



Torrefaction effects on the pyrolysis of pineapple crown (*Ananas comosus*)—kinetic triplet and model validation

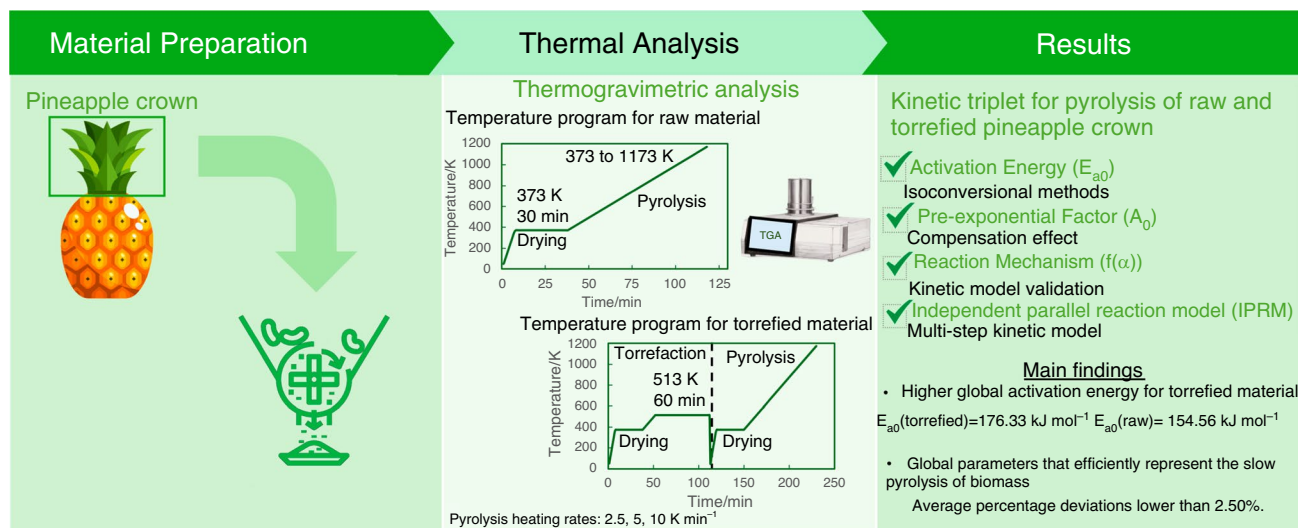
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Abstract

The aim of this study is to suggest pyrolysis as a possible route for pineapple crown, by estimating the kinetic triplet that efficiently represents the slow pyrolysis of raw and previously torrefied pineapple crown. Thermogravimetric analyses were performed at heating rates of 2.5, 5, and 10 K min⁻¹, and global methods were applied (isoconversional methods and compensation effect). The raw material was characterized by proximate analysis and chemical composition, and these values were consistent with other biomasses. The stages verified for the decomposition of the raw and torrefied biomass were dehydration, volatilization and carbonization. The torrefaction process mainly decomposed the hemicellulose. Furthermore, an increase in the activation energy of the pyrolysis of the torrefied material was observed, which occurs due to the degradation of the most reactive portion of the material. The slow pyrolysis of the raw pineapple crown presented an activation energy of 154.56 kJ mol⁻¹, a global pre-exponential factor of 1.75×10^{12} s⁻¹, and a global conversion function N3 (third-order reaction). The pyrolysis of torrefied biomass presented an activation energy of 176.33 kJ mol⁻¹, a global pre-exponential factor of 1.34×10^{13} s⁻¹, and a global conversion function N2 (second-order reaction). This work proposed a methodology based on the reconstruction of experimental kinetic curves using all conversion functions, and the results indicate that the methodology effectively determined the parameters that represent the decomposition of the heterogeneous material.

Graphical Abstract



Keywords Kinetic compensation effect · Pineapple residues · Pyrolysis · Isoconversional model · Kinetic triplet · Mathematical modeling

Extended author information available on the last page of the article

Introduction

The excessive use of fossil fuels to meet growing energy demand generates negative environmental impacts, mainly due to the high greenhouse gas emissions, such as carbon dioxide (CO_2). Alternative renewable and sustainable sources have been investigated to mitigate harmful effects. Lignocellulosic biomass from animal and vegetable sources, such as agricultural, industrial, and forestry residues, can be converted into energy-rich products. The use of these residues for energy purposes helps reduce the emission of harmful gases and minimizes the damage caused by improper disposal [1, 2].

Pineapple (*Ananas comosus*) is a tropical fruit from the Bromeliaceae family. According to FAO (Food and Agriculture Organization of the United Nations) [3], 29.36 million tons of pineapple were produced worldwide in 2022. Brazil ranked as the fourth largest producer with 2.34 million tons in 2022, behind Costa Rica, the Philippines, and Indonesia. Furthermore, pineapple is the fifth most produced fruit in the country, which indicates that the fruit is very relevant to Brazilian agriculture [3]. Lignocellulosic residues from pineapple processing (peel, stalk, crown, and base) represent 60% of the mass of the fruit. The pineapple crown is the main residue, corresponding to around 25% to 30% of the mass of the fruit. A large volume of waste is generated, requiring treatment technologies to add value [3, 4].

A possible route for waste treatment is converting biomass into energy through physical, biological, or thermochemical processes. Thermochemical processes use heat to decompose biomass, generating energy-rich products. The main thermochemical processes are combustion, gasification, and pyrolysis. In pyrolysis, biomass decomposition occurs at moderate temperatures (between 623 and 973 K) in the total or partial absence of oxygen, producing solid, gaseous, and liquid compounds for energy use. However, some properties of biomass, such as heterogeneous composition, low energy density, and high moisture content, make thermochemical processes difficult. Pretreatment processes, such as pelletization, briquetting, and torrefaction, can improve the characteristics of the biomass [5, 6].

Torrefaction is a heat treatment process carried out between 473 and 573 K, at heating rates below 50 K min^{-1} , in the absence of oxygen, and under atmospheric pressure. Torrefied biomass is the most viable solid fuel due to lower moisture content, higher energy density, greater grinding capacity, and increased C/H and C/O ratios. The temperature range in the pretreatment process leads to the dehydration of the biomass and the decomposition of a large part of the hemicellulose and extractives, which are the less thermally stable compounds. These changes

occurring during the pretreatment process validate the study on pyrolytic decomposition of torrefied biomass [6, 7].

Meng et al. [8] studied the pyrolysis of pine wood coupled to a torrefaction system and compared the properties of bio-oil (pyrolysis liquid product) produced from raw and torrefied biomass. The authors found that the bio-oil from torrefied biomass presented higher quality, with lower oxygen and moisture content. Lopes, Tannous and Carmazini [9] compared the thermal behavior of torrefied coconut fiber (498 K and 15 min) with the raw material. The authors reported a 12.8% increase in the higher calorific value after biomass torrefaction. Chen et al. [10] investigated the properties and pyrolysis kinetics of raw and torrefied rice husks at different temperatures. They observed an increase of 8%, 11%, and 22% in the energy density of torrefied biomass at 473, 523, and 573 K, respectively.

The design and optimization of the pyrolysis reactors on an industrial scale require an understanding of hydrodynamics, transport simulation, and kinetic analysis of the biomass decomposition reactions. According to the International Confederation of Thermal Analysis and Calorimetry (ICTAC), the kinetic analysis aims to obtain the relationship among conversion rate, the extent of decomposition, and temperature. This relationship can be obtained by determining the kinetic triplet in which the activation energy (E_a) is related to the energy barrier, the pre-exponential factor (A) is the frequency of collisions, and the conversion function $f(\alpha)$ is the reaction mechanism [11]. Thermogravimetry is the main experimental thermal analysis used to evaluate the thermal decomposition of biomass. It is based on measuring the mass variation of a sample under heating conditions and in a controlled atmosphere [9, 11].

Mathematical methods are applied to process thermogravimetric data and determine the pyrolysis kinetic parameters. The distributed activation energy model (DAEM), the independent parallel reaction model (IPRM), the model adjustment methods, and the isoconversional methods are used to determine the activation energy. Integral and differential isoconversional methods are developed for homogeneous materials and a single-step decomposition reaction. This enables the determination of a global activation energy and a comparison with other lignocellulosic biomasses. Isoconversional methods do not require prior knowledge of the reaction model (model-free method). Furthermore, the global activation energy (E_{a0}) can be used to determine the other kinetic parameters using the compensation effect method and compare experimental and theoretical conversion functions [10, 11].

In the compensation effect, a model adjustment method is associated with different theoretical reaction models to obtain a set of E_{ai} and $\ln(A)_i$ values where the index refers to the number of reaction models. The slope and intercept

coefficients of the linear relationship between a set of Arrhenius parameters are called compensation parameters and enable us to determine the global pre-exponential factor using the isoconversional activation energy value. Based on these global parameters, a curve is constructed with conversion function values calculated for each degree of conversion and compared with the theoretical reaction models to analyze the model fit quality [11].

Kinetic analyses of the pyrolysis of urban and agricultural residues have been widely developed in literature. Marquez et al. [12] evaluated the pyrolysis of urban solid waste using five isoconversional methods and the IPRM. Chilla and Suranami [13] applied three isoconversional methods to determine the activation energy of the pyrolysis of orange peel. Chen et al. [10] used three isoconversional methods, the compensation effect, and the master-plots methodology to determine the kinetic triplet for the pyrolysis of raw and torrefied rice husks and straw. Arenas, Navarro and Martinez [14] studied the pyrolysis of five different residues, including pineapple peel, applying five isoconversional methods. The authors used the DAEM to determine the kinetic parameters for the different biomass decomposition reactions.

The estimated kinetic parameters must represent the decomposition of the material efficiently. Therefore, ICTAC recommends that the kinetic triplet be used to reconstruct the experimental curves, in order to verify the adjustment of the estimated parameters [11]. During the preparation of this work, a proposal was implemented to investigate the conversion functions in the curve reconstruction stage, which is based on performing the reconstruction with the estimated global activation energy and pre-exponential factor values but applying different theoretical conversion functions in order to evaluate the best model for reproducing the experimental kinetic curve.

Thus, this study aims to evaluate the slow pyrolysis of raw and torrefied pineapple crown using isoconversional methods, compensation effect, and reconstruction of experimental curves to determine the kinetic triplet. Kinetic modeling studies on raw and pre-treated pineapple crown using this methodology are not common in the literature, and the present study seeks to contribute to the kinetic study and evaluation of the effect of torrefaction for this residual biomass.

Experimental and kinetic analysis methods

Material

Pearl pineapples (*Ananas comosus*) were purchased from markets in the Uberaba region, Minas Gerais state, Brazil. The pineapple crown was removed from the fruit and cut into slices of approximately 5 cm. The material was crushed in a knife mill to obtain a fine powder. The raw biomass was

characterized by chemical composition (cellulose, hemicellulose, lignin, and extractive contents) according to standard methods reported by Setter et al. [15]. The moisture, ash, fixed carbon, and volatile contents (proximate analysis) were determined according to ASTM D3172, ASTM D3173, and ASTM D3174. All characterization techniques were performed in triplicate. The proximate analysis enables us to estimate the higher calorific value (HHV) using the correlation proposed by Yin [16].

Thermogravimetric analysis and torrefaction pretreatment

Thermogravimetric analyses were performed using a Shimadzu DTG-60H TGA/DTA analyzer. Samples of approximately 10 mg, sieved in 80 mesh, were analyzed in an alumina crucible, using nitrogen at a flow rate of 50 mL min⁻¹ as a purge gas. The ICTAC recommends using at least three temperature programs with heating rates ranging from 1 to 20 K min⁻¹ [11, 17]. Higher heating rates greater may generate inefficient temperature and mass values [17, 18]. Thus, we selected the following heating rates: 2.5, 5, and 10 K min⁻¹.

The thermal analysis of raw biomass was conducted with a previous drying step (heating from room temperature to 373 K at a heating rate of 50 K min⁻¹ and maintained at that temperature for 30 min). After drying, the raw biomass was heated to 1173 K at heating rates of 2.5, 5, and 10 K min⁻¹.

The torrefaction pretreatment was performed in the thermogravimetric analyzer before subjecting the material to the same temperature program. Firstly, the material was subjected to a drying step and then the temperature was raised from 373 to 513 K at a heating rate of 50 K min⁻¹ and this temperature was maintained for 60 min for torrefaction. These torrefaction conditions were selected based on Yang et al. [6]. Then, the torrefied biomass was cooled down to room temperature and subjected to the same heating conditions as the raw biomass, with three heating rates. The exclusion of error points in the thermogravimetric data and data derivation were carried out based on Tibola et al. [17]. Analyses were performed in duplicate.

Thermogravimetric analyses at heating rates of 2.5, 5, and 10 K min⁻¹ are performed to estimate the kinetic parameters. New analyses were carried out at heating rates of 7.5, 15, 30, and 50 K min⁻¹ for model validation at different rates from those used for its determination, according to ICTAC recommendation [11].

