple-step process. Usually, when the activation energy is independent of the conversion degree, this indicates a single-step process. For fibers, the linear dependency between these parameters is observed in the conversion degree range $\alpha = 0.1\text{-}0.8$,[15] and this is attributed to cellulose. Lignocellulosic materials are well-known to have three main components that contribute to the main degradation steps: hemicelluloses, cellulose and lignin. Hemicellulose is the main contributor to the reaction order, cellulose plays a major role in the activation energy values[24,38] and lignin is responsible for the “tail” in the final of the degradation process, besides char formation, and has little effect on Arrhenius parameters.[19-20] At higher conversion degrees, there are changes in the reaction mechanism, probably indicating unification of multiple reaction mechanisms caused by the complex reactions in the decomposition process of the main fiber components.[15,19-20] In the case of wood fibers, it may be attributed to the pyrolysis of the biomass, considered as a matrix of its three solid global components – hemicelluloses, cellulose and lignin.[19] In the final decomposition process, the remaining parts of cellulose, hemicelluloses and lignin degrade, besides the respective charcoals; so multiple reactions occur at the same time, which makes modeling very complex.

At lower conversion degrees, α < 0.1, there is mass loss related to water evaporation and sublimation of low molecular components. The degradation of lignocellulosic fiber starts with the degradation of hemicelluloses. Therefore, the main thermal decomposition stage (215-310 °C), which corresponds to 60% of the thermal decomposition of the fiber, can represent the degradation process as a whole and it will be emphasized in the present study. This process may offer a simplified and more meaningful way of modeling the thermal decomposition behavior of wood fibers. Also, it can help to understand how biomass conversion takes place by simultaneously comparing the most common degradation mechanisms in the solid state.

The activation energy was calculated using the Friedman and the KAS (Fig. 3 a-b) methods. These methods are complementary rather than competitive and should to be used for comparison.[38-39] The results obtained for all the wood fibers studied in accordance with the typical thermal decomposition behavior of cellulose:[40] 195-213 kJ.mol^{-1}. This result suggests that Arrhenius parameters are mainly related to cellulose, in spite of the differences in chemical composition, as demonstrated in Figure 1.

It is well known that E_a alone cannot provide an integral prediction or modeling for any thermal decomposition process. As the energy barrier, E_a itself may provide information of the critical energy needed to start a reaction. From a modeling perspective, a narrow range of activation energy can help calculate the other parameters of thermal kinetics.

The pre-exponential factor follows the same dependence of E_a on conversion degree, indicating the interdependence of apparent magnitudes of Arrhenius parameters for a set of related rate processes. This compensation effect is approximately linear and regardless of the reliability of the A and E_a values obtained, they can express levels of reactivity and enable comparisons of kinetics being valid for substances of similar reactivity.[6,39-40,43]

