Elucidating the thermal decomposition mechanism and pyrolysis characteristics of biorefinery-derived humins from sugarcane bagasse and rice husk

Julio César de Jesus Gariboti1 · Marina Gontijo Souza Macedo1 · Vinícius Matheus Silva Macedo1 · Yesid Javier Rueda-Ordóñez2 · Emília Savioli Lopes1 · Jonathan Tenorio Vinhal3 · Eliezer Ladeia Gomes1 · Jorge Alberto Soares Tenório4 · Romilda Fernandez Felisbino1 · Melina Savioli Lopes5 · Laura Plazas Tovar1

Received: 25 November 2021 / Accepted: 4 February 2022 / Published online: 26 February 2022 © The Author(s), under exclusive licence to Springer Science+Business Media, LLC, part of Springer Nature 2022

Abstract
Biomass-derived humins produced in the biorefining of biomass represent an attractive feedstock for thermochemical processes. This work examines the purification and characterization of humins derived from sugarcane bagasse and rice husks (H-SCB and H-RH, respectively), followed by the kinetic and thermodynamic analysis of its pyrolysis. Pyrolysis was assessed via thermogravimetric analysis, and a global reaction model was adopted to address pyrolysis kinetics. To boost the quality of fit between the kinetic model and thermoanalytical data, the analyses are based on Vyazovkin's method. The activation energy of H-SCB increased from 166.09 to 329.76 kJ mol⁻¹. In contrast, the activation energy of H-RH decreased from 163.31 to 84.99 kJ mol⁻¹. According to the results of the generalized master-plot approach, the governing reaction mechanism shifted among order-based models, nucleation, and diffusion-controlled particle mechanisms. Thermo-dynamic properties showed that the process is endothermic, with the thermal decomposition of H-SCB being more reactive (ΔS_average = -0.004 kJ mol⁻¹ K⁻¹) compared to H-RH (ΔS_average = -0.05 kJ mol⁻¹ K⁻¹). Also, the heat absorbed helps the humins to achieve a more ordered state close to a conversion of 0.50. Furthermore, a difference of about 7 kJ mol⁻¹ between the enthalpy of the reaction and the average activation energy indicates the formation of favorable product with humins' considerable bioenergy potential. These findings are the first reported data on the forecast kinetic curves and pyrolysis mechanism of biorefinery-derived humins, and these results will enable process design for the thermochemical conversion of these emerging materials to produce energy and other products.

Keywords Biomass · Humins · Isoconversional methods · Kinetic analysis · Thermochemical processes

Introduction
Circular chemistry is proposed as a solution to secure the development of a sustainable future. Levulinic acid is currently suggested as a promising platform chemical because of its many possible derivatives [1]. However, the production of levulinic acid in the concept of circular chemistry is broken because of the formation of a carbonaceous by-product, known as humins, during the acid-catalyzed dehydration of carbohydrates to produce levulinic acid [1–4]. Humins are currently considered green precursors or potential fuel for biorefinery process [5]. They are formed of macromolecules with a maximum carbon composition of 65% [6–8]. Their chemical structure is rich in furans, carboxyl groups, ketones, and hydroxyl groups [9, 10]. Furthermore, humins have a variety of components in smaller quantities, such as
carbohydrates, peptidoglycans, and peptides derived from lignin [1].

Currently, most of the research on the valorization of humins-based products is focused on the synthesis of thermoset polymers [11], copolymers with elastomer properties [12], support for catalysts [13], preparation of resins [14], and production of cyclic and aromatic hydrocarbons [15], or as a fuel for cogeneration of heat and power [16]. According to the results reported in these studies, there are thermal properties of humins that indicate a great potential for their application in thermochemical conversion processes. Humins are extremely important because they are powerful sources of energy when submitted to the pyrolysis process [1, 17]. Pyrolysis, a technology in which the material is thermally decomposed under inert atmosphere at high temperatures, produces bio-oil, biochar, and pyrolysis gas, which are products that can be used as feedstock in the production of fuels and chemicals [18].