Determination of the activation energy (E_a)

We estimated the activation energy of slow pyrolysis of raw and torrefied biomass by using the classic integral isoconversional methods of Ozawa–Flynn–Wall (OFW), Starink

Table 1 Equations of the isoconversional methods [11, 17]

Symbol	Model	Equations
FDM	$\ln\left(\beta_1 \frac{d\alpha}{dT}\right)_\alpha = \ln[A_\alpha f(\alpha)] - \frac{E_\alpha}{RT_\alpha}$	(1)
OFW	$\log \beta_i = \left[\log\left(\frac{A_\alpha E_\alpha}{R}\right) - \log[g(\alpha)] - 2.315 \right] - 0.4567 \frac{E_\alpha}{RT_\alpha}$	(2)
KAS	$\ln\left(\frac{\beta_1}{T_\alpha^2}\right) = \ln\left[\frac{A_\alpha R}{g(\alpha)E_\alpha}\right] - \frac{E_\alpha}{RT_\alpha}$	(3)
STK	$\ln\left(\frac{\beta_1}{T_\alpha^{1.92}}\right) = \ln\left[\frac{A_\alpha R}{g(\alpha)E_\alpha}\right] - 1.0008 \frac{E_\alpha}{RT_\alpha}$	(4)
VZK	$\varphi = \left \sum_{i=1}^n \sum_{j \neq i}^n \frac{\beta_j I(E_\alpha, T_\alpha)}{\beta_i I(E_\alpha, T_\alpha)} \right = \min$	(5)
	$I(E_\alpha, T_\alpha) = (E_\alpha/R) [p(x)]$	(6)
	$x = E_\alpha/RT_\alpha$	(7)
	$p(x) = \frac{e^{-x}}{x^2} \left(\frac{x^4 + 16x^3 + 86x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \right)$	(8)

(STK), Kissinger–Akahira–Sunose (KAS), the Friedman differential method (FDM), and the Vyazovkin method (VZK). Table 1 shows these isoconversional methods.

For Eqs. (1)–(5), A is the pre-exponential factor, α is the conversion range, $f(\alpha)$ is the differential form of the conversion function, $g(\alpha)$ is the integral form of the conversion function, R is the ideal gas constant, β_i is the heating rate, E_α is the activation energy in a conversion range α , and T_α is the temperature. The activation energies in Eqs. (1)–(4) were estimated using the slope coefficient in the linear regressions obtained from the isoconversional equations as a function of the inverse of temperature for each degree of conversion.

The conversion ranged from 0.05 to 0.95, with a step size of 0.05. This procedure was performed for the heating rates of 2.5, 5.0, and 10.0 K min⁻¹, according to ICTAC recommendations [11].

The Vyazovkin method (VZK) uses Eqs. 5–8 in order to obtain the optimal value of the activation energy for each conversion (α), E_α . It considers that the optimal value of E_α would minimize the value of the function φ in Eq. 5. The starting value of E_α used is the value of calculated by the model that presented the best results (FDM, OFW, MCR, or STK) in previous analyses.

Table 2 Differential ($f(\alpha)$) and integral ($g(\alpha)$) kinetic models for solid-state reactions [11]

Reaction model	Symbol	$f(\alpha)$	$g(\alpha)$
<i>Nucleation</i>			
Power law I	P ₁	$4\alpha^{3/4}$	$\alpha^{1/4}$
Power law II	P ₂	$3\alpha^{2/3}$	$\alpha^{1/3}$
Power law III	P ₃	$2\alpha^{1/2}$	$\alpha^{1/2}$
Power law IV	P ₄	$2/3\alpha^{-1/2}$	$\alpha^{3/2}$
Avrami–Erofe'ev I	AE ₁	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
Avrami–Erofe'ev II	AE ₂	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
Avrami–Erofe'ev III	AE ₃	$4(1-\alpha)[- \ln(1-\alpha)]^{3/4}$	$[- \ln(1-\alpha)]^{1/4}$
<i>Geometric contraction</i>			
Cylinder contraction	CC	$2(1-\alpha)^{1/2}$	$1 - (1-\alpha)^{1/2}$
Sphere contraction	EC	$3(1-\alpha)^{2/3}$	$1 - (1-\alpha)^{1/3}$
<i>Reaction order</i>			
First order	N ₁	$(1-\alpha)$	$-\ln(1-\alpha)$
<i>n</i> th order	N _n	$(1-\alpha)^n$	$[1 - (1-\alpha)^{(1-n)}]/(1-n)$
<i>Diffusional phenomena</i>			
One-dimensional	D1	$1/2\alpha$	α^2
Two-dimensional	D2	$[- \ln(1-\alpha)]^{-1}$	$\alpha + (1-\alpha)\ln(1-\alpha)$
Jader three-dimensional equation	D3	$(3/2)[(1-\alpha)^{2/3} [1 - (1-\alpha)^{1/3}]^{-1}]$	$[1 - (1-\alpha)^{1/3}]^2$
Ginstling–Brounstein three-dimensional equation	D4	$(3/2)[(1-\alpha)^{1/3} - 1]^{-1}$	$(1 - 2\alpha/3) - (1-\alpha)^{2/3}$

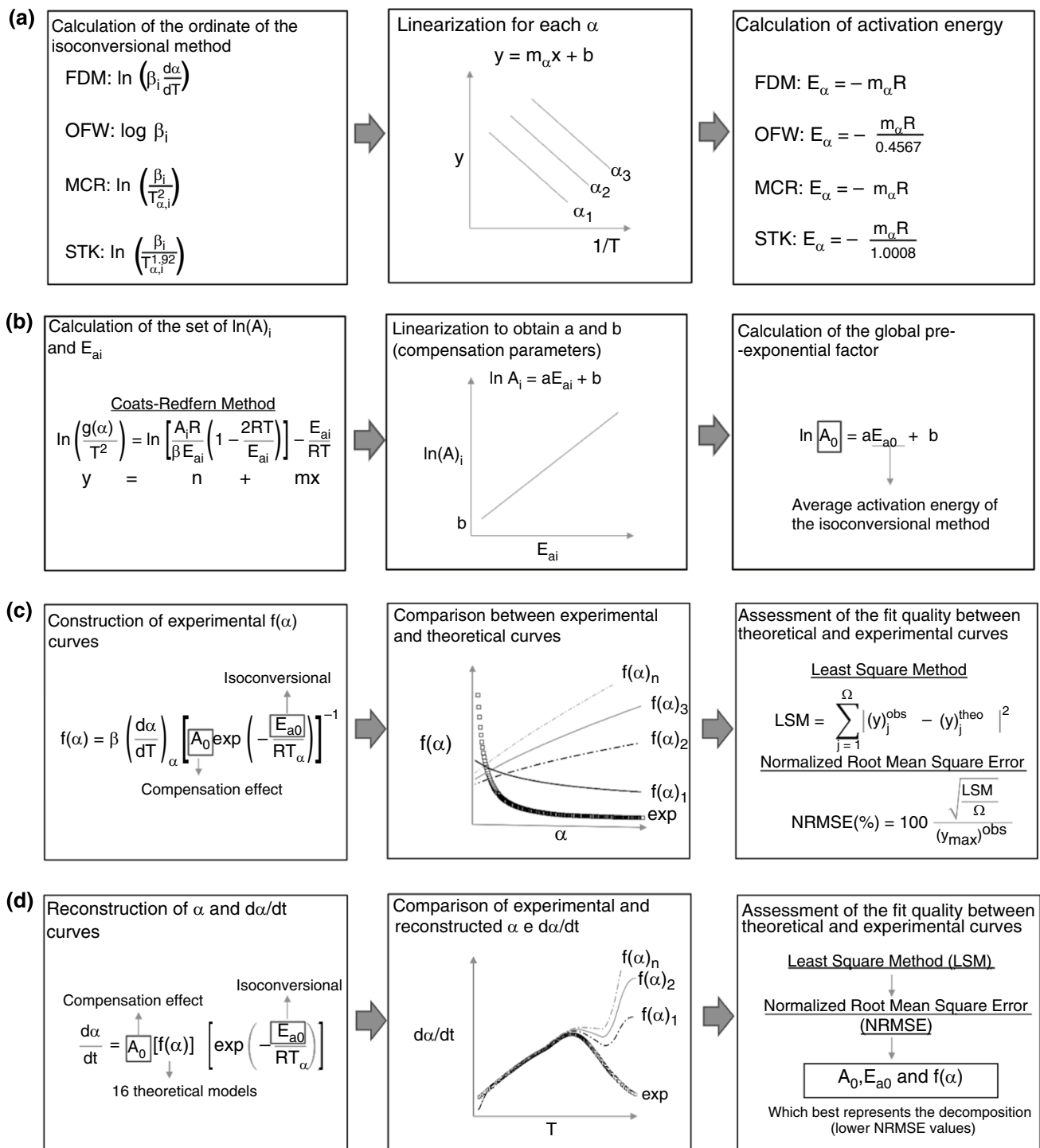


Fig. 1 Schematic flowchart to determine the activation energy (a), the pre-exponential factor (b), the conversion function (c), and to reconstruct the α and $d\alpha/dT$ curves

In Microsoft Excel, besides the initial $E\alpha$ values, it is necessary to input the values of α , β , and temperature of the conversion T_α for each β . With those values, for each heating rate, the values of x (Eq. (7)), $p(x)$ (Eq. (8)), and $I(E_\alpha, T_\alpha)$

(Eq. (6)) were calculated. Finally, all these values were used to minimize the value of φ (Eq. (6)) for each α . After that, using the Solver add in [19], it was informed the objective cell, which contains the value to be minimized (φ), and the cell that contains the variable ($E\alpha$). In order to minimize φ

Table 3 Chemical composition and proximate analysis of the raw pineapple crown and other lignocellulosic biomasses

Characterization analysis	Lignocellulosic biomass				
	Pineapple crown	Peach pit	Lemon peel	Sugarcane straw	Pineapple peel
<i>Proximate analysis (%)</i>					
Moisture**	8.15 ± 0.28	5.70	6.10	3.12	6.78 ± 1.32
Volatile materials*	87.69 ± 0.45	84.80	87.16	87.61	68.96 ± 1.41
Fixed carbon*	9.25 ± 0.28	13.90	1.34	3.22	19.52 ± 0.74
Ashes*	3.06 ± 0.17	1.30	5.40	9.17	4.75 ± 0.22
<i>Chemical composition (%)</i>					
Cellulose**	45.50 ± 0.71	31.58	23.10	52.60	20.90 ± 0.60
Hemicellulose**	20.75 ± 0.63	21.02	8.09	12.05	31.80 ± 1.90
Total lignin**	14.12 ± 0.34	27.53	7.60	22.50	10.40 ± 1.05
Extractives**	6.78 ± 0.26	—	13.50	11.68	28.10 ± 2.50
HHV/MJ kg ⁻¹	19.04 ± 0.03	21.77	—	16.42	—
Reference	This study	Alejandra et al. [24]	Adeniyi et al. [25]	Ferreira et al. [26]	Tran et al. [27]

**Wet basis, *Dry basis

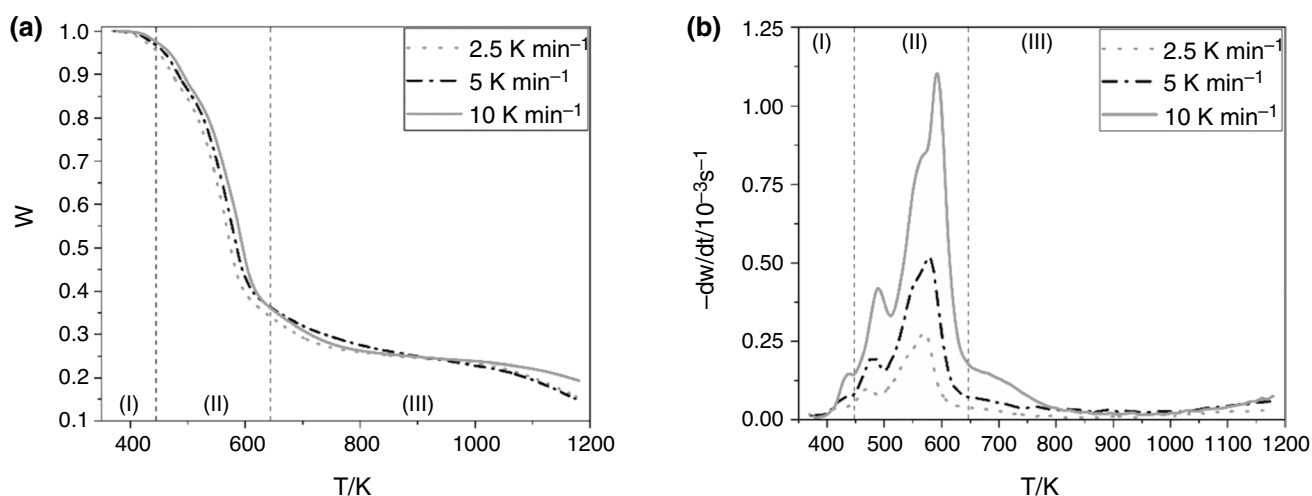
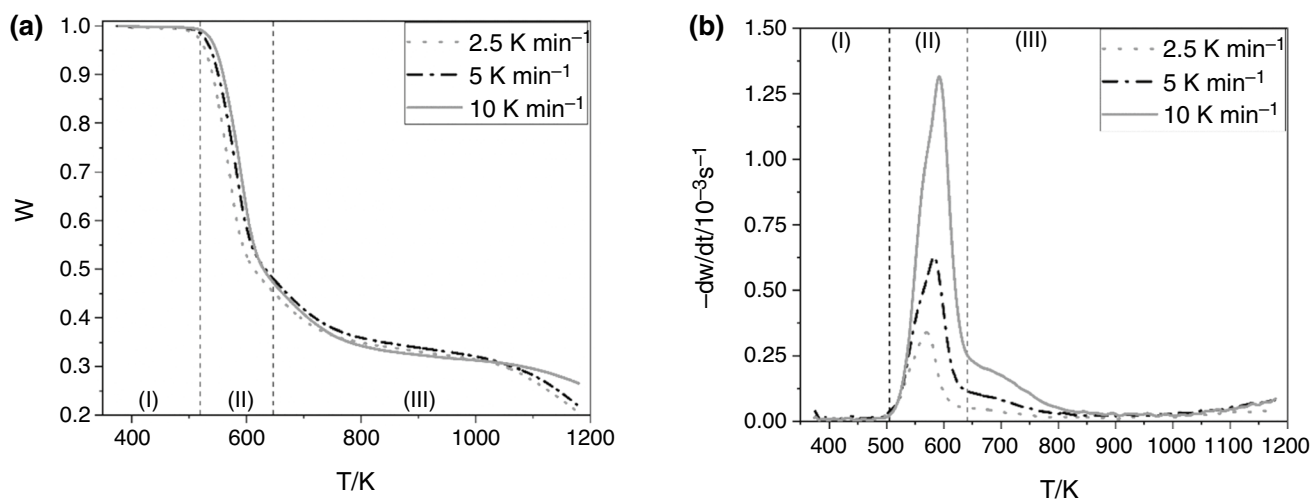
**Fig. 2** Profiles of mass loss (a) and mass loss rate (b) for the raw biomass**Fig. 3** Profiles of mass loss (a) and mass loss rate (b) for the torrefied biomass

Table 4 Parameters of the stages of pyrolysis

Stage	Material	$\beta/K\text{min}^{-1}$	T_i/K	T_f/K	T_{max}/K	$(dw/dt)_{\text{max}}/10^{-3}s^{-1}$
Dehydration (stage I)	Raw biomass	2.5	369.28	441.59	439.95	0.05
		5.0	373.70	451.40	449.93	0.09
		10.0	375.89	462.39	461.13	0.19
	Torrefied biomass	2.5	373.60	524.11	522.87	0.09
		5.0	375.57	532.47	530.15	0.16
		10.0	378.17	543.10	541.86	0.38
Volatilization (stage II)	Raw biomass	2.5	441.59	597.32	570.96	0.28
		5.0	451.40	607.30	579.92	0.52
		10.0	462.39	619.58	595.44	1.10
	Torrefied biomass	2.5	524.11	601.35	570.77	0.34
		5.0	532.47	611.98	583.33	0.63
		10.0	543.10	622.35	592.58	1.30
Carbonization (stage III)	Raw biomass	2.5	597.32	1178.30	598.44	0.09
		5.0	607.30	1179.07	608.27	0.19
		10.0	619.58	1180.41	620.73	0.37
	Torrefied biomass	2.5	601.35	1176.76	602.45	0.10
		5.0	611.98	1177.93	612.77	0.23
		10.0	622.35	1179.57	623.28	0.45

values, it was used the preset option “GRG nonlinear” as solving method. A detailed explanation of the other isoconversional methods was presented in previous work by the research group [17].