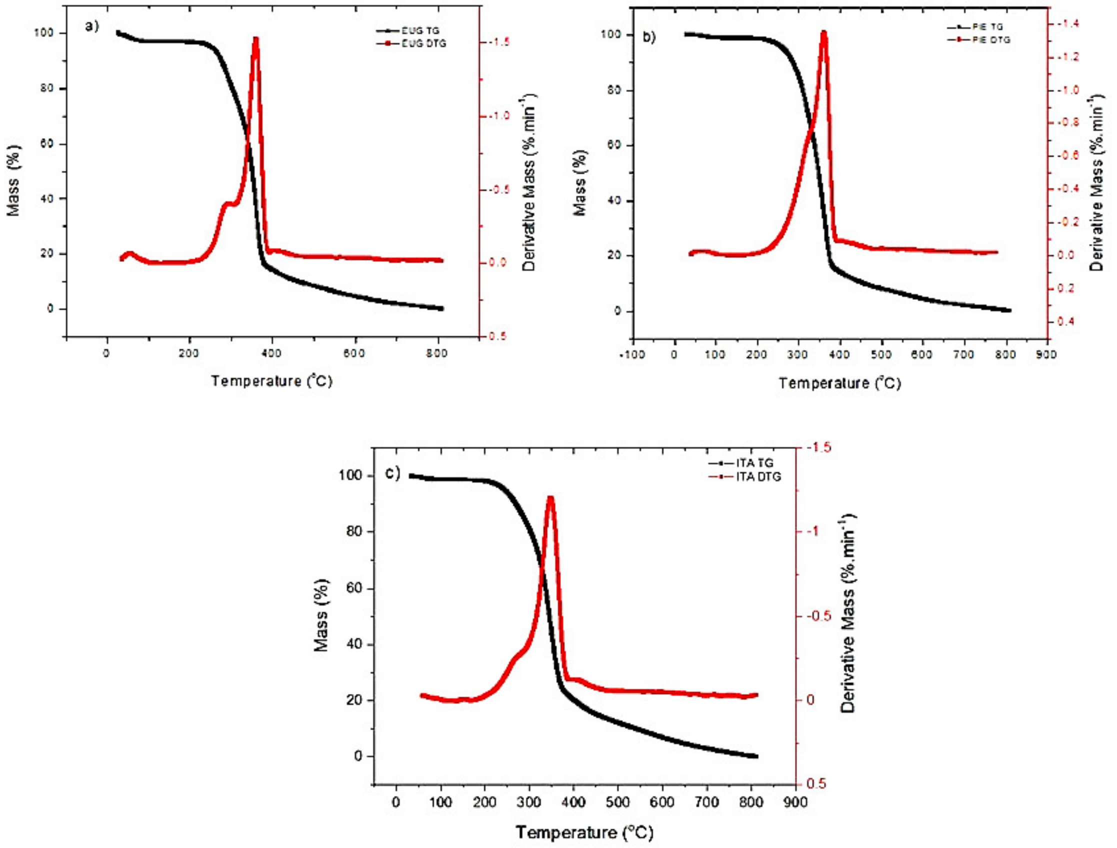


Figure 2: Representative TG and DTG curves at 10 °C.min^{-1} for a) EUG, b) PIE and c) ITA wood fibers

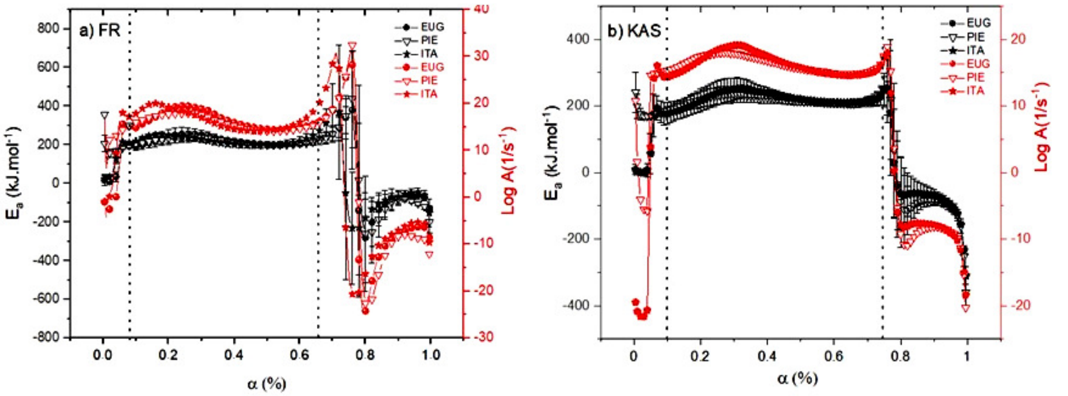


Figure 3: Activation energy and pre-exponential factor as a function of conversion degree using a) Friedman, and b) KAS methods (dotted lines represent the range used for simulation)

Modeling of thermal behavior

To model the kinetic behavior, besides E_a and A dependence on α, it is necessary to have previous knowledge of the degradation model and mechanism. For determining the degradation model, a reasonable reaction pathway, which physically represents the pyrolysis process of the wood fiber, has to be assumed. In the present study, it was assumed that the reaction pathway follows Waterloo's model[19-20] and a simplified single-step global reaction mechanism. This mechanism assumes that all the components of the wood fiber, *i.e.*, cellulose, hemicelluloses and lignin, decompose in volatiles (gas) and charcoal (solid followed by gas) in the pyrolysis process. With the degradation model assumed, model-fitting methods can be used for determining the degradation mechanism more accurately.[19-20] Examples of the degradation mechanism are diffusion, autocatalytic or geometrical contraction. In our case, a statistical (F-test) tool was applied aiming to determine the most probable degradation mechanism by comparing all the theoretical mechanisms with the experimental results.