Humins resulting from the acidic treatment of carbohydrates [11] or synthesized in industrial processes [11, 19] showed the volatilization of residual water and volatile organic components under pyrolysis conditions. The humins produced by Avantium Chemicals exhibited in their degradation profile a devolatilization (120 to 270 °C), followed by dehydration, decarboxylation, and decarbonylation reactions [20]. Two previous works determined the kinetic parameters of humin pyrolysis through linear differential and integral isoconversional methods [21, 22]. Cortés and Bridgewater [22] described the pyrolysis of the solid residue of hydrolysis of miscanthus by the third-order reaction mechanism and estimated activation energy of 155 kJ mol⁻¹. However, there was not enough evidence to support the mechanism selection given the significant discrepancy when compared to the experimental data. Wang et al. [21] interpreted the pyrolysis of humins by the one-step global reaction. Also, they determined the mean pyrolysis energy of humins obtained by acid hydrolysis of commercial xylose (150.68 kJ mol⁻¹) and glucose (163 kJ mol⁻¹). Sbirrazzuoli [23] and Sangregorio et al. [24] calculated the activation energy for humins (supplied by Avantium N.V.) using non-isothermal rheometry and the data were interpreted by isoconversional methods. Sbirrazzuoli [23] stated that the activation energy ranged from 25 to 110 kJ mol⁻¹, highlighting some individual processes: (i) uncatalyzed cross-linking of crude humins, (ii) diffusion as a rate-controlling step at the end of the reaction, and (iii) molecular mobility intensification, where the conversion rate is governed by movements of longer chain segments. Similarly, Sangregorio et al. [24] reported a decrease between 10 and 60 kJ mol⁻¹, attributing this decrease to the predominance of the kinetic diffusion mechanism for conversion greater than 40%.

However, there are no reports on the investigation of the pyrolysis behavior of humins derived from sugarcane bagasse or rice husks, which are two agro-industrial residues with great potential to be used in biorefineries [1]. In this work, humins obtained from hydrolysis/dehydration reactions of sugarcane bagasse and rice husk were investigated. The humins were purified and characterized. Thermoanalytical data and kinetic calculations were performed to analyze the behavior of pyrolysis considering a one-step global single reaction [21, 22]. The kinetic parameters were computed using the model-free kinetics method, based on Vyazovkin’s isoconversional technique to describe an advanced nonlinear isoconversional method. The reaction mechanism was revealed from the master-plot methodology that allowed the investigation of 39 kinetic mechanisms. Furthermore, a shift in the reaction mechanism was shown by variations in the activation energy. This work overcomes the main drawback with numerical instabilities introduced by the linear isoconversional methods reported by other authors [21, 22] and presents an analysis of the thermodynamic parameters of the thermal/pyrolysis decomposition of humins from sugarcane bagasse and rice husks. Therefore, these results represent an important milestone in the design of new processes for the valorization of humins in advanced and integrated biorefineries, thus contributing to the development of circular chemistry in biorefinery processes focused on the production of levulinic acid.

Materials and Method

Agro-industrial acid hydrolysis residue and chemicals

Acid hydrolysis residues (AHR) were obtained from the biorefining of the agro-industrial residues sugarcane bagasse (SCB) and rice husk (RH) in a three-step process which consisted of an acid pretreatment followed by alkaline treatment and catalytic cellulose depolymerization to produce levulinic acid, as proposed in previous works [2–4]. In the first step, biomass (SCB or RH) was pre-treated with a solution of sulfuric acid (1.0% w/v) at 121 °C for a residence time of 90 min with 20% of solids loading. In the second step of the process, the insoluble solid fraction (ISF-I) obtained from the previous step was treated with sodium hydroxide (0.5% w/v for SCB and 2.0% w/v for RH) at 121 °C for 90 min with 20% of solids loading. This stage produced a second water-insoluble solid fraction (ISF-II). Using ISF-II, the last stage was performed under optimized conditions determined by Lopes et al. [3]: 190 °C, 7.0% w/v sulfuric acid for 75 min with 12% of solids loading. After the reaction, the products were separated by vacuum filtration (0.22 µm polyvinylidene fluoride membrane) into a liquid fraction (characterized in previous work [3]) and a water-insoluble solid fraction, which corresponded to the AHR. The AHR
was resuspended in distilled water to remove residual sugars and organic acids. The remaining solid material was dried in an oven at 60 °C for 24 h and stored in a vacuum desiccator for purification and physicochemical characterization.

