# Application of the artificial neural network (ANN) approach for prediction of the kinetic parameters of lignocellulosic fibers

Heitor Luiz Ornaghi Júnior[1*], Roberta Motta Neves[2], Francisco M. Monticeli[3]

[1]Federal University for Latin American Integration (UNILA), Edifício Comercial Lorivo - Av. Silvio Américo Sasdelli, 1842 - Vila A, Foz do Iguaçu - PR, 85866-000, Brazil

[2]Post-Graduation Program in Mining, Metallurgical and Materials, Federal University of Rio Grande do Sul (UFRGS), Av. Bento Gonçalves, 9500 - Setor 4 - Prédio 74 - Sala 211, Porto Alegre-R, 91501-970, Brazil

[3] Departament of Materials and Technology, São Paulo State University (Unesp), School of Engineering, Guaratinguetá. 12516-410. São Paulo, Brazil

**Abstract**

Lignocellulosic fibers are widely applied as composite reinforcement due to their properties. The thermal degradation behavior determines the maximum temperature in which the fiber can be applied without significant mass loss. It is possible to determine these temperatures using Thermogravimetric Analysis (TG). In particular, when curves are obtained at different heating rates, kinetic parameters can be determined and more detailed characteristics of the material are obtained. However, every curve obtained at a distinct heating rate demands material, cost, and time. Methods to predict thermogravimetric curves can be very useful in the materials science field and in this sense mathematical approaches are powerful tools if well employed. For this reason, in the present study, curaua TG curves were obtained at three different heating rates (5, 10, 20, and 40 °C.min-1) and Vyazovkin kinetic parameters were obtained. After, the experimental curves were fitted using an artificial neural network (ANN) approach followed by a Surface Response Methodology (SRM). Curves at any heating rate between the minimum and maximum experimental heating rates were obtained with high reliability. Finally, Vyazovkin kinetic parameters were tested again with the new curves showing similar kinetic parameters from the experimental ones. In conclusion, due to the capability to learn from the own data, ANN combined with SRM seems to be an excellent alternative to predict TG curves that do not test experimentally, opening the range of applications.

***Keywords**:* lignocellulosic fiber, thermal degradation, kinetic analysis, artificial neural network.

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## 1. Introduction

Lignocellulosic fibers are versatile materials used in different applications. Their use englobes the entire fiber for reinforcement in composite materials [1,2], or the use of their derivatives (cellulose, hemicellulose, or lignin) in different uses as shape memory of lignin-rubber composites [3], to obtain nanocellulose [4], to reinforce expanded composites [5] or cellulose biomedical applications [6], for example. This potential of application can be attributed to the wide variety of chemical components (cellulose, hemicellulose, lignin, waxes, low molecular weight components, oil, etc.) presented in the lignocellulosic fibers [7,8]. Also, the same fiber can have different properties depending on the plant age, climate, soil among others [9].

Yao et al. [10] studied the thermal degradation behavior of ten different lignocellulosic fibers, focusing on the Arrhenius kinetic parameters. The activation energy in the function of the conversion degree presented similar values, independently of the chemical content of the fiber. A linear dependency in the conversion range $\alpha$ = 0.2-0.8 was observed for all fibers with an apparent activation energy of 160-170 kJ.mol$^{-1}$ for most of the fibers studied. Sunphorka et al [11] studied an artificial neural network (ANN) model using 150 data from different lignocellulosic fibers in relation to Arrhenius kinetic parameters. The main results indicated that cellulose plays a major role in the pre-exponential factor while the hemicellulose on the reaction order. According to the authors, all components affected the activation energy. Ornaghi Jr. et al. [7] studied the mechanisms involved in the thermal degradation of lignocellulosic fibers based on the chemical composition. The main results indicate that the activation energy of the fibers followed similar values to the cellulose component and that the thermogravimetric curves followed a similar pattern, independently of the chemical composition. Monticeli et al [12] studied the optimal training data for ANN application using thermogravimetric analysis. The results indicated 50-60 as the optimal number of training datasets for all fibers. Also, a reliable prediction of TG curves was obtained at different heating rates did not obtained experimentally.

Most of the fibers found in the literature follow a similar curve format, independently of the amount of the chemical components, indicating that the degradation process may follow certain degradation rules. For example, a mass loss of about 5-10% is obtained at 100 °C due to moisture evaporation and from 300 °C from the degradation of cellulose. In some cases, a shoulder is observed at DTG (derivative thermogravimetric analysis) due to the higher amount of hemicellulose in a small range before cellulose degradation [13,14]. Hence, the prediction of the thermogravimetric curves of a particular lignocellulosic fiber can be extended to most of the fibers due to these similarities.