The degradation mechanism can be obtained by master plot curves[42] or using model-fitting methods.[17,42] Master plot curves compare the theoretical degradation curves with the experimental ones. The mechanism is visually obtained by similarities in the curve format. Model-fitting methods, such as F-test, allow simultaneously fitting multiple data sets under different temperature programs. Besides, linear and multi-variate nonlinear regression methods, together with advanced statistical analysis and prediction, can be incorporated into the calculus. The selected models are fitted by minimizing the difference between the measured and calculated data. Master plots are easier to evaluate, but statistic tools seem to produce more reliable results. Statistic tools, as presented in Netzsch software, are necessary to inform of the degradation models, different from master plots, improving the reliability of the results obtained.

The degradation model is based on the characteristics of the material. In a previous study, Moukhina[26] described how to assign the best degradation mechanism, based on thermal degradation curves performed at different heating rates. Our study was based on it, considering that cellulose plays a major role in activation energy. Three different hypotheses are assumed: (i) a single degradation mechanism (from cellulose) overlaps all preceding and subsequent reactions (from hemicelluloses and lignin); hence cellulose is the main contributor to E_a – hemicelluloses and lignin can contribute to the reaction order; (ii) two and (iii) three degradation steps, respectively. For stages (ii) and (iii), in spite of the linear dependence of activation energy on conversion degree, it is considered that the other steps exist, but do not substantially contribute to changes in the thermogravimetric curves. To increase the reliability of the results obtained, a two-degradation step mechanism was fitted, considering all the results from a one-step degradation mechanism, and a three-degradation step mechanism considers the results of the one- and two-step degradation mechanisms. Hence, all the degradation steps and all the mechanisms for any step were compared.

(i) *One-step degradation mechanism*: the chemical degradation model that describes a one-step degradation mechanism is A → B, where A represents the biomass and B represents the decomposed components (cellulose, hemicelluloses and lignin). This model considers that cellulose plays a major role in the Arrhenius parameters (since the values obtained by FR and KAS models are close to the cellulose component), as well as in the degradation mechanism. The theoretical degradation mechanisms were simultaneously fitted with the experimental curves. The following theoretical degradation mechanisms were used: A-type (nucleation and growth), D-type (diffusion), F-type (order-based), C- and B-type (autocatalytic) and R-type (geometrical contraction). The best fit of the EUG wood fiber is presented in Figure 4.

The best fit found for each fiber was: A-type (nucleation and growth) with $E_a = 268.28$ kJ.mol^{-1} and log A = 19.97 (s^{-1}) for PIE wood, $E_a = 221.19$ kJ.mol^{-1} and log A = 15.97 (s^{-1}) for EUG wood and $E_a = 220.86$ kJ.mol^{-1} and log A = 16.21 (s^{-1}) for ITA wood. This type of mechanism was also found in a previous study.[20] It is important to have in mind that a model is a theoretical, mathematical description of what occurs experimentally, describing a particular reaction type and translating it into a rate equation.[43] For example, nucleation and growth mechanisms are mathematically similar to the autocatalytic ones, but have distinct physical meanings.[43] Since the curves presented a poorer fit and values higher than the ones found in the literature, it is reasonable to believe in the existence of at least one more mechanism and the existence of a single degradation mechanism must be discarded. Also, according to A. Cabeza *et al.*,[19] it is reasonable to think that the autocatalytic mechanism must play a major role in the thermal degradation behavior, since it is physically realistic.

(ii) *two-step degradation mechanism*: different chemical models were used aiming to obtain the best fit, as shown in Scheme 1.