Determination of the global pre-exponential factor (A)

The global pre-exponential factor for raw and torrefied biomass was estimated through the compensation effect using the average activation energy from the isoconversional method with the lowest standard deviation. This methodology uses the Coats–Redfern method [20] associated with different reaction models reported in the literature to obtain a set of E_{ai} and $\ln(A)_i$ values. A set of 48 pairs of E_{ai} and $\ln(A)_i$ values were obtained by linear regression of the Coats–Redfern method (Eq. 9), which is 16 for each heating rate. The linearization of the Arrhenius parameters enabled us to obtain the compensation parameters “a” and “b.” These parameters allowed us to determine the global pre-exponential factor for the average activation energy. Table 2 shows the kinetic models used to define the set of E_{ai} and $\ln(A)_i$ values (with reaction order model up to third-order—N3).

$$\ln\left(\frac{g(\alpha)}{T^2}\right) = \ln\left[\frac{A_i R}{\beta E_{ai}}\left(1 - \frac{2RT}{E_{ai}}\right)\right] - \frac{E_{ai}}{RT} \quad (9)$$

where E_{ai} and $\ln(A)_i$ are the activation energy and pre-exponential factor values for each conversion function ($g(\alpha)$) and i is the number of conversion functions.

Determination of the reaction model ($f(\alpha)$)

The experimental curves of $f(\alpha)$ were numerically constructed for each heating rate based on the average activation energy and global pre-exponential factor values determined previously. The experimental curves were compared to the theoretical reaction models presented in Table 2. The conversion ranged from 0.05 to 0.95, with a step size of 0.05. We used the least squares method (LSM) and normalized root-mean-square error (NRMSE) to evaluate the fit quality of the theoretical and experimental curves. The theoretical reaction model with the smallest NRMSE value in the experimental curve was established as the most suitable to represent biomass pyrolysis.

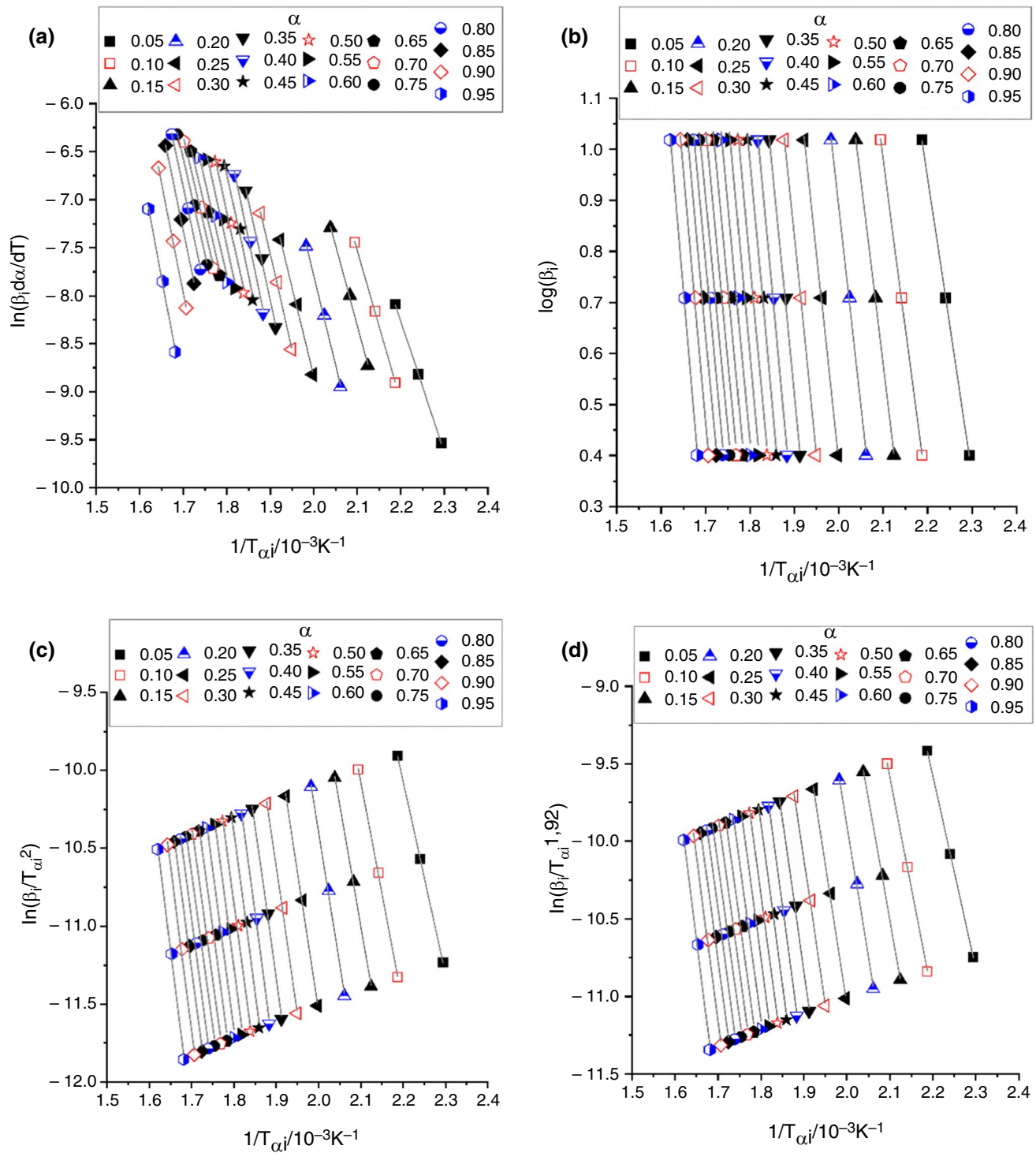


Fig. 4 Linearization of the FDM (a), OFW (b), KAS (c), and STK (d) methods for the pyrolysis of raw biomass

Reconstruction of α and da/dT curves

The numerical reconstruction of the conversion (α) and conversion rate (da/dt) curves as a function of temperature was performed using the kinetic triplet. This numerical

reconstruction can validate the kinetic triplet by comparing the reconstructed curves with the experimental curves obtained from thermogravimetric data. In this study, the numerical reconstruction of the α and da/dt curves was performed using each reaction model shown in Table 2 to

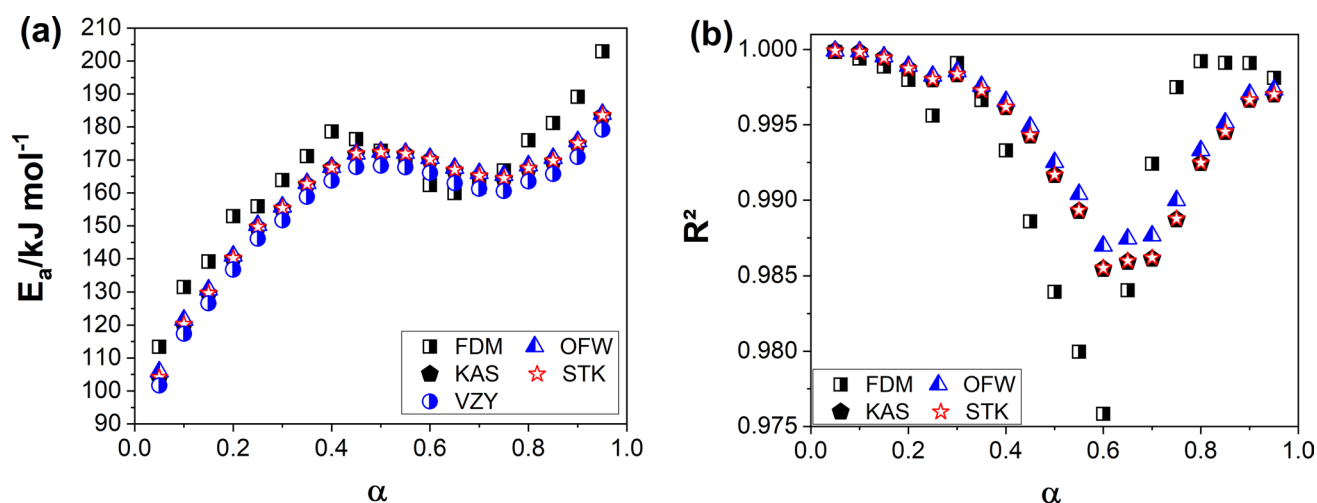


Fig. 5 Activation energy (a) and coefficient of determination (b) for the pyrolysis of raw biomass

Table 5 Average activation energy values for raw pineapple crown and other biomasses

Biomass	$\beta/K\text{min}^{-1}$	Models	$E_{a0}/kJ\text{mol}^{-1}$	References
Pineapple crown	2.5, 5.0, 10.0	FDM, OFW, KAS, STK, VZK	158.87 ± 20.49	This work
Watermelon seed	5.0, 10.0, 20.0, 40.0	KAS, STK	131.23 ± 17.90	Gözke [34]
Onion peel	5.0, 10.0, 20.0	FDM, OFW, KAS, STK	168.60	Açikalin and Gözke [35]
Pequi shell	5.0, 10.0, 15.0, 20.0, 25.0	FDM, OFW	231.80	Martins et al. [36]
Coconut fiber	5.0, 10.0, 15.0, 20.0	FDM, OFW, STK, MCR, VZK	173.38 ± 10.04	Lopes and Tannous [23]
Corn cob	5.0, 10.0, 20.0, 40.0	OFW, KAS	247.86	Phuakpunk et al. [37]
Rice husk	5.0, 10.0, 20.0	FDM	193.72	Hu et al. [38]

reevaluate the most suitable reaction model for biomass pyrolysis. The α and $d\alpha/dt$ curves were reconstructed for the heating rates of 2.5, 5, and 10 K min⁻¹. The LSM and NRMSE were used to analyze the fit quality of the experimental curves. Figure 1 shows schematic flowcharts of the steps to determine the kinetic triplet. The index Ω is the number of experimental measurements, $(y)_j^{\text{obs}}$ and $(y)_j^{\text{theo}}$ are experimental and theoretical data, respectively, and $(y_{\text{max}})^{\text{obs}}$ refers to the maximum experimental value.

Application of the kinetic triplet

After determining the most suitable kinetic triplet that represents the slow pyrolysis of the pineapple crown, we performed the numerical reconstruction of the α and $d\alpha/dt$ curves at heating rates of 7.5, 15, 30, and 50 K min⁻¹. These heating rates are also classified as slow pyrolysis, since fast pyrolysis occurs at heating rates above 10³ K min⁻¹ [21, 22]. This analysis aims to verify whether the kinetic triplet

efficiently represent the pyrolysis of the biomass at heating rates different from those used to determine these parameters (7.5 K min⁻¹ for intermediate and 15, 30, and 50 K min⁻¹ for higher conversion rates). New thermogravimetric analyses were carried out for the experimental curves of α and $d\alpha/dt$ at extra heating rates according to the methodology described in Sect. "Thermogravimetric analysis and torrefaction pretreatment". The numerical reconstruction of the α and $d\alpha/dt$ curves and the fit quality analysis were carried out as presented in Sect. "Reconstruction of α and $d\alpha/dt$ curves".