Suppliers and purities of chemicals are listed in Table S1—Supplementary Information. Ultrapure deionized water (18 MΩ cm resistivity, Milli-Q, Millipore) was used.

**Purification**

The purification of AHR from SCB and RH was performed based on the method presented by Song et al. [25], with adaptations. Samples were acidified with a 1 mol L⁻¹ HCl until reaching a pH between 1 and 2; then, the samples were washed with deionized water to remove the acid solution. The resulting solid was subjected to three extraction processes. Firstly, a 1 mol L⁻¹ NaOH solution was used repetitively till a pH of 12.6 was reached. Then, the second extraction was performed with a 6 mol L⁻¹ urea ((NH₂)₂CO) and 0.1 mol L⁻¹ NaOH, in each extraction. The solution was centrifuged (2500 rpm for 30 min) and kept at 25 °C for 24 h. The supernatant fraction was removed, and its pH was adjusted to 7–8 with a 1 mol L⁻¹ HCl solution. To remove the alkaline solution and urea, the supernatant fraction was washed with deionized water and then dried in an oven at 60 °C for 48 h. Finally, the resulting solid was extracted with a solution of DMSO (dimethylsulfoxide) and H₂SO₄ in a volume ratio of 94:6 for 18 h. The solids were then separated from the DMSO/H₂SO₄ solution by centrifugation at 15,000 × g. The solutions collected for each extraction were combined and diluted with water until a pH of 2 was obtained. The solution was kept overnight at 4 °C to allow precipitation of humins. The released solids were isolated and dehydrated with 0.3 mol L⁻¹ HF/0.1 mol L⁻¹ HCl (50 mL), washed with distilled water, and dried to obtain the humins, referred here as H-SCB and H-RH for humins derived from SCB and humins derived from RH, respectively. Humins were weighed and their yield was expressed in g per 100 g of biomass, in dry weight. The samples were stored in a desiccator for further characterization and analysis.

**Structural characterization**

The surface morphology of the humins was investigated using scanning electron microscopy (SEM, JEOL JSM-7401F, Jeol Ltd., Japan). The samples were deposited on a carbon strip and inserted into a vacuum chamber to be covered with a gold film before analysis. The Fourier transform infrared spectroscopy (FT-IR, Shimadzu/IR Prestige 21 spectrometer, Shimadzu Corporation, Japan) was used as a qualitative verification of functional groups. All humin samples were analyzed under ambient conditions. A portion of the sample was ground with KBr (1% w/w) and compressed under a pressure of 10 kN for 5 min. The spectra were acquired under a transmittance mode, performing 100 scans over 4000 to 50 cm⁻¹ with a 4 cm⁻¹ resolution. To ensure the quality of the analysis, all spectra were corrected with the blank spectrum obtained before each scan. The selected spectra were normalized to a total area of 100.

Moisture content was determined in accordance with the ASTM D3173 standard method [26] as the mass loss after drying at 105 °C. Ash content was determined according to the standardized method ASTM D3174 [27]. To determine volatile matter (VM), the standardized method ASTM D3175 [28] was used. Fixed carbon (FC) was determined by difference (FC = 100%—VM—ashes).