The best degradation model fit found for all the fibers was model (3), where B represents hemicelluloses and C represents cellulose, s in model (2) represents solid. When the two-step mechanism was tested, all the wood fibers changed from A-type to D-type in the first stage and C-type in the second stage. This change of the degradation mechanism has a more realistic approach, since the heat is transferred to the sample and after diffusion of the heat, the cleavage of polymer chains produces oligomers that accelerate the degradation process.

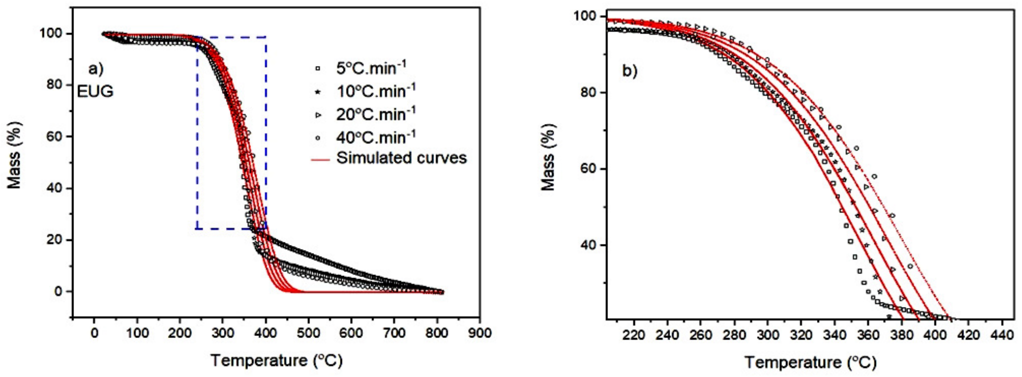
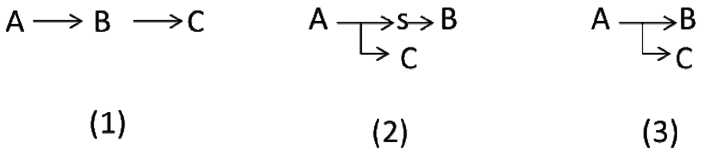


Figure 4: a) Experimental and theoretical fitting of EUG wood fiber degradation considering a one-step mechanism, b) magnification of the range tested (dotted lines are guide for the eye and represent the range used for simulation)



Scheme 1: Chemical models used to fit TG curves considering a two-step mechanism
(A: biomass, B: hemicelluloses, C: cellulose and D: lignin)

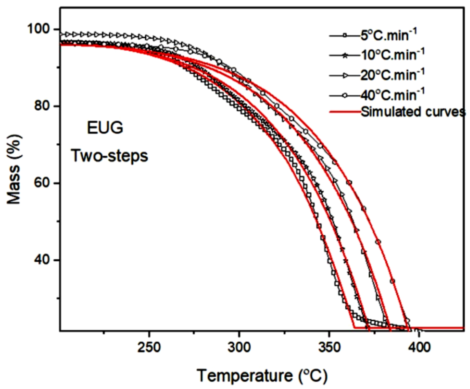


Figure 5: Experimental and theoretical of EUG wood fiber considering a two-step mechanism (dotted lines are guide for the eye and represent the range used for simulation)

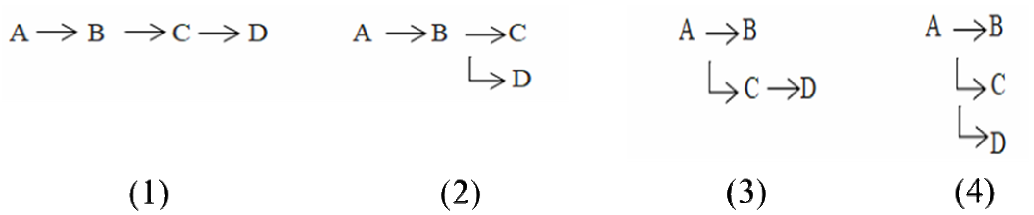
The typical activation energies of the individual components lie in the range of 105-111 kJ.mol^{-1} for hemicelluloses, 195-213 kJ.mol^{-1} for cellulose, and 35-65 kJ.mol^{-1} for lignin.[15] All the wood fibers showed the best fitting and more realistic Arrhenius parameters, when compared to the single-step mechanism. For the EUG wood fiber, the values found in the first degradation step indicated D-type, with E_a = 130.00 kJ.mol^{-1} and log A = 8.20 (s^{-1}), and the second degradation step was C-type, with E_a = 200.00 kJ.mol^{-1} and log A = 14.54 (s^{-1}). For the PIE wood fiber, the same degradation mechanism was found in the first and second degradation steps, with E_a = 113.55 kJ.mol^{-1} and log A = 4.99 (s^{-1}) for D-type and E_a = 200.00 kJ.mol^{-1} and log A = 13.07 (s^{-1}) for C-type. Finally, for the ITA wood fiber, E_a = 128.87 kJ.mol^{-1} and log A = 8.29 (s^{-1}) for the first degradation step, and E_a = 180.00 kJ.mol^{-1} and log A = 8.96 (s^{-1}) for the autocatalytic mechanism.