Independent parallel reaction model

Unlike the global methods described in the previous sections, the independent parallel reactions model (IPRM) approach is a multi-step kinetic study, i.e., it considers the heterogeneity of the biomass and the presence of multiple decomposition reactions [17, 23]. Thus, the overall theoretical conversion rate can be described as a linear combination

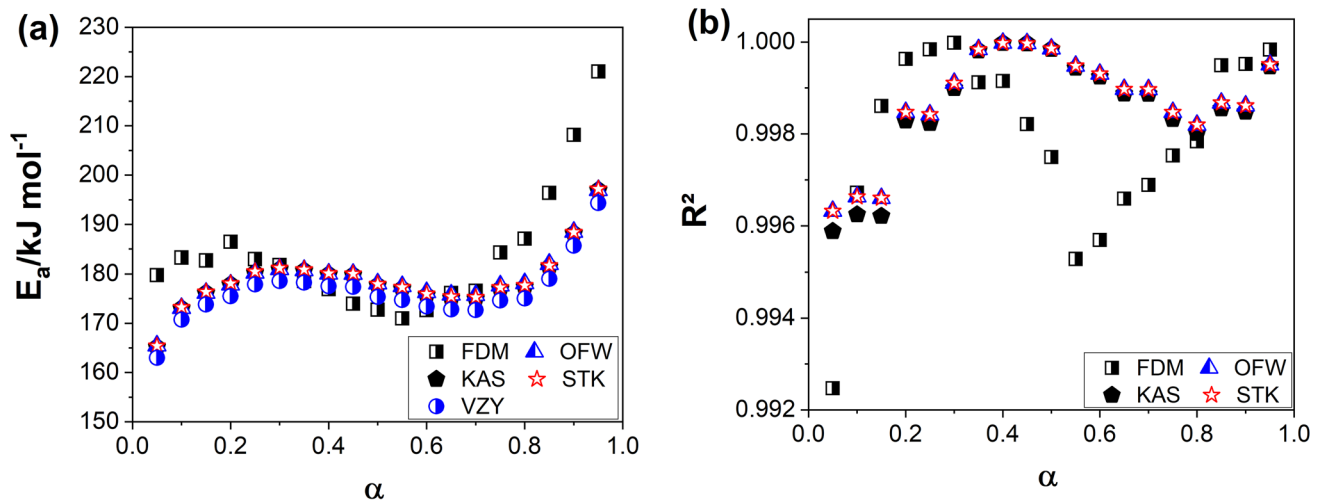


Fig. 7 Activation energy (a) and coefficient of determination (b) for the pyrolysis of the torrefied biomass

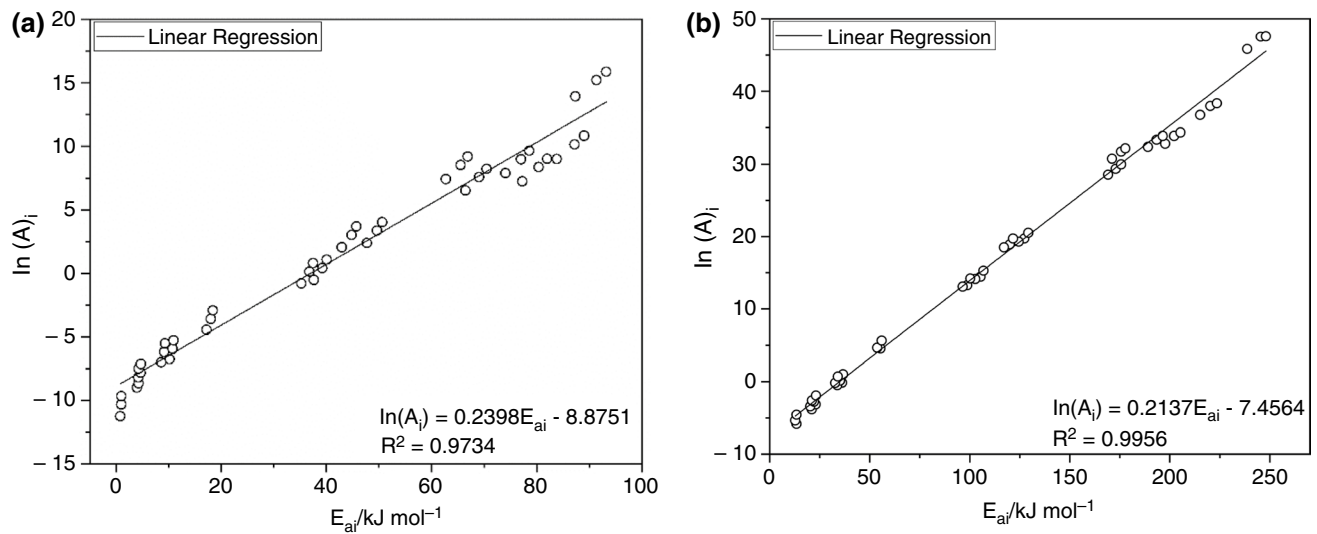


Fig. 8 Linear regression to obtain the compensation effect parameters for raw (a) and torrefied (b) biomass

$$\beta \frac{d\alpha_p}{dT} = k_p (1 - \alpha_p)^{n_p} \quad (11)$$

$$k_p = A_p \exp\left(\frac{-E_{ap}}{RT}\right) \quad (12)$$

where α_p , k_p e n_p are the conversion value, the rate constant, and the reaction order for the pseudo-component p , respectively; z is the number of pseudo-components; and A_p e E_{ap} is the Arrhenius pre-exponential factor and the activation energy for the pseudo-component p . The theoretical conversion and conversion rates were determined by using the fourth-order Runge–Kutta method. The kinetic parameters

were estimated through optimization by the evolutionary differential method using the objective function (OF) shown by Eqs. (13) and (14).

$$\text{LSM_DC}_\sigma = \sum_{j=1}^{\Omega} \left| \left(\beta_\sigma \frac{d\alpha}{dT} \right)_j^{\text{obs}} - \left(\beta_\sigma \frac{d\alpha}{dT} \right)_j^{\text{theo}} \right|^2 \quad (13)$$

$$\text{OF} = \left[\sum_{\sigma=1}^4 \text{LSM_DC}_\sigma \right] \left[\sqrt{\frac{\sum_{\sigma=1}^4 (\text{LSM_DC}_\sigma - \overline{\text{LSM_DC}})^2}{\sigma - 1}} \right] \quad (14)$$

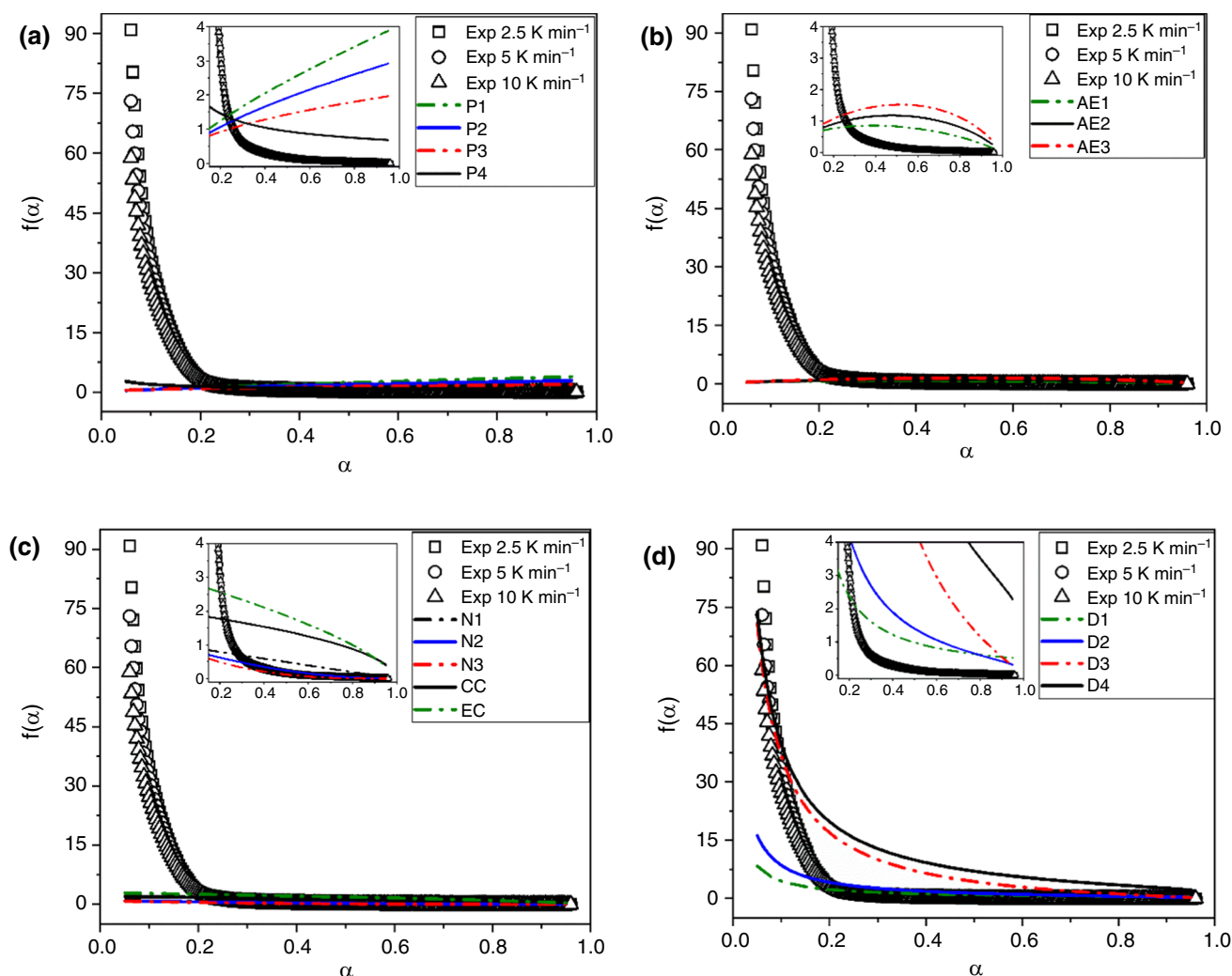


Fig. 9 Theoretical and experimental curves for raw biomass considering **a** Power laws, **b** Avrami–Erofe'ev, **c** Reaction order and contraction geometric, and **d** Diffusional phenomena models

where LSM_DC_σ is the least square method for the derivative conversion and σ is the heating rate counter, which varies from β_1 corresponding to 2.5 K min^{-1} to β_3 of 10 K min^{-1} . The optimization was performed for all heating rates simultaneously to achieve greater robustness of the estimated parameters, in accordance with ICTAC recommendations [18]. The initial parameters were used in accordance with what was explained by Tibola et al. [17] in a previous work of the research group. The numerical calculation was performed using Scilab software (version 6.1.1).

Results and discussion

Table 3 compares the characterization of the raw pineapple crown obtained in this study with other agricultural and industrial residues. The proximate analysis and chemical

composition were consistent with other lignocellulosic biomasses.

Thermal decomposition profile

We used mass loss (TG) and mass loss rate (DTG) curves at heating rates of 2.5, 5, and 10 K min^{-1} to evaluate the behavior of the pineapple crown under thermal decomposition. We did not consider the drying temperature range (first 30 min at 375 K) to eliminate the influence of mass reduction due to biomass moisture [11]. The replicates showed good reproducibility for all heating rates. Figures 2 and 3 show the TG and DTG curves for raw and torrefied biomass, respectively.

The TG (w) and DTG (dw/dt) curves showed similar behavior at different heating rates. However, a higher heating rate slightly shifted the TG curves to the right (Figs. 2a and 3a), which indicates that a certain degree of conversion is

Table 6 Normalized root-mean-square error between theoretical and experimental curves for raw biomass

Model	Normalized Root-Mean-Square Error— NRMSE/ %		
	2.5 K min ⁻¹	5.0 K min ⁻¹	10.0 K min ⁻¹
<i>Nucleation</i>			
P1	15.42	16.55	17.25
P2	15.35	16.44	17.08
P3	15.28	16.35	16.94
P4	14.70	15.60	16.00
AE1	15.24	16.29	16.85
AE2	15.25	16.30	16.87
AE3	15.25	16.30	16.88
<i>Contraction geometric</i>			
CC	14.83	15.76	16.20
EC	14.57	15.43	15.80
<i>Reaction order</i>			
N1	15.12	16.14	16.66
N2	15.15	16.18	16.71
N3	15.18	16.21	16.76
<i>Diffusion phenomena</i>			
D1	13.55	14.16	14.21
D2	11.92	12.11	11.68
D3	7.82	9.69	13.37
D4	10.18	12.83	17.25

achieved at higher temperatures by applying higher heating rates. Furthermore, the height of the DTG peaks increased by increasing the heating rates (Figs. 2b and 3b), representing an increase in the mass loss rate. Previous works have also verified this behavior in the thermogravimetric analysis of sunflower seed husks [17], coconut fiber [28], and cattle manure [29]. This behavior is related to the reduced residence time of the sample at lower temperatures with higher heating rates, leading to degradation at higher temperatures. The increase in the height of the DTG peaks is due to more thermal energy supply that increases the temperature difference between the sample and the surroundings, which favors the mass loss rate [28, 30].

The thermal decomposition of the raw and torrefied biomass occurred in three stages: dehydration (stage I), volatilization (stage II), and carbonization (stage III). Volatilization is an important stage in kinetic analysis since it includes the decomposition of hemicellulose and cellulose and the partial decomposition of lignin. Hemicellulose is the less thermally stable compound since it comprises several branched polysaccharides with low molecular mass. The decomposition of hemicellulose occurs between 513 and 663 K. The decomposition of cellulose occurs between 533 and 633 K, and its thermal stability is attributed to the linear and unbranched structure formed by D-glucose units. Lignin is the most

difficult compound to decompose, mainly because it is a complex and amorphous molecule formed by several phenylpropane units, and its decomposition occurs between 473 and 1123 K [11, 30, 31].

Considering these decomposition temperature ranges, the first peak in the DTG curves of raw biomass (Fig. 2b) corresponded to the devolatilization of hemicellulose, and the second main peak referred to the devolatilization of cellulose. A specific peak for lignin is not observed since it gradually decomposes over a wide range of temperatures [11, 30]. The DTG curves for torrefied biomass (Fig. 3a) showed only one peak. This occurs because torrefaction partially decomposes hemicellulose, the less thermally stable compound [32].