The main objective of this study is to perform the thermal degradation kinetic behavior of curaua fiber using the Vyazovkin kinetic method and ANN approach. The experimental curves were kinetically tested, and curves do not tested experimentally were predicted, and new kinetic tests were done. The results presented reliable and robust data without the necessity of further experimental curves.

## 2. Materials and Methods

Curaua fiber received from CEAPAC (support center for community action projects) was used in this study. More details about the fiber characteristics can be found on [15,16].

Thermogravimetric analysis was carried out using a TA instrument model TGA-50 Shimadzu under nitrogen atmosphere from 25 to 900 °C. It was used ~10 mg of each sample at three distinct heating rates (5, 10, 20, and 40 °C.min$^{-1}$). The curves were used

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to calculate the kinetic parameters according to the Vyazovkin method. The theoretical and ANN predicted curves were used to calculate the kinetic parameters. It was used in the previous study of Monticeli et al. [12] as a base for the obtaining of the new ANN curves at distinct heating rates. The predicted curves were used to calculate again the kinetic parameters.

### 2.1 Kinetic approach

The thermal degradation kinetic of lignocellulosic fibers follows the kinetics of the reaction of solids:

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

where $d\alpha/dt$ is the degradation rate, $k(T)$ is the rate constant, and $f(\alpha)$ is a function of the conversion.

The degradation kinetic follows Arrhenius (Equation 2) and the heating rate changes linearly with temperature (Equation 3):

$$k(T) = Ae^{-\frac{Ea}{RT}} \tag{2}$$

$$\beta = \frac{dT}{dt} = constant \tag{3}$$

where $A$ is the pre-exponential factor, $Ea$ is the activation energy, $R$ is the gas constant, $T$ is the temperature, $\beta$ is the heating rate, and $dT/dt$ is the temperature in function of time.

The reaction model follows equation (4):

$$f(\alpha) = \alpha^m(1-\alpha)^n - ln(1-\alpha)^p \tag{4}$$

where $m$, $n$, and $p$ are constants.

In combining Equations (1) (2) (3) and (4) we obtain equation (5):

$$\frac{d\alpha}{dT} = \frac{A}{\beta}e^{-\frac{Ea}{RT}}\alpha^m(1-\alpha)^n - ln(1-\alpha)^p \tag{5}$$

Vyazovkin equation is proposed according to Equations (6) (corrected heating rate) and (7):

$$\sum_{i=1}^{S}\sum_{j=1}^{L}(T_{ij}(\beta.t_{ij} + T_0))^2 \tag{6}$$

$$\sum_{i}^{n}\sum_{j\neq 1}^{L}\frac{[I(Ea, T_{\alpha,i})\beta_j]}{[I(Ea, T_{\alpha,j})\beta_i]} = min \tag{7}$$

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where $S$ is the number of files for the corresponding heating rate, $L$ is the number of rows in the $i$-file, $T_{ij}$ is a value of the temperature in the $i$-file in the $j$-row, and $t_{ij}$ is the value of the time in the $i$-file in the $j$-row measurements. $\beta$ and $T_0$ are unknown parameters of the equation. $I(E,T)$ if found by numerical integration.

The kinetic calculation was performed with the help of the Software developed by Drozin et al. [17] with the experimental and predicted curves.

### 2.2 Artificial neural network

An ANN is conventionally constructed with three layers, i.e. an input, an output, and a hidden layer. Each layer has different numbers of neuronal elements. In the present case, we use as input vectors a set of *i*TG curves at different heating rates. In this sense, the network will modify the weight of the interconnections between neurons in order to reproduce the given parameters. Figure 1 shows the scheme of the calculation process.