Figure 5 presents the best fit for the EUG fiber (the representative curve). So far, depending on the number of degradation steps, there were changes in the degradation mechanisms, proving this to be a more realistic approach. The best fitting was found when compared to the single-degradation mechanism.

(iii) *three-step degradation mechanism*: considering that the main degradation curve is governed by hemicelluloses, cellulose and lignin components, the mechanism shown in Scheme 2 was considered.

Figure 6 presents the experimental and the simulated data for the wood fibers, in the conversion range α = 0.1-0.8, totalizing more than 60% of total mass loss. All the wood fibers followed the autocatalytic model in all the degradation stages as the most probable degradation mechanism. As a matter of fact, hemicellulose is the major contributor to thermal stability, lignin – to the "tail" in the final part of the degradation process, and cellulose – to the activation energy or Arrhenius parameters. All Arrhenius parameters obtained are in accordance with the KAS and the Friedman methods.[15] The use of one more component gives the best fit at the final part of the curve. Also, the autocatalytic models obtained seem to represent a more realistic approach and are in accordance with other studies found in the literature using other model-fitting procedures.[19-20,22]

Table 1 presents the five best fittings for all the wood fibers. It can be noted that the three-step degradation mechanism, with an autocatalytic degradation mechanism, predominates. All the results followed the general Waterloo's degradation model, which considers that all the compounds present in the biomass decompose into volatiles and char. However, the specific degradation model differed for each fiber, as well as Arrhenius parameters. In spite of the excellent fit using three steps, the activation energy and the pre-exponential factor of the fibers studied seem not to follow the activation energy of the main individual components: cellulose, hemicelluloses and lignin. Probably, this is caused by consecutive/parallel reactions, which change the expected thermal characteristics of the individual components.



Scheme 2: Chemical models used to fit TG curves considering a three-step mechanism (A: biomass, B: hemicelluloses, C: cellulose and D: lignin)