Table 4 presents the parameters of the three stages of material decomposition, where T_i and T_f are the initial and final temperature, respectively, and $T_{\max}$ is the temperature at which the maximum mass loss rate occurs $((dw/dt)_{\max})$. These results indicate that the volatilization stage occurred in a narrower range for torrefied biomass. This fact confirms that the torrefaction pretreatment decomposed the less thermally stable portion of the raw biomass [9, 23]. The value of $T_{\max}$ for volatilization, which is the temperature of highest mass loss related to the decomposition of cellulose, did not change after the torrefaction process. This indicates that the pretreatment did not decompose the cellulose [23].

Isoconversional methods

The thermogravimetric data from the volatilization stage are applied to the isoconversional methods FDM, OFW, KAS, STK, and VZK to obtain the activation energy for the decomposition of raw and torrefied biomass.

Determination of the activation energy for raw biomass

Figure 4 presents the linear regressions for the FDM, OFW, KAS, and STK methods for the volatilization stage of the raw biomass. The degree of conversion (α) varied between 0.05 and 0.95, with a step size of 0.05. We can observe that the FDM method (Fig. 4a) showed a distinct behavior from other methods, presenting zones of concavity change between the straight lines. This behavior occurs because the FDM method is the only differential method and depends on the conversion rate $(d\alpha/dt)$, presenting higher sensitivity than integral methods. The changes in concavities indicate the occurrence of multiple reactions. The first zone ($0.05 \leq \alpha \leq 0.35$) probably represents the decomposition of hemicellulose, while the second zone ($0.40 \leq \alpha \leq 0.95$) corresponds to the decomposition of cellulose [23].

The linearization of the integral methods (OFW, KAS, and STK) also presented two conversion zones, represented by groups of parallel straight lines. The first group

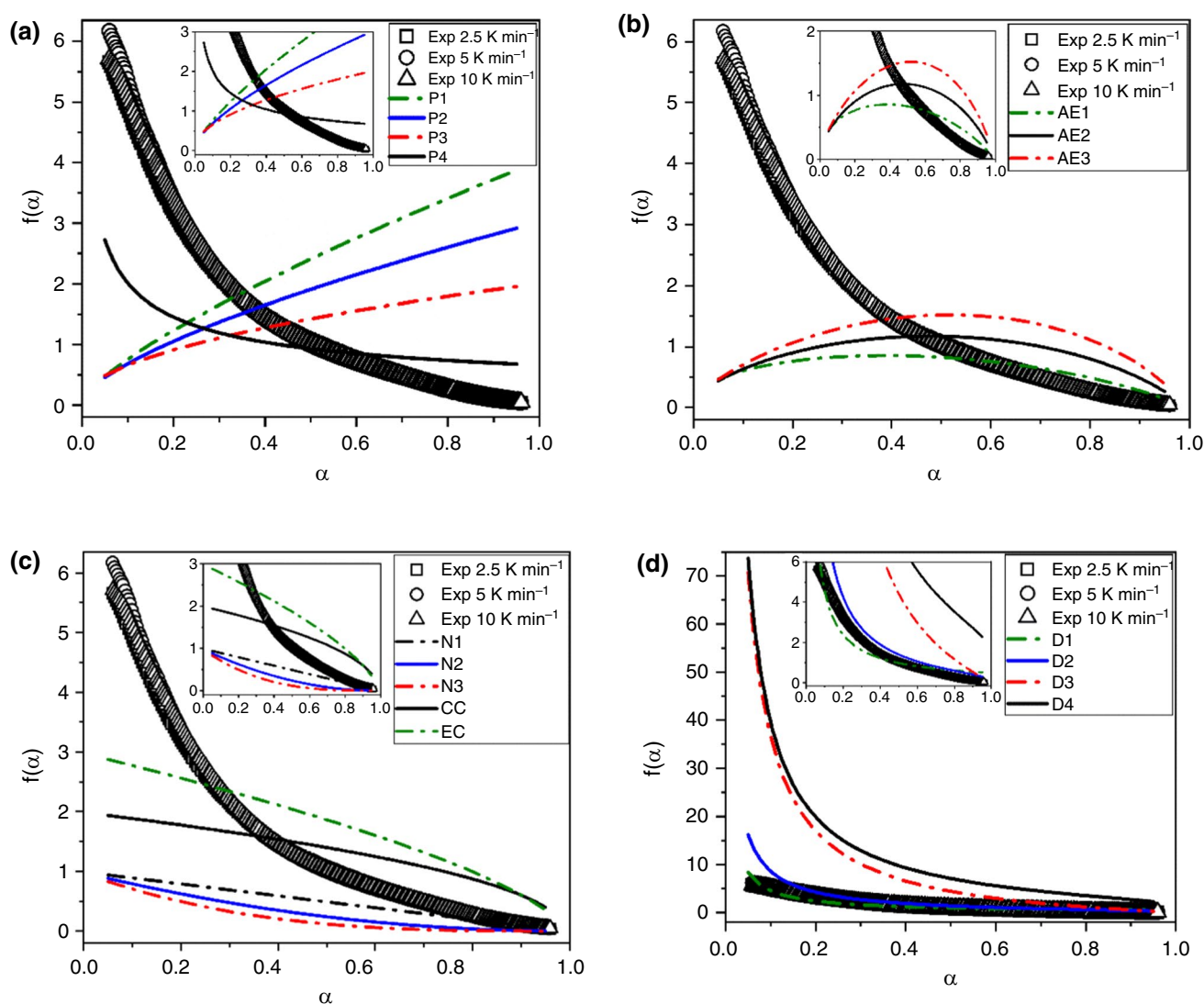


Fig. 10 Theoretical and experimental curves for torrefied biomass considering **a** Power laws, **b** Avrami–Erofe'ev, **c** Reaction order and contraction geometric, and **d** Diffusional phenomena models

($0.05 \leq \alpha \leq 0.35$) corresponds to more distant lines and is probably equivalent to the decomposition of hemicellulose. The second group ($0.40 \leq \alpha \leq 0.95$) corresponds to the closest lines and is equivalent to the decomposition of cellulose [23]. We did not identify a specific zone for the decomposition of lignin since it has a wide decomposition temperature range [10]. Figure 5 presents the activation energy for the FDM, OFW, KAS, STK, and VZK methods and the coefficient of determination (R^2) for the classical isoconversional methods.

Figure 5 shows several fluctuations in the distribution of E_a values for all isoconversional methods, tending to increase as the conversion progresses. In addition, the variation of E_a with conversion indicates the existence of multi-step reactions. This behavior is related to the difference

in the thermal stability of the biomass compounds. The decomposition of hemicellulose, which is the less thermally stable compound, occurs between $0.05 \leq \alpha \leq 0.35$ ($E_{a0} = 138.77 \pm 19.64 \text{ kJ mol}^{-1}$), and the decomposition of cellulose occurs between $0.40 \leq \alpha \leq 0.95$. Therefore, more energy is required for decomposition in the final conversion phase ($E_{a0} = 170.60 \pm 7.43 \text{ kJ mol}^{-1}$). Arenas, Navarro and Martinez [14] and He et al. [33] also observed an increase in E_a values in the pyrolysis of orange peel and pine wood, respectively. The average E_{a0} value for the entire process, considering all isoconversional methods, was $158.87 \pm 20.49 \text{ kJ mol}^{-1}$. Figure 5 shows that the linear regressions for the isoconversional methods presented a good fit, with R^2 higher than 0.990 for the conversion range of $0.05 \leq \alpha \leq 0.40$ and $0.80 \leq \alpha \leq 0.95$. The lower values for

Table 7 Normalized root-mean-square error between theoretical and experimental curves for torrefied biomass

Model	Normalized Root-Mean-Square Error—NRMSE (%)		
	2.5 K min ⁻¹	5.0 K min ⁻¹	10.0 K min ⁻¹
<i>Nucleation</i>			
P1	44.78	42.76	45.27
P2	38.28	37.04	39.07
P3	33.21	32.62	34.31
P4	20.23	20.81	21.70
AE1	29.89	29.74	31.30
AE2	29.44	29.39	30.81
AE3	29.49	29.44	30.78
<i>Contraction geometric</i>			
CC	20.56	21.27	21.91
EC	16.83	17.62	17.78
<i>Reaction order</i>			
N1	28.89	28.68	30.30
N2	30.81	30.34	32.17
N3	32.21	31.56	33.54
<i>Diffusion phenomena</i>			
D1	8.70	8.18	9.43
D2	33.41	28.43	31.84
D3	250.37	227.10	246.32
D4	281.60	255.83	277.22

R^2 in the range of $0.45 \leq \alpha \leq 0.75$ can be attributed to the heterogeneity of biomass and complex reactions [18].

Table 5 compares E_a values for different biomasses using isoconversional methods. The average E_a value obtained in this study aligned well with those calculated in previous studies, presenting an intermediate value compared to those shown in Table 5. Among the isoconversional methods, VZK presented the lowest standard deviation, with E_{a0} of 154.56 ± 20.22 kJ mol⁻¹. Thus, we considered the average E_a value from the VZK method to determine the other kinetic parameters.

Determination of the activation energy for torrefied biomass

Figure 6 shows the linear regressions for the same isoconversional methods for the decomposition of torrefied biomass. Similar to raw biomass results, the FDM method showed a distinct behavior from the other methods due to the presence of concavities. However, we can observe a single conversion zone ($0.20 \leq \alpha \leq 0.85$) in Fig. 6a, which mainly refers to the decomposition of cellulose. The OFW, KAS, and STK methods presented a group of parallel straight lines in the same decomposition range. The E_{a0} value for this conversion range was 178.23 ± 3.14 kJ mol⁻¹. The presence of a single

conversion zone is due to torrefaction pretreatment in which the temperature was sufficient to decompose hemicellulose [10]. Figure 7 shows the E_a and R^2 values as a function of the conversion for torrefied biomass.

Figure 7a shows that the E_a value variation decreased compared to the raw biomass. The NRMSE values in the range of $0.20 \leq \alpha \leq 0.85$ were 3.65% for the KAS, OFW, STK, and VZK methods. For the FDM method, the NRMSE values were 14.87% due to the greater sensitivity of the method. The E_{a0} value for the entire conversion range was 179.35 ± 7.52 kJ mol⁻¹. The VZK method presented the lowest standard deviation, with $E_{a0} = 176.33 \pm 6.20$ kJ mol⁻¹. Then, it was used to determine the other kinetic parameters. Figure 7b shows that the linearization of the isoconversional methods presented a good fit, with R^2 higher than 0.995 for almost all conversion values.

The energy barrier for the decomposition of torrefied biomass was higher than the raw biomass. Chen et al. [10] and Lopes and Tannous [23] reported similar results for rice husk and coconut fiber, respectively. The torrefaction reduces the portion of the less thermally stable compounds (hemicellulose) and can remove hydroxyl bonds from cellulose, producing an intermediate cellulose with double bonds between carbons and higher thermal stability. Despite the increase in activation energy, the improvement in the properties of pyrolysis products justifies the pretreatment [10].

Determination of the global pre-exponential factor

The global pre-exponential factor (A) is a kinetic parameter related to the frequency of molecular collisions. It can be obtained by the compensation effect based on the activation energy previously estimated. We generated a set of 48 pairs of E_{ai} and $\ln(A)_i$ for raw and torrefied biomass using the Coats–Redfern method associated with 16 reaction models (Table 2). Figure 8a and b presents the linear regressions for this set of pairs of E_{ai} and $\ln(A)_i$ for raw and torrefied biomass, respectively.

Figure 8 shows that the linear regression fitted to the data well, with R^2 of 0.973 and 0.996 for raw and torrefied biomass, respectively. The compensation parameters were $a = 0.2398$ and $b = -8.8751$, for raw biomass, and $a = 0.2137$ and $b = -7.4564$ for torrefied biomass. Based on the compensation parameters, we determined the global pre-exponential factor (A_0) from the E_{a0} of the isoconversional methods. The A_0 for raw and torrefied biomass was 1.75×10^{12} and 1.34×10^{13} s⁻¹, respectively.