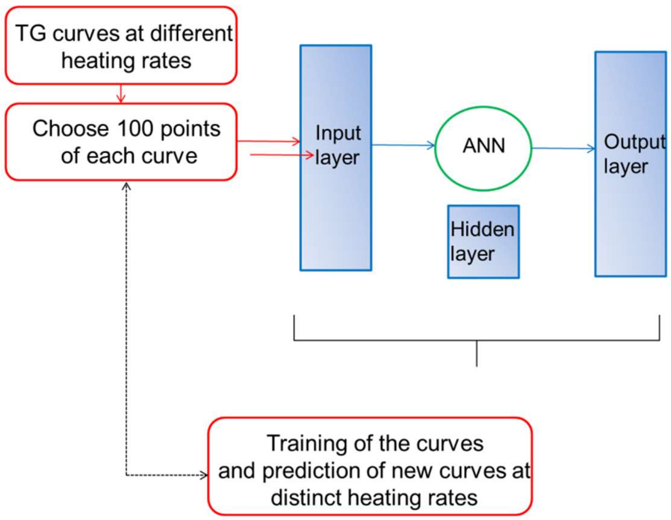


**Figure 1**. Flowchart of the calculation process.

The main issues necessary to be defined before using the networks are the quality and number of the initial TG curves, the training algorithm, and the number of neurons in the hidden layer. The number of initial TG curves used for the training should not be excessively large in order to avoid the over-training of the network, and it has to be distributed correctly, in the sense that normally it is a good idea to avoid sets of input vectors with the same output vectors. These kinds of orthogonal combinations produce better results than using random sets of parameters [18].

The following conditions (Table 1) were used to training the ANN network:

Table 1 – Parameters used to perform the ANN fit.

| Technique | Number of layers | Number of hidden neurons in each layer | Training Repetitions | Neural network algorithm | Error function | Threshold of error function | Activation Function |
|---|---|---|---|---|---|---|---|
| TGA | 1 | 12 | 3 | Resilient backpropagation with back tracking | Sum of squared errors | 0.01 | Tangent hyperbolicus |

With the training of the network, we can feed the network with different curves and predicted new curves. The main drawback is that the curves outside the lower and higher heating rate cannot be created due to the accumulation of errors [18,19]

### 2.3 Surface Response Methodology (SRM)

The SRM is a statistical approach for modeling and analyzing a process in which the response of interest is affected by various variables [12,20,21]. Equation 8 describes the degradation curve interaction among the combination of temperature and heating rate. In using this method, the statistical relevance is kept and the number of experiments can be reduced.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{j=1}^{k} \beta_j x_j + \sum_{j=1}^{k} \beta_{jj} x_j^2 + \sum_{i=1}^{k-1} \sum_{j=i}^{k} \beta_{ji} x_i x_j \qquad (8)$$

where $Y$ represents the predicted response (i.e., degradation curve – $W_{ANN}$ (%)), $x_i$ and $x_j$ are variations parameter, in which $i$ represents the $x$-axis (temperature T (ºC)) and $j$ is the $y$-axis (heating rate HR (ºC.min$^{-1}$)). $\beta_0$ is the constant coefficient; $\beta_i$ is the linear coefficient; and $\beta_{ij}$ is the interaction coefficient.

## 3. Results and discussion

Figure 2 a-b) shows the experimental thermogravimetric curves and the respective derivatives of curaua fiber at different heating rates. The curves maintain the same format independently of the heating rate used only shifting the curve to higher temperature due to the thermal lag. Three visible main loss stages are visualized: i) at around 100 °C a mass loss of 5% can be mainly attributed to the evaporation of intrinsic moisture, ii) at around 300 °C a more abrupt mass loss attributed mainly to hemicellulose that extends up to 350 °C and, iii) from 350 °C to 400 °C the degradation of cellulose (the main component) in a narrower range, representing the main degradation stage. Lignin degrades overall extension range [7,22,23].

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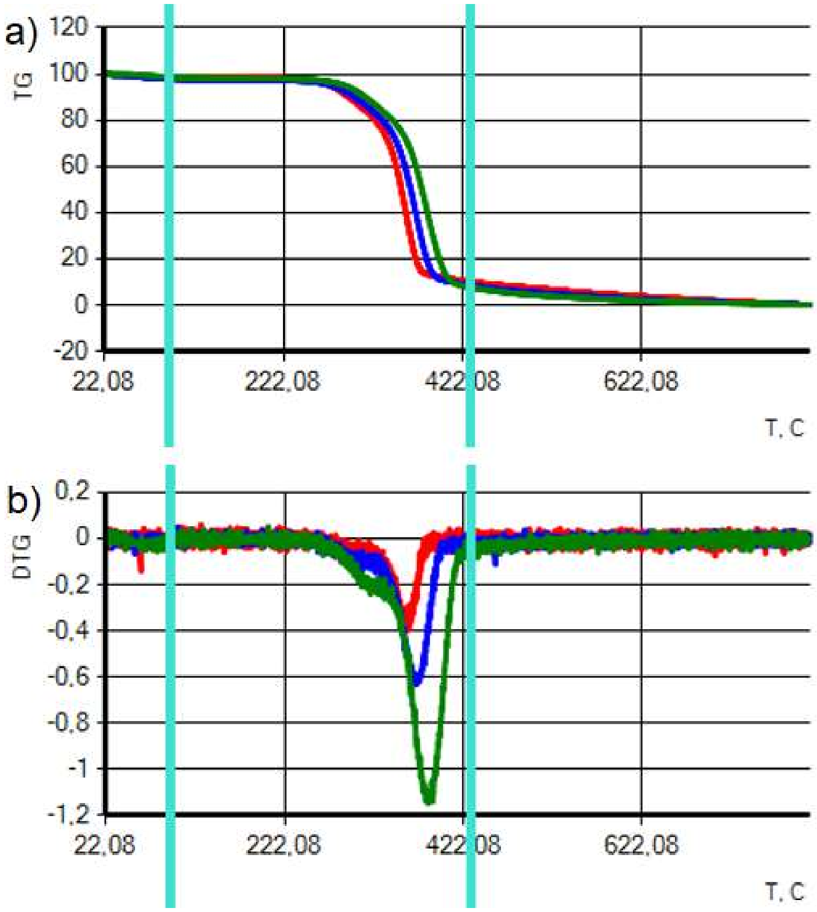