The higher heating value (HHV) was determined with a bomb calorimeter (Adiabatic Calorimeter, Parr Instrument Company, USA) with excess oxygen at a pressure of 30 bar. The equipment was calibrated with benzoic acid (C₆H₅COOH). The composition of elements C, H, and O was determined from empirical correlations presented in Equations (1) to (3) developed by Nhuchhen [29], with average absolute error of 0.45%, 2.82%, 2.01%, respectively.

\[
H = 55.36778 - 0.4830VM - 0.5319FC - 0.56 Ashes \quad (1)
\]

\[
C = -35.9972 + 0.7698VM + 1.3269FC + 0.3250 Ashes \quad (2)
\]

\[
O = 223.6805 - 1.7226VM - 2.2296FC - 2.2463 Ashes \quad (3)
\]

**Thermogravimetric analysis (TGA)**

Thermal/pyrolysis degradation of humins was conducted using a DTG-60H thermogravimetric analyzer (Shimadzu Corporation, Japan). Initially, to remove all atmospheric gases, the thermogravimetric analysis began with the priming of the furnace cell with nitrogen gas (50 mL min⁻¹ for 20 min) at 30 °C. Then, to ensure complete evaporation of moisture, the temperature was increased to 120 °C. Thermogravimetric analysis was performed under non-isothermal conditions at three different heating rates (15, 20, and 30 °C min⁻¹ for SCB and 10, 20, and 30 °C min⁻¹ for RH), selected in previous tests between 5 and 40 °C min⁻¹, up to 800 °C (data not shown) showing lower noise in the TGA mass/temperature curves. Using an analytical computer system, the loss of mass as a function of temperature and the derivative thermogravimetry (DTG) were recorded. Solid residue yield at 800 °C was reported. To eliminate or reduce heat and mass transfer limitations, approximately 7 mg of sample was used in each analysis in alumina crucibles with a circular base (6 mm in diameter and 3 mm in height, 70 µL). The accuracy of the TGA thermal balance is 0.001 mg.
The evolved gas was analyzed using an MS-QMID (mass spectroscopy with quasi multiple ion detection, QMID). Analysis to detect released ions was performed on a thermal balance (Netzsch, STA 449 F1 model), coupled to a quadrupole mass spectrometer (QMS 403 C Aëolos). Crude humins samples of approximately 10 mg were placed in an alumina crucible and the analysis was carried out at a temperature range of 30–120 °C, heating rate of 15 °C min\(^{-1}\), with 20 min of residence time at 120 °C. After the 120 °C plateau, the temperature was risen to 800 °C with a heating rate of 15 °C min\(^{-1}\). The analysis was carried out under N\(_2\) atmosphere with gas flow rate of 50 mL min\(^{-1}\) and a balance protective N\(_2\) flow rate of 20 mL min\(^{-1}\). The measuring module in the mass spectrometer was set to scan bargraph mode and m/z range of 10–100 u to continuously detect the ions from gaseous products released during sample decomposition.

**Kinetics of the solid-state reaction**

The pyrolysis reaction of humins is given below:

\[
\text{Humins} \rightarrow \text{Volatile} + \text{Biochar}
\]

Solid-state reactions assume: (i) one-step chemical reaction and it is irreversible; (ii) humins are spherical particle sufficiently small for heat and mass transport limitations to be negligible; (iii) all mass changes result from thermal decomposition; (iv) gas flow rate is higher than the release rate of pyrolysis gases; and (iv) the heat of pyrolysis is negligible.

The thermogravimetric and kinetic behavior of the thermal/pyrolysis decomposition of humins was interpreted based on the mass loss profiles as a function of temperature and time, as well as the conversion. Therefore, the sample dehydration step was ignored, and the pyrolysis was analyzed in the interval of 150–800 °C.

The conversion reaction rate is defined as:

\[
\frac{d\alpha}{dt} = k(T)\alpha
\]

where \( f(\alpha) \) is a mathematical function that represents the reaction mechanism (Table 1), \( k(T) \) is the conversion rate constant, and \( \alpha \) is defined by Equation (6):

\[
\alpha_{\text{exp}} = \frac{W_{150} - W}{W_{150} - W_{800}} \quad \text{[} 0.150 < \alpha < 0.800 \text{]} \quad (6)
\]

where \( W_{150} \), \( W \), and \( W_{800} \) are the normalized mass at 150 °C, at a time \( t \), and at 800 °C, respectively.