Determination of the reaction model

We can evaluate the predominant reaction mechanism in the decomposition of raw and torrefied biomass by comparing experimental curves, constructed with A_0 and E_{a0} values,

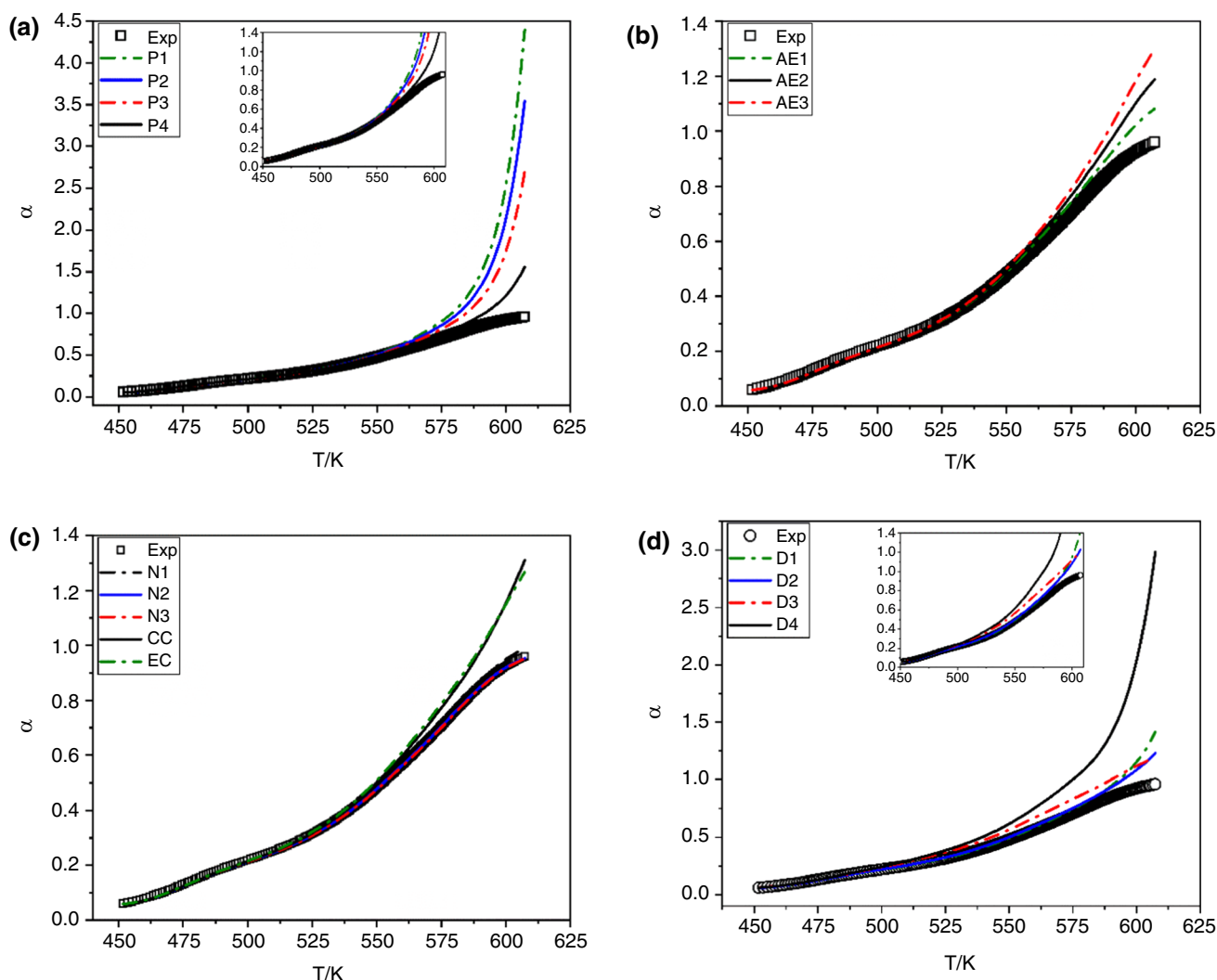


Fig. 11 Theoretical and experimental curves of α as a function of T for raw biomass ($\beta = 5.0 \text{ K min}^{-1}$) using **a** Power laws, **b** Avrami–Erofe'ev, **c** Reaction order and contraction geometric, and **d** Diffusional phenomena models

and theoretical curves, representing the conventional kinetic models.

Comparison of $f(\alpha)$ curves for raw biomass

Figure 9 presents the numerically constructed curves with the Arrhenius parameters calculated for raw biomass compared to theoretical conversion functions for heating rates of 2.5, 5, and 10 K min^{-1} . We can observe that no model completely overlapped the experimental data, which was expected due to the complexity of biomass pyrolysis. In general, the behavior of experimental curves shows a decrease in $f(\alpha)$ as conversion progresses until $f(\alpha)$ reaches zero, meaning that there is consumption of the material as conversion values increase and the material is completely consumed at the end of the reaction. Some theoretical models do not respect this behavior, as is the case with power law models

(from P1 to P4). Diffusional phenomena model best fitted to the experimental data (Fig. 9d).

The LSM and NRMSE evaluated the fit quality of the $f(\alpha)$ curves. Table 6 presents the NRMSE values for all conversion functions studied. The D3 diffusional model presented the smallest deviations for heating rates of 2.5 and 5 K min^{-1} , with an NRMSE of 7.82% and 9.69%, respectively. At the heating rate of 10 K min^{-1} , the D2 diffusional model best represented the process, with an NRMSE of 11.68%. Therefore, the D3 diffusional model is more suitable for modeling the slow pyrolysis of the pineapple crown since it showed the smallest deviations at 2.5 and 5 K min^{-1} and a small deviation at 10 K min^{-1} . Diffusional models were also the most suitable for representing the pyrolysis of other biomasses. El-Sayed and Mostafa [39], Tibola et al. [17], and Lopes and Tannous [23] also determined the D3 diffusional model to represent the pyrolysis of olive pomace,

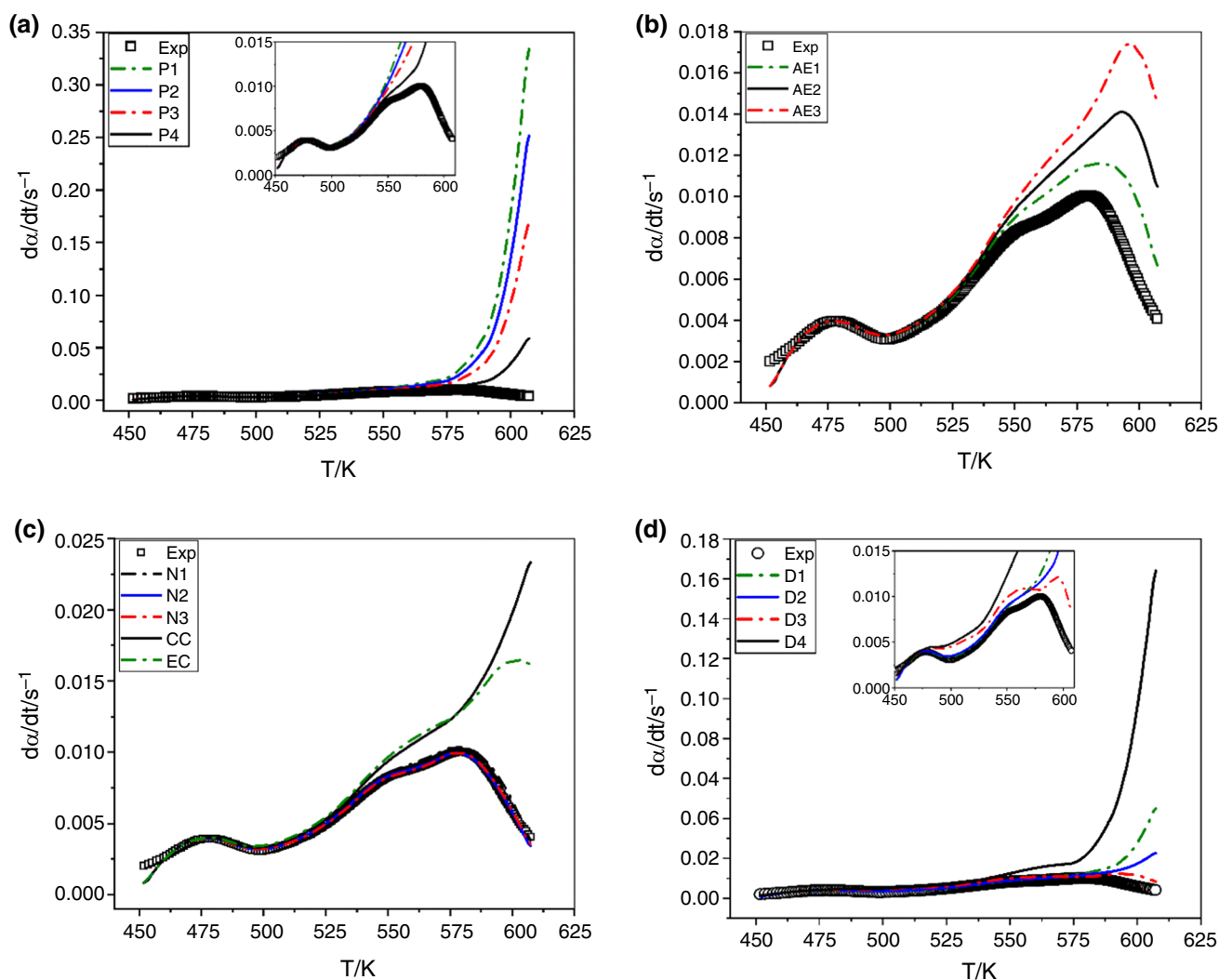


Fig. 12 Theoretical and experimental curves of da/dt as a function of T for raw biomass ($\beta = 5.0 \text{ K min}^{-1}$) using **a** Power laws, **b** Avrami-Erofe'ev, **c** Reaction order and contraction geometric, and **d** Diffusional phenomena models

coconut fiber, and sunflower seed husk, respectively. Some studies described the reaction order model as more appropriate, such as the pyrolysis of sewage sludge in which the N2 reaction order model (second-order) mechanism was predominant during the process [40].

Comparison of $f(\alpha)$ curves for torrefied biomass

Figure 10 shows the theoretical and experimental curves for the pyrolysis of torrefied biomass at heating rates of 2.5, 5, and 10 K min^{-1} . Table 7 presents the NRMSE values for the torrefied biomass.

We can observe that the D1 diffusional model ($f(\alpha) = 1/2\alpha$) best fitted to the data, presenting an NRMSE of 8.70%, 8.18%, and 9.43% for the heating rates of 2.5, 5, and 10 K min^{-1} , respectively. Lignocellulosic biomass is a

heterogeneous material, and its thermal decomposition is complex, with parallel and competitive reactions and different conversion functions. However, determining a global conversion function is sufficient to mathematically represent the pyrolysis process if the theoretical representation of the experimental data is efficient [41]. The ICTAC recommends the numerical reconstruction of the α and da/dt curves to validate the calculated kinetic triplet [11].

Reconstruction of the α and da/dt curves

The experimental α and da/dt curves as a function of temperature were reconstructed to assess whether the kinetic parameters efficiently represent the pyrolytic decomposition of the pineapple crown. We considered the 16 reaction models presented in Table 2.

Table 8 Normalized root-mean-square error between theoretical and experimental curves of α and $d\alpha/dt$ for raw biomass

Model	NRMSE $_{\alpha}$ /%			NRMSE $_{d\alpha/dt}$ /%		
β / K min $^{-1}$	2.5	5.0	10.0	2.5	5.0	10.0
<i>Nucleation</i>						
P1	76.50	62.95	55.90	718.44	602.55	506.40
P2	57.67	47.45	42.14	539.57	452.40	380.03
P3	38.84	31.96	28.39	360.68	302.23	253.64
P4	13.84	11.38	10.14	121.90	101.75	84.88
AE1	4.90	4.10	3.81	18.61	15.17	12.37
AE2	8.63	7.25	6.71	35.38	28.91	23.54
AE3	12.45	10.48	9.68	53.04	43.42	35.44
<i>Contraction geometric</i>						
CC	10.95	9.14	8.37	59.74	48.91	40.08
EC	11.20	9.41	8.76	47.70	38.77	31.43
<i>Reaction order</i>						
N1	1.49	1.21	1.15	4.65	3.85	3.81
N2	0.40	0.43	0.43	1.76	1.74	2.59
N3	0.58	0.60	0.60	1.48	1.52	2.29
<i>Diffusion phenomena</i>						
D1	10.79	8.87	7.93	91.88	76.54	63.63
D2	7.89	6.54	6.00	48.12	39.44	32.24
D3	13.06	11.01	10.86	27.35	21.24	18.48
D4	54.13	45.08	41.12	377.89	313.23	259.66

Validation of the kinetic triplet for raw biomass

Figures 11 and 12 show theoretical and experimental curves of α and $d\alpha/dt$ as a function of T , respectively, for raw biomass at the heating rate of 5 K min $^{-1}$. We focused on discussing the results for the heating rate of 5 K min $^{-1}$ since the behavior of the curves at different heating rates was similar. Table 8 presents the NRMSE values for all models and heating rates.

Although the results presented in Sect. "Determination of the reaction model" showed that the D3 diffusional model was the most suitable, Figs. 11 and 12 indicate that it was not the best fit to the thermogravimetric experimental curves. The numerical reconstruction of the α and $d\alpha/dt$ curves using the D3 diffusional model showed an NRMSE of 11.01% and 21.24%, respectively, for the heating rate of 5 K min $^{-1}$. However, the reaction order models practically overlapped with the experimental data. The N2 reaction order model was the most suitable to represent the α curves, with an NRMSE of 0.43%, and the N3 reaction order model was the most suitable for the $d\alpha/dt$ curves, with an NRMSE of 1.52%. Since the $d\alpha/dt$ curves have greater sensitivity, the N3 reaction order model proved to be more suitable to represent the pyrolysis reaction. This divergence is because the methodology was developed for homogeneous materials with a single-step decomposition reaction. Furthermore, the kinetic

triplet with $E_{a0} = 154.56$ kJ mol $^{-1}$, $A_0 = 1.75 \times 10^{12}$ s $^{-1}$, and $f(\alpha) = (1 - \alpha)^3$ (third-order reaction model) effectively represented the slow pyrolysis of the raw pineapple crown, with an NRMSE of 1.52%.

Validation of the kinetic triplet for torrefied biomass

Figures 13 and 14 present the theoretical and experimental curves of α and $d\alpha/dt$ as a function of T , respectively, for the heating rate of 5 K min $^{-1}$. (The behavior of the curves for the rates of 2.5 and 10 K min $^{-1}$ was similar.) Table 9 presents the NRMSE values for all reaction models at all heating rates. The NRMSE values for the D1 diffusional model, which was the most suitable model in Sect. "Results and discussion", were 1.05% and 7.95% for α and $d\alpha/dt$ curves, respectively, for the heating rate of 5 K min $^{-1}$. However, the reaction order "n" models presented small deviations. The N2 reaction order model showed the smallest NRMSE value for the $d\alpha/dt$ curves (curves that present greater sensitivity) with an NRMSE of 2.50%.