**Figure 2. a)** thermogravimetric and **b)** derivative TG curves of curaua fiber at different heating rates. The heating rates of 10, 20 and 40 °C.min$^{-1}$ are represented by the red, blue and green lines. The vertical cyan lines represent the limit of calculation of the kinetic parameters

All the curves above were used to calculate the kinetic parameters using the Vyazovkin kinetic model in the temperature range from 100 to 435 °C (main degradation stage). The corrected heating rates (provided by the Software) using the Vyazovkin method were 10.09, 20.1, and 39.79 °C.min$^{-1}$. Figure 3a represents the activation energy in the function of the conversion and while Figure 3b the degradation rate in the function of conversion degree. A very good correlation between the theoretical and calculated degradation rate vs alpha is obtained. The results presented the following values: $E_a$ = 192.02 KJ/mol$^{-1}$, A = 10.6 E15, m =0.9, n = 1.71 and p = 0.

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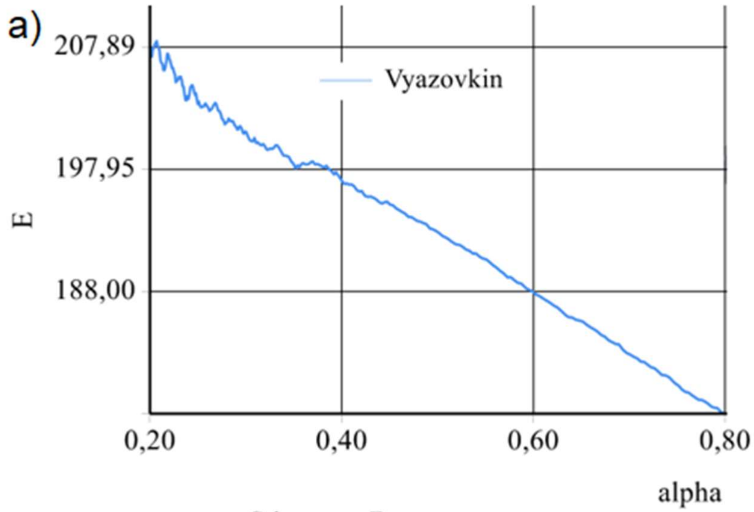


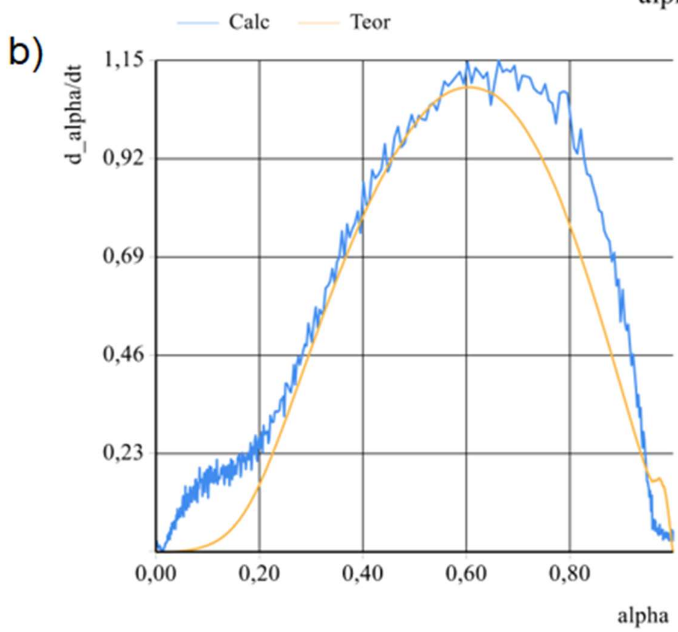


**Figure 3.** Kinetic calculation of the experimental curves. **a)** activation energy in function of conversion degree, and **b)** degradation rate in function of conversion degree

Based on experimental degradation curves, the ANN fit was constructed with parameters variation, in which temperature and heating rate as the input parameters and the loss of mass (kinetic behavior) as output. The experimental dots were used to training the ANN. The number of training data influences the predictive curve, which was thoroughly investigated in previous work to optimize the ANN method [12]. Figure 4a presents the trained curves with the experimental ones, and Figure 4b exhibits the enlargement of initial degradation. An excellent fit was obtained for all heating rates tested. The coefficient of determination was $R^2 > 0.99$ for all curves.