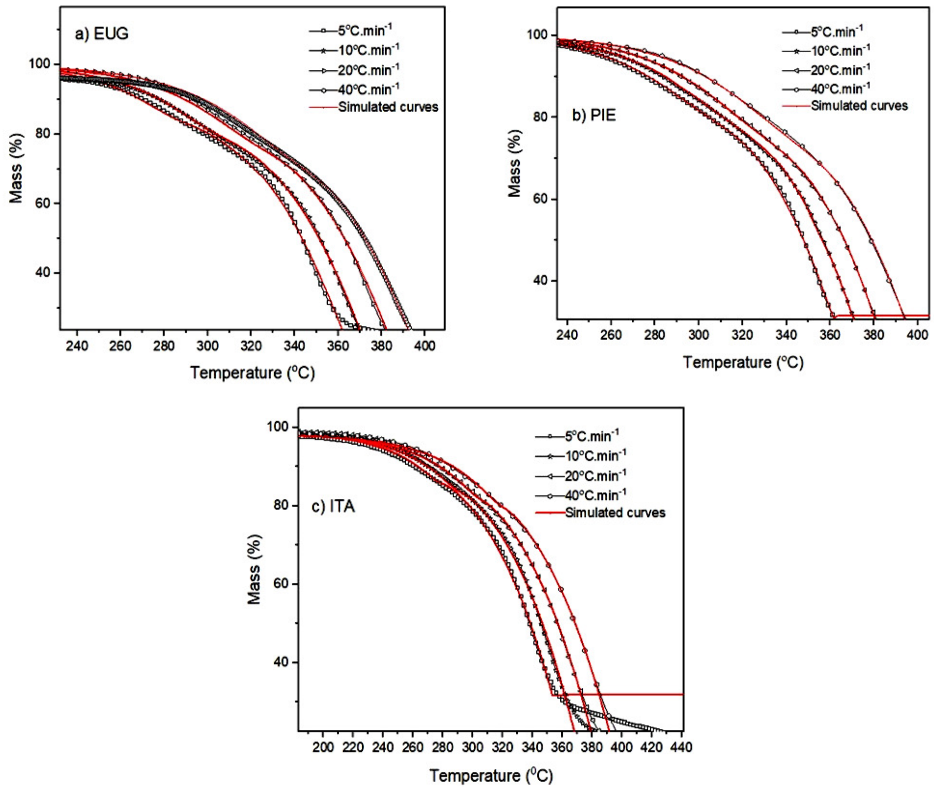


Figure 6: Experimental and theoretical of a) EUG, b) PIE and c) ITA wood fibers, considering a three-step degradation mechanism (dotted lines are guide for the eye and represent the range used for simulation)

Table 1
Best fits to the respective mechanism model, and Arrhenius parameters for all fibers studied

Wood fiber	Degradation model	Type	E_a (kJ/mol)	Log A (s^{-1})	F_{exp}
EUG	2	Cn	70.22	3.01	1.00
		Cn	200.00	15.00	
		Cn	124.96	10.08	
	3	D1	152.61	10.13	1.15
		Cn	111.00	4.25	
		Cn	175.61	1.57	
	1	D1	102.73	5.96	1.21
		Cn	200.00	14.40	
		Cn	391.39	31.49	

	2	D1	105.3	6.14	1.53
		Cn	111.00	6.70	
		Cn	2070.20	183.80	
	1	Cn	103.96	6.17	1.90
		Cn	200.00	15.00	
		Cn	83.75	69.46	
	1	Cn	80.01	3.97	1.00
		Cn	111.00	11.00	
		Cn	169.22	13.31	
	3	D3	113.49	4.89	4.82
		Cn	200.00	13.05	
PIE	3	D1	113.07	5.03	5.32
		Cn	200.00	13.06	
	3	D	113.48	4.05	5.44
		Cn	200.00	12.99	
	3	D2	113.49	4.90	5.47
		Cn	200.00	13.06	
	3	D1	174.66	12.17	1.00
		Cn	111.00	4.55	
		Cn	120.68	11.88	
	2	D1	89.85	4.97	2.09
		Cn	111.00	6.92	
		Cn	64.60	6.84	
ITA	2	D1	128.97	8.30	3.19
		Cn	180.00	8.96	
	2	D1	128.99	8.30	3.19
		Bn	180.00	8.96	
	1	Cn	84.01	4.43	3.53
		Cn	111.00	11.00	
		Cn	102.39	12.02	

CONCLUSION

The autocatalytic degradation mechanism was predominant for all the wood fibers, cellulose being the major contributor to Arrhenius parameters, while hemicelluloses and lignin seem to play a major role in reaction order. The activation energy and the pre-exponential factor followed the same trend and reached close values for both the Friedman (derivative) and the KAS (integral) methods (E_a ~ 200 kJ.mol^{-1} and log A ~16 s^{-1}). Such similarity is indicative of the fact that any of the two methods can be used for initial prediction for the further fit of the curves and to determine the reaction model. The method applied in the present work is more robust, in comparison with the ones found in the literature so far, because it simultaneously compares multiple experimental and theoretical models. The results obtained are physically plausible and are in accordance with those reported in recent literature, using other model-fitting methods. The dissimilarities among the wood fibers are attributed to differences in their chemical composition and are essential to improve the understanding of the pyrolysis process.

ACKNOWLEDGMENTS: The authors would like to thank CAPES and CNPq for financial support (Process number: 153335/2018-1).

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