The methodology for determining kinetic triplet using isoconversional methods and the compensation effect recommended by ICTAC were based on homogeneous materials, with constant activation energy or small variation by increasing the conversion. However, the kinetic triplet considering a single conversion function has been efficiently

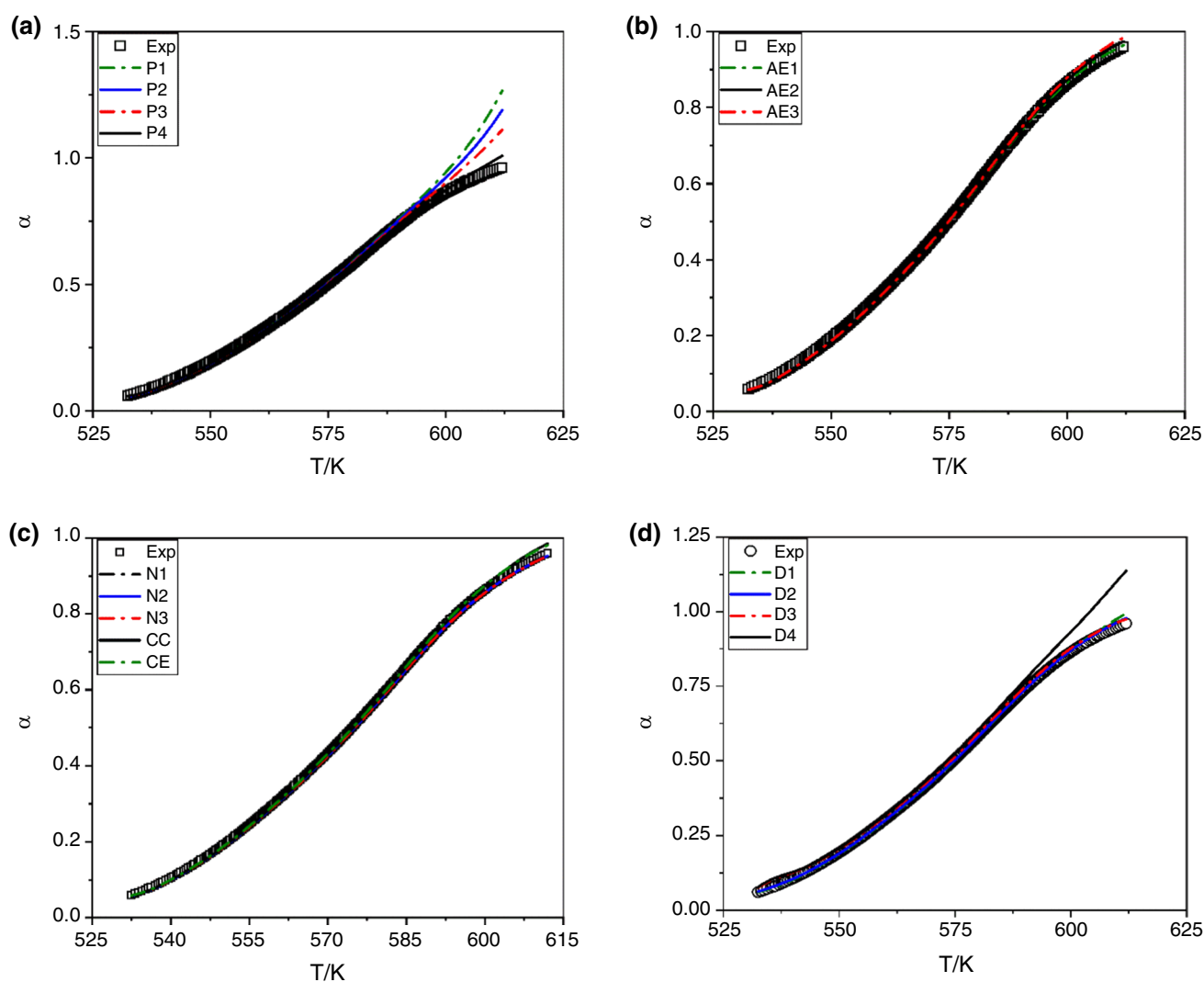


Fig. 13 Theoretical and experimental curves of α as a function of T torrefied biomass ($\beta = 5.0 \text{ K min}^{-1}$) using **a** Power laws, **b** Avrami–Erofe'ev, **c** Reaction order and contraction geometric, and **d** Diffusional phenomena models

used to represent pyrolytic reactions of various heterogeneous biomasses [13, 14, 17, 34, 35, 37, 38, 41–43], resulting in a mathematical representation of a single-equation and facilitating the simulation and optimization of the pyrolysis process.

This study identified the kinetic triplet for the pyrolysis of pineapple residues via the compensation effect. The results for the theoretical curves of α and da/dt were accurate since the NRMSE values for experimental data were low, achieving a maximum magnitude of 2.50%. Therefore, this study compared the theoretical and experimental curves of α and da/dt considering all reaction models shown in Table 2 since the comparison between theoretical and experimental conversion functions did not identify the best possible mathematical representation for the

kinetic triplet. The results highlighted the efficiency of the compensation effect in determining the kinetic triplet for the pyrolysis of heterogeneous materials. They also suggested that the numerical reconstruction of theoretical and experimental curves of α and da/dt can be carried out for all possible conversion functions to determine the kinetic triplet that provides the best theoretical representation for the pyrolytic reaction. Table 10 presents the kinetic triplet obtained for the raw and torrefied pineapple crown.

Application of the kinetic triplet

The kinetic triplet estimated for the raw and torrefied biomass were applied to the numerical construction of α and da/dt curves for the heating rates of 7.5 (intermediate value

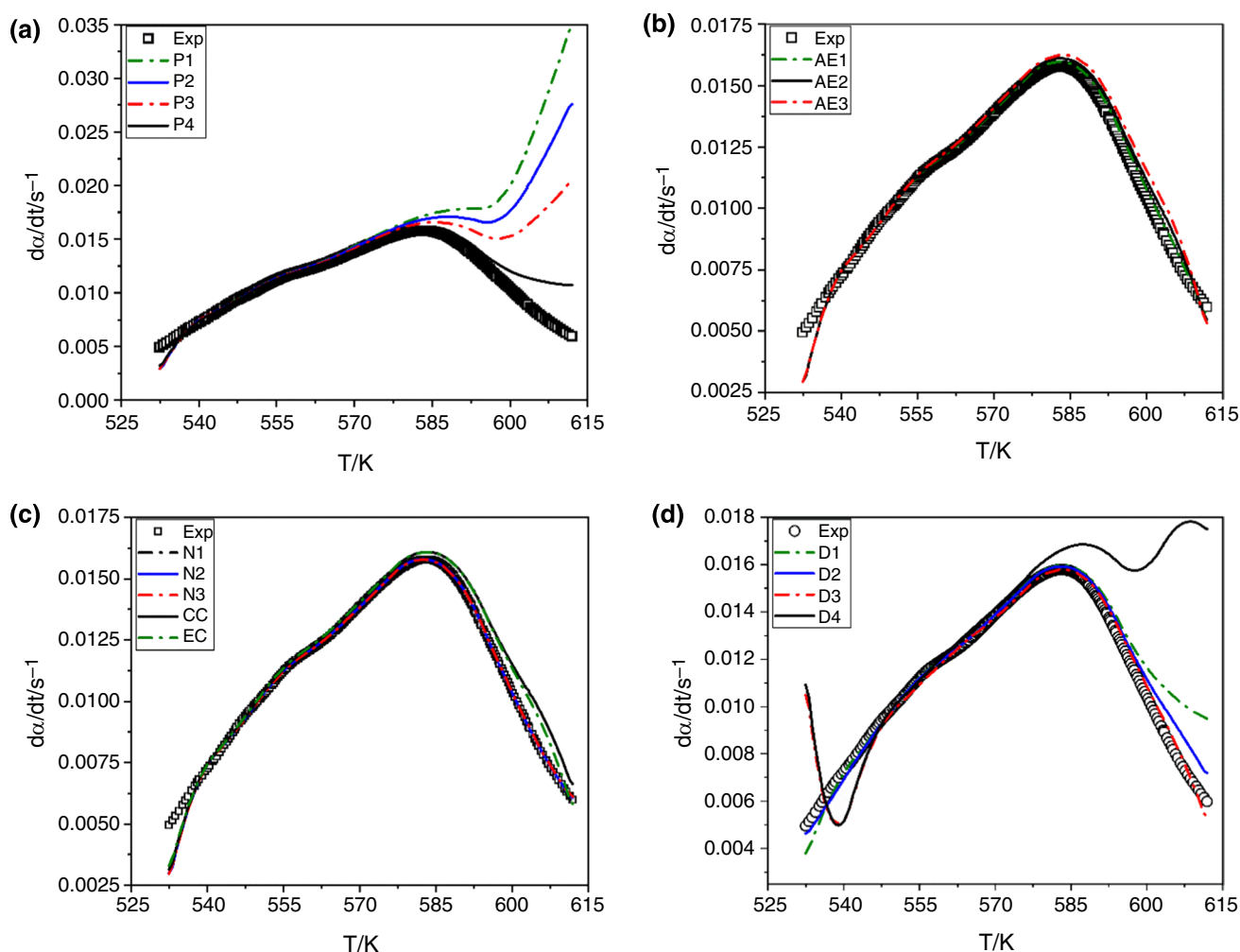


Fig. 14 Theoretical and experimental curves of $d\alpha/dt$ as a function of T for torrefied biomass ($\beta = 5.0 \text{ K min}^{-1}$) using **a** Power laws, **b** Avrami-Erofe'ev, **c** Reaction order and contraction geometric, and **d** Diffusional phenomena models

between those used to estimate the parameters) and 15, 30, and 50 K min^{-1} (higher heating rates). We compared the theoretical and experimental curves of α and $d\alpha/dt$ to evaluate the efficiency in representing the decomposition of the biomass at different heating rates. Figures 15 and 16 show the theoretical and experimental curves of α and $d\alpha/dt$ for raw and torrefied biomass, respectively, and Table 11 shows the NRMSE values. The results indicated that the kinetic triplet estimated in this study can efficiently represent the slow pyrolysis of the raw and torrefied pineapple crown in reactor simulation and optimization, including at different heating rates. The highest NRMSE value was 4.62%.

Independent parallel reaction model

The parallel and independent reactions model allows multi-step kinetic modeling and the estimation of kinetic

parameters for the different decomposition reactions of a heterogeneous material independently. Figures 17 and 18 show the adjustment for the conversion and conversion rate curves considering the heating rate of 5 K min^{-1} for the raw pineapple crown and after the torrefaction treatment, respectively. The adjustment of the curves for the rates of 2.5 and 10 K min^{-1} is presented in supplementary material.

It can be observed in Fig. 17b that four reactions were modeled for the decomposition of the raw pineapple crown: the main decomposition of extractives (R1), hemicellulose (R2), cellulose (R3), and lignin (R4). The adoption of four pseudo-components for the representation of biomass decomposition has already been reported in the literature [44, 45]. According to Mészáros et al. [46], the decomposition of extractives begins at lower temperatures (around 450 K), and thus, the first reaction (R1) was related to the majority decomposition of these components. The large

Table 9 Normalized root-mean-square error between theoretical and experimental curves of α and $d\alpha/dt$ for torrefied biomass

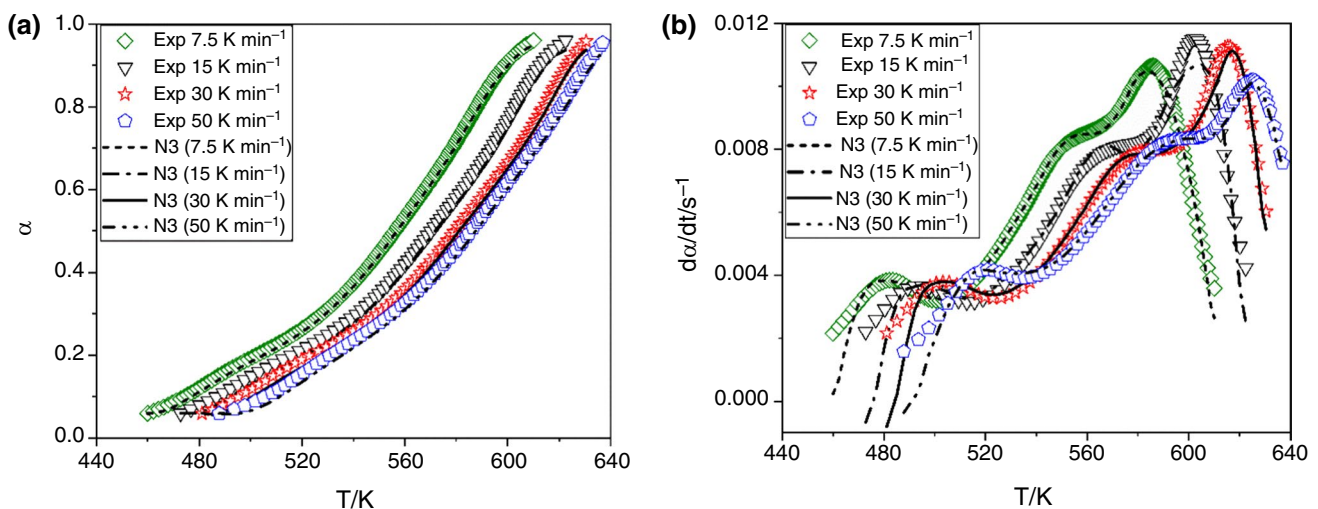
Model	NRMSE $_{\alpha}$ (%)			NRMSE $_{d\alpha/dt}$ (%)		
β / K min $^{-1}$	2.5	5	10.0	2.5	5	10.0
<i>Nucleation</i>						
P1	10.23	8.90	7.95	65.16	62.14	57.26
P2	7.63	6.62	5.90	48.94	46.67	42.98
P3	5.03	4.36	3.87	32.73	31.21	28.72
P4	1.65	1.42	1.26	11.15	10.64	9.74
AE1	0.69	0.66	0.65	3.07	3.14	3.02
AE2	0.95	0.86	0.78	4.32	4.18	3.85
AE3	1.39	1.25	1.10	5.83	5.50	4.96
<i>Contraction geometric</i>						
CC	1.18	1.04	0.92	5.81	5.44	4.94
EC	1.14	1.01	0.88	4.89	4.54	4.07
<i>Reaction order</i>						
N1	0.77	0.78	0.79	2.34	2.54	2.57
N2	0.94	0.94	0.94	2.29	2.50	2.56
N3	0.99	0.99	0.99	2.30	2.52	2.57
<i>Diffusion phenomena</i>						
D1	1.22	1.05	0.94	8.35	7.95	7.23
D2	0.72	0.60	0.53	4.32	3.95	3.54
D3	1.81	1.72	1.63	8.60	7.96	8.76
D4	7.31	6.58	5.92	34.43	31.90	29.78

Table 10 Kinetic triplet for the pyrolysis of raw and torrefied pineapple crown

Material	Kinetic triplet		
	$E_{a0}/\text{kJ mol}^{-1}$	A_0/s^{-1}	$f(\alpha)$
Raw biomass	154.56	1.75×10^{12}	N3
Torrefied biomass	176.33	1.34×10^{13}	N2

peak with shoulder observed in Fig. 16b encompasses the main decomposition of hemicelluloses, celluloses, and lignin according to the degradation temperature ranges reported for these components in the literature [11, 30, 31].