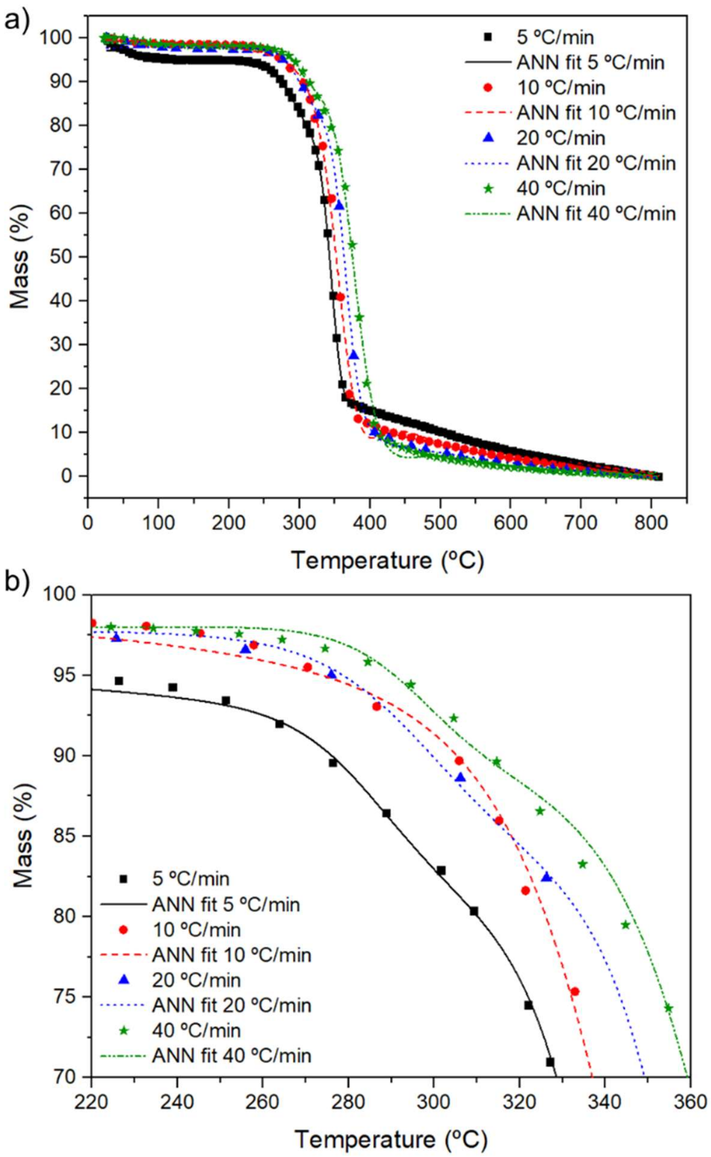


**Figure 4. a)** Thermogravimetric curves of curaua fiber at different heating rates trained using ANN approach according to Monticeli et al [12], and **b)** enlargement of initial degradation

Only 1/10 of the experimental dataset has been used for training the ANN, resulting in a perfect fitting, resulting in an appropriate predictive result. Regarding the ANN application, new degradation behavior could be predicted with no need for long experiments [24].

From the ANN predicted curves, intermediate heating rates were predicted using the surface response methodology (SRM), resulting in a 3D Surface response to predict mass loss as a function of temperature and heating rate variation. Dot curves give the experimental data. The coefficient of determination $R^2 = 0.96$, indicating high reliability of predicted results. For the lowest heating rate (i.e., 5 ºC/min), the degradation curve initiates at the lowest temperature for onset and endset, resulting in the slowest degradation of the remaining residue (15%), between 375 - 810 ºC. With the increased heating rate, more abrupt degradation occurs, increasing the onset and endset temperature.

A well-trained ANN could develop a degradation mechanistic understanding of the natural fiber considered, considering that the ANN method is a purely phenomenological approach. For a better approximation of the theoretical and experimental results, the equation of the three-dimensional curve in Figure 5 was divided into three, presented in Eq. (9) – for the temperature range of 25 – 250 ºC, Eq. (10) – for the temperature range of 250 – 410 ºC, and Eq. (11) – for the temperature range of 410 – 810 ºC.

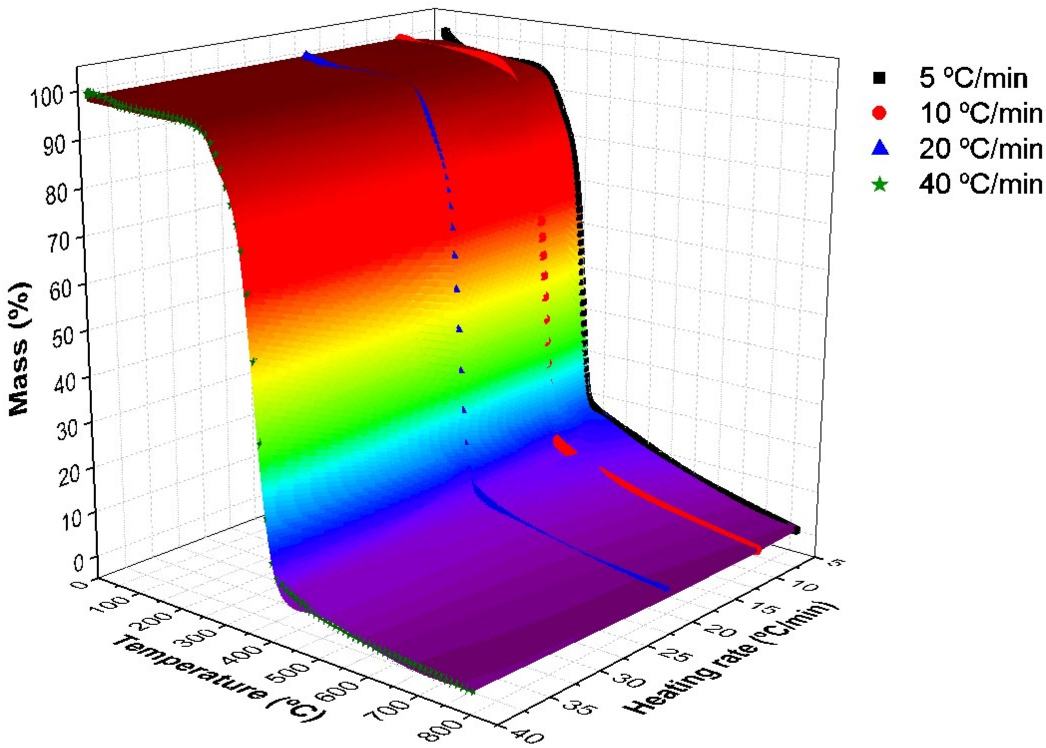


**Figure 5**. Surface Response Methodology for the thermogravimetric curves

$$W_{ANN} = 97.5 + 0.17HR - 0.007T - 0.004HR^2 - 2.4 \cdot 10^{-5}T^2 + 3.1 \cdot 10^{-4}T \cdot HR \quad (9)$$
$$W_{ANN} = -272.7 - 1.2HR + 2.83T - 0.01HR^2 - 0.005T^2 + 0.006T \cdot HR \quad (10)$$
$$W_{ANN} = 44.4 - 0.5HR - 0.09T + 0.0054HR^2 + 4.9 \cdot 10^{-5}T^2 + 3.14 \cdot 10^{-4}T \cdot HR \quad (11)$$

Following Figure 5 and Eqs. (9) - (10), Figure 5 exhibits the predicted values of curaua fiber degradation using the heating rates of 7, 15, 30, and 50 ºC.min$^{-1}$. Through the ANN and RSM combination, it is possible to predict other degradation curves with different analysis parameters not accessed experimentally, which decreases costs and time related to tests repetitions with high reliability