It can be observed in Fig. 18b that the decomposition of the torrefied material was modeled with two main reactions, referring to the majority decomposition of cellulose and

**Fig. 15** Theoretical and experimental curves for raw biomass at heating rates of 7.5, 15.0, 30.0, and 50 K min $^{-1}$: **a** α versus T ; **b** $d\alpha/dt$ versus T

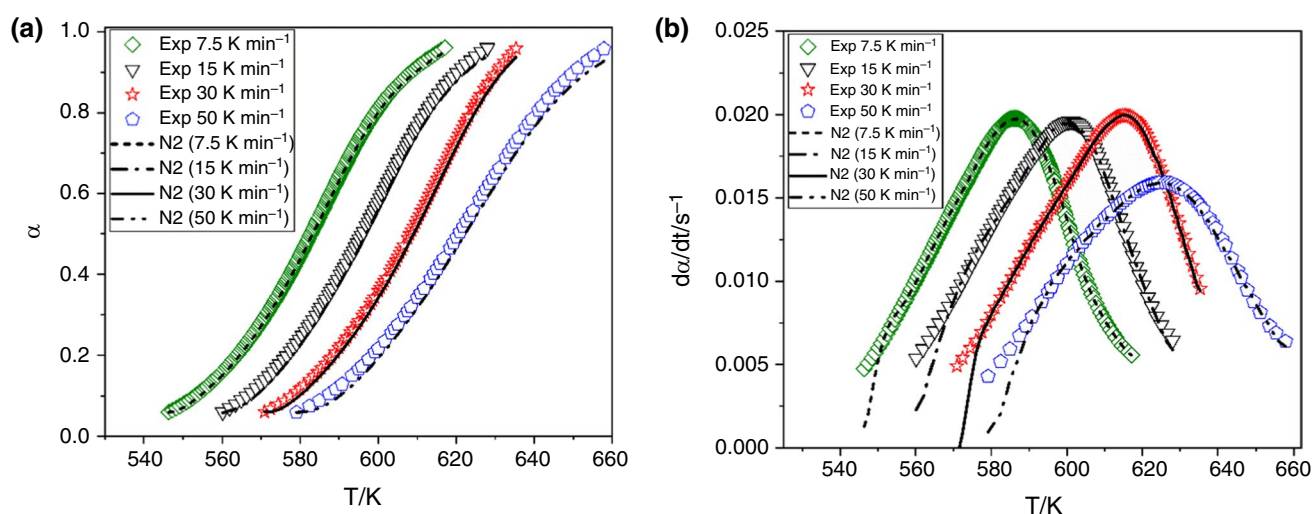


Fig. 16 Theoretical and experimental curves for biomass torrefied at the heating rates of 7.5, 15.0, 30.0, and 50 K min⁻¹: **a** α versus T ; **b** $d\alpha/dt$ versus T

Table 11 Normalized root-mean-square error for theoretical and experimental curves of α and $d\alpha/dt$

Heating rates /K min ⁻¹	Raw biomass		Torrefied biomass	
	NRMSE $_{\alpha}$ (%)	NRMSE $_{d\alpha/dt}$ (%)	NRMSE $_{\alpha}$ (%)	NRMSE $_{d\alpha/dt}$ (%)
7.5	0.87	2.50	0.93	2.01
15.0	1.67	4.62	1.84	2.91
30.0	1.72	4.14	1.84	3.99
50.0	1.76	3.00	2.61	4.22

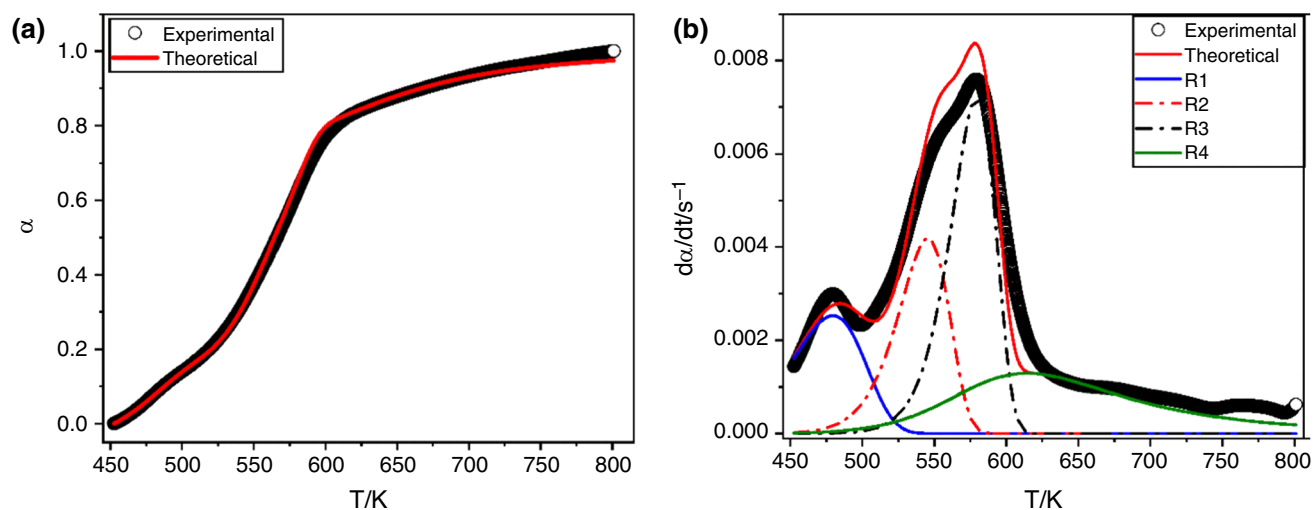


Fig. 17 Modeling of the conversion **(a)** and conversion rate **(b)** for raw biomass obtained by IPRM for 5 K min⁻¹

lignin (R3 and R4). The reduction of pseudo-components occurs due to compositional changes caused by the torrefaction treatment. The optimal kinetic parameters E_{ap} , A_p e n_p obtained for the pseudo-components of the decomposition of

raw and torrefied pineapple crown are presented in Table 12. It is important to highlight that the optimization was performed for the heating rates of 2.5, 5, and 10 K min⁻¹ simultaneously, according to the ICTAC recommendation [18].

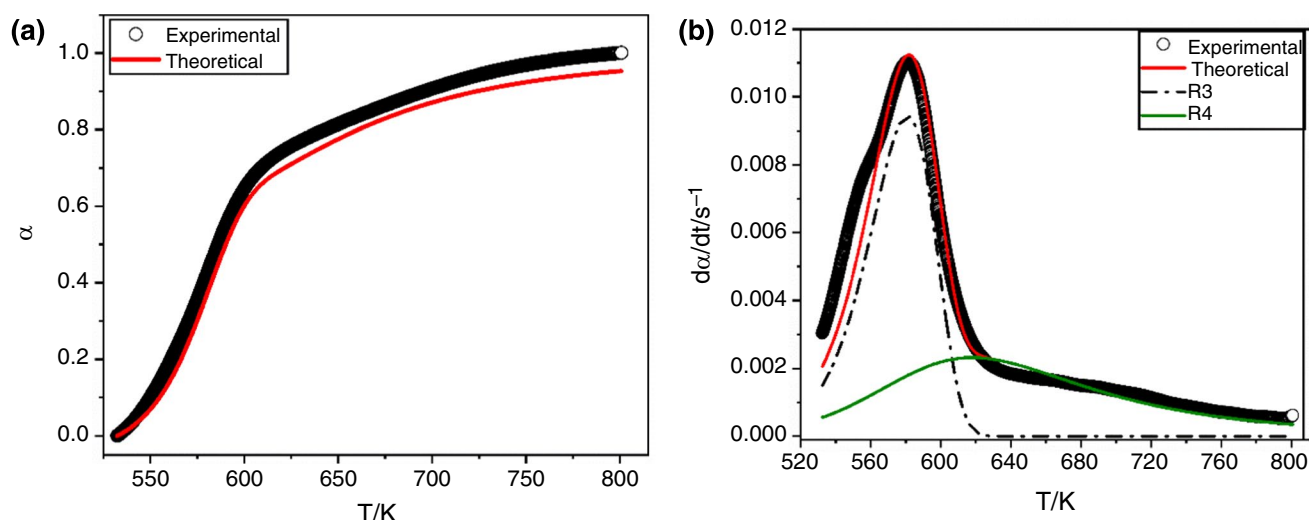


Fig. 18 Modeling of the conversion **(a)** and conversion rate **(b)** for torrefied biomass obtained by IPRM for 5 K min⁻¹

Table 12 Kinetic parameters and their respective deviations for IPRM

Material	Parameters	R1	R2	R3	R4	β	NRMSE _{α} (%)	NRMSE _{dα/dt} (%)
Raw biomass	c_p	0.15	0.23	0.27	0.15	2.5	2.76	6.63
	A_p/s^{-1}	1.99×10^5	5.74×10^{10}	4.02×10^{13}	2.91×10^4	5	1.24	5.72
	$E_{ap}/\text{kJ mol}^{-1}$	71.61	136.68	176.12	84.59	10	2.34	7.58
	n_p	1	1	1	3	—	—	—
Torrefied biomass	c_p	—	—	0.53	0.47	2.5	1.72	3.99
	A_p/s^{-1}	—	—	4.48×10^{10}	2.89×10^4	5	4.22	5.11
	$E_{ap}/\text{kJ mol}^{-1}$	—	—	144.72	85.43	10	7.37	7.47
	n_p	—	—	1	3	—	—	—

The estimated activation energy values are in the same range of values obtained in studies presented in the literature for different biomasses. The activation energy for the decomposition of extractives was estimated in the range of 43.0–208.0 kJ mol⁻¹, according to Sfakiotakis and Vamvuka [44] and Xavier et al. [45]. The values obtained for the decomposition of hemicellulose, cellulose, and lignin were verified in the ranges of 90.45–150.60 kJ mol⁻¹, 132.10–196.30 kJ mol⁻¹, and 32.2–100.0 kJ mol⁻¹, respectively [17, 18, 45, 47].

The parallel and independent reactions methodology presented good adjustments to the experimental data (with a maximum NRMSE value of 7.58% for the conversion rate), but the deviations verified for the IPRM were higher compared to the global methods, a fact that highlights the efficiency of the parameters obtained in global method.

The curves were reconstructed for rates of 7.5, 15, 30, and 50 K min⁻¹ for IPRM. The adjustments and NRMSE values are shown in supplementary material. The deviations obtained are in the range 1.76–9.49% for the conversion

curves and 4.81–13.85% for conversion rate curves. The higher NRMSE values compared to the reconstruction performed using the global parameters indicate that the models obtained by IPRM did not reproduce the biomass pyrolysis as efficiently for heating rates different from those used in the estimation of these parameters.

Conclusions

This study evaluated the pyrolysis of raw and torrefied pineapple crown by determining the kinetic triplet. The single-step kinetic modeling exposed that the global activation energy values were higher for torrefied biomass (176.33 kJ mol⁻¹) than for raw biomass (154.56 kJ mol⁻¹) due to the decomposition of the less thermally stable compound during torrefaction. The other global kinetic parameters estimated were A_0 of 1.75×10^{12} s⁻¹ and N3 as $f(\alpha)$ for raw biomass; A_0 of 1.34×10^{13} s⁻¹ and N2 as $f(\alpha)$ for the previously torrefied material. The compensation effect

methodology was effective in determining the kinetic triplet for the heterogeneous material with NRMSE values lower than 2.50%. These parameters also successfully represented the pyrolysis at different heating rates from those used in determining these parameters. Obtaining such effective kinetic parameters was possible due to numerical reconstruction of the conversion and conversion rate curves for all theoretical conversion functions, and therefore, this study highlights the need to perform this step to obtain the most suitable kinetic triplet to represent the pyrolysis. This work focused on the kinetic study of the raw and torrefied pineapple crown, and the results were effective; future work can be carried out to expand the study of pyrolysis as a possible destination for this residue. As suggestions for the continuation of the study on pineapple crown pyrolysis, we cite: additional characterization analyses, including ultimate analysis, bulk density, characterization of the volatile products, and chemical composition of ash; investigation of pyrolysis of raw and torrefied pineapple crown in a pilot plant; and evaluation of the properties of the products generated.

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Author contributions AECS contributed to investigation; data curation; and roles/writing—original draft. JASJ was involved in methodology and data curation. TJPO contributed to visualization; roles/writing—original draft; and writing—review and editing. NGS was involved in data curation; validation; visualization; roles/writing—original draft; and writing—review and editing. DAC contributed to conceptualization; methodology; roles/writing—original draft; and writing—review and editing. CRC was involved in conceptualization; data curation; resources; supervision; visualization; and writing—review and editing.

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Data availability Thermogravimetric data will be available on request.

Declarations

Competing interests The authors have no relevant financial or non-financial interests to disclose.

Ethical approval We declared that this manuscript does not involve researching about humans or animals.

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