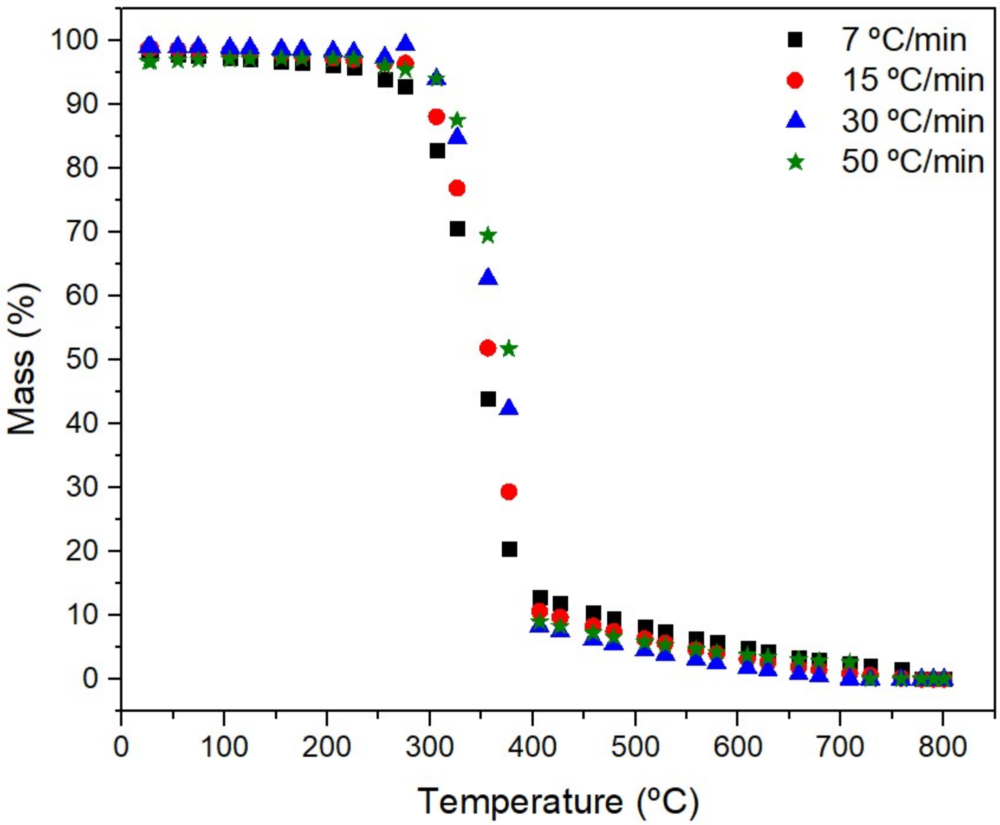


**Figure 6**. Predicted thermogravimetric curves of curaua fiber

The new kinetic modeling was done using the following curves predicted at the heating rates of a) 7, 15, and 30 °C.min$^{-1}$ and b) 7, 15, 30, and 50 °C.min$^{-1}$. The results using Vyazovkin model presented the following values for condition a): $E_a$ = 228.74 KJ/mol$^{-1}$, A = 3.59 E19, m = 0.1, n = 1.00 and p = 0 and for condition b) $E_a$ = 226.92 KJ/mol$^{-1}$, A = 6.92 E18, m = 0.1, n = 1.53 and p = 0.

The values obtained, mainly the activation energy is close to the experimental curves. Also, the extrapolated curve (at 50 °C.min$^{-1}$) used in condition b) seems to be satisfactory in the present study. Of course that the extrapolation of data using ANN is not well recommended due to the accumulation of errors. However, it can be used carefully and seems to work if the behavior did not change drastically from the previous behavior.

## 4. Conclusions

The present study proposed obtaining new thermogravimetric curves for curaua fiber at any heating rate situated between the minimum and maximum heating rates experimentally tested. For this, an Artificial Neural Network (ANN) followed by the Surface Response Methodology (SRM) was used to obtain new TG curves. Vyazovkin kinetic method was used in the experimental curves and in the newly obtained curves. The kinetic results presented similar values for the experimental and predicted curves. This approach can be extended to any material to obtain properties, parameters or to optimize processes.

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## REFERENCES

1. Angrizani CC; Ornaghi HL; Zattera AJ; Amico SC. Thermal and Mechanical Investigation of Interlaminate Glass/Curaua Hybrid Polymer Composites. J *Nat Fibers*. **2017**, 14, 271–277.

2. Silva HSP; Ornaghi HLJ; Almeida JHSJ; Zattera AJ; Amico SC. Mechanical Behavior and Correlation Between Dynamic Fragility and Dynamic Mechanical Properties of Curaua Fiber Composites. *Polym Compos*. **2014**, 35, 1078-1086.

3. Nguyen NA; Meek KM; Bowland CC; Naskar AK. Data of thermally active lignin-linkages and shape memory of lignin-rubber composites. *Data Br* **2019**, 22, 392–399.

4. Neves RM; Lopes KS; Zimmermann MGV; Poletto M; Zattera AJ. Cellulose Nanowhiskers Extracted from Tempo- Oxidized Curaua Fibers. *J Nat Fibers* **2019**, 17, 1355-1365.

5. Neves RM; Lopes KS; Lazzar LK; Monticeli FM; Zattera AJ. Characterization of expanded polystyrene and its composites by supercritical carbon dioxide foaming approach. *J Porous Mater*. **2021,** 1-10.

6. Seddiqi H; Oliaei E; Honarkar H; Jin J; Geonzon LC; Bacabac RG; Klein-Nulend J. Cellulose and its derivatives: towards biomedical applications. *Cellulose,* **2021,** 28, 1893-1931.

7. Ornaghi HL; Ornaghi FG; Neves RM; Monticeli F; Bianchi O. Mechanisms involved in thermal degradation of lignocellulosic fibers: a survey based on chemical composition. *Cellulose*. **2020**, 27, 4949-4961.

8. Yang J; Ching YC; Chuah CH. Applications of lignocellulosic fibers and lignin in bioplastics: A review. *Polymers*, **2019**, 11, 751-776.

9. Abdul Khalil HPS; Hossain MS; Rosamah E; Azli NA; Saddon N; Davoudpoura Y, Islam, N; Dungani, R. The role of soil properties and it's interaction towards quality plant fiber: A review. *Renew Sustain Energy Rev*. **2015**, 43, 1006–1015.

10. Yao F; Wu Q; Lei Y; Guo W; Xu Y; Thermal decomposition kinetics of natural

 doi:10.20944/preprints202105.0561.v1


fibers : Activation energy with dynamic thermogravimetric analysis. *Polym Degrad Stab*, **2008**, 93, 90–98.

11. Sunphorka S; Chalermsinsuwan B; Piumsomboon P. Artificial neural network model for the prediction of kinetic parameters of biomass pyrolysis from its constituents. *Fuel*, **2017**, 193, 142–158.
12. Monticeli FM; Neves RM; Ornaghi HL Jr. Using an artificial neural network ( ANN ) for prediction of thermal degradation from kinetics parameters of vegetable fibers. *Cellulose.* **2021**, 28, 1961-1971
13. Asim M; Paridah MT, Chandrasekar M, Shahroze RM, Jawaid M, Nasir M, Siakeng. Thermal stability of natural fibers and their polymer composites. *Iran Polym J.* **2020**, 29, 625–648.
14. Monteiro SN; Calado V; Margem FM; Rodriguez RJS. Thermogravimetric stability behavior of less common lignocellulosic fibers - A review. *J Mater Res Technol.* **2012**, 1, 189–99.
15. Ornaghi HL Jr; Zattera AJ; Amico SC. Thermal behavior and the compensation effect of vegetal fibers. *Cellulose*, **2014**, 21, 189–201.
16. Neves RM; Lopes KS; Zimmermann MGV; Poletto M; Zattera AJ. Cellulose Nanowhiskers Extracted from Tempo-Oxidized Curaua Fibers. *J Nat Fibers* **2019**.
17. Drozin D; Sozykin S; Ivanova N; Olenchikova T; Krupnova T; Krupina N, Advin V. Kinetic calculation: Software tool for determining the kinetic parameters of the thermal decomposition process using the Vyazovkin Method. *SoftwareX* **2020**, 11, 100359.
18. Schmidhuber J. Deep Learning in neural networks: An overview. *Neural Networks* **2015**, 61, 85–117
19. Dall Agnol L; Ornaghi HL Jr; Monticeli F; Dias FTG, Bianchi, O. Polyurethanes synthetized with polyols of distinct molar masses: Use of the artificial neural network for prediction of degree of polymerization. *Polym Eng Sci.* **2021**
20. Debnath S; Reddy MM; Yi QS. Influence of cutting fluid conditions and cutting parameters on surface roughness and tool wear in turning process using Taguchi method. *Meas J Int Meas Confed.* **2016**, 78, 111–119.
21. Aydar AY. Utilization of Response Surface Methodology in Optimization of Extraction of Plant Materials. *Statistical Approaches With Emphasis on Design of Experiments Applied to Chemical Processes*, Chapter 10, **2018.**
22. Patwardhan PR, Brown RC, Shanks BH. Understanding the fast pyrolysis of lignin. *ChemSusChem,* **2011**, 4, 1629–1636.
23. Cabeza A, Sobrón F, Yedro FM, García-Serna J. Autocatalytic kinetic model for thermogravimetric analysis and composition estimation of biomass and polymeric fractions. *Fuel* **2015**, 148, 212–225.
24. Fernández-Fdz D, López-Puente J, Zaera R. Prediction of the behaviour of CFRPs against high-velocity impact of solids employing an artificial neural network methodology. *Compos Part A Appl Sci Manuf.* **2008**, 39, 989–996.