The corresponding thermogravimetric conversion rate \( (d\alpha/dt) \) is represented by Equation (7):

\[
\frac{d\alpha}{dt} = \frac{dW}{dt} \left( \frac{1}{W_{800} - W_{150}} \right)
\]

The pyrolysis reaction kinetics are defined through the conversion rate presented by Equation (8):

\[
\frac{d\alpha}{dT} = \frac{A}{\beta} \cdot f(\alpha) \cdot \exp \left( \frac{-E_a}{RT} \right)
\]

where \( A \) is the pre-exponential factor (min\(^{-1}\)), \( E_a \) the activation energy (kJ mol\(^{-1}\)), \( R \) is the universal gas constant \((8.3145 \text{ J mol}\(^{-1}\) K\(^{-1}\)) \( T \) is the temperature (K), and \( \beta \) is the heating rate, which can be expressed by Equation (9):

\[
\frac{dT}{dt} = \beta
\]

Equation (10) represents an integral form of Equation (8), where \( g(\alpha) \) is the integral form of \( f(\alpha) \), \( I(E_a, T) \) is the integral of temperature, without analytical solution, being commonly replaced by empirical approximations \((p(u))\), in which \( u \) is defined as \( E_a/RT \).

\[
g(\alpha) = \int_{0}^{\alpha} f(\alpha) = \frac{A}{\beta} \int_{T_o}^{T} \exp \left( \frac{-E_a}{RT} \right) dT \equiv \frac{1}{\beta} I(E_a, T) = \frac{AE_a}{\beta R} p(u)
\]

Table 1 presents different kinetic functions \( f(\alpha) \) used to represent the pyrolysis reaction mechanisms and their respective integral forms \( g(\alpha) \), such as kinetic mechanisms based on chemical reaction, one-dimensional and three-dimensional diffusion, nucleation and nuclei growth, and models based on phase boundary reactions [30].

**Isoconversional kinetic methods**

The thermogravimetric and kinetic behavior of non-catalytic pyrolysis of humins was evaluated using three isocconversional methods developed by Flynn–Wall–Ozawa (FWO) [31], Starink (STK) [32], and Vyazovkin (VYZ) [33].

The FWO method (Equation (11)) describes the reactions independent of the reaction rates and uses the linear Doyle approximation for the temperature integral.

\[
\ln \beta_i = \ln \left[ \frac{A_a E_{e_a}}{R g(\alpha)} \right] - 5.331 - 1.052 \frac{E_{e_a}}{RT_{a.i}}
\]

The STK method (Equation (12)) presents another approximation for the temperature integral, but it is considered more accurate when compared to the FWO method [34].

\[
\ln \left( \frac{\beta_i}{T_{a,i}^{0.92}} \right) = \ln \left[ \frac{R^{0.92} A_a}{E_{e_a} 0.92 g(\alpha)} \right] - 1.0008 \frac{E_{e_a}}{RT_{a,i}}
\]
### Table 1 Kinetic mechanisms, $f(\alpha)$, and their integral forms, $g(\alpha)$, used in solid-state reactions

| Model | $g(\alpha)$ | $f(\alpha)$ | Rate-determining mechanism |
|-------|-------------|-------------|----------------------------|
| 1. Chemical process or mechanism non-involving equations | | | |
| $F_{1/3}$ | $1 - (1 - a)^{2/3}$ | $(3/2)(1 - a)^{1/3}$ | Chemical reaction |
| $F_{3/4}$ | $1 - (1 - a)^{1/3}$ | $4(1 - a)^{1/4}$ | Chemical reaction |
| $F_{2/3}$ | $(1 - a)^{-1/3} - 1$ | $2(1 - a)^{1/2}$ | Chemical reaction |
| $F_3$ | $(1 - a)^{-1} - 1$ | $(1/2)(1 - a)^{3}$ | Chemical reaction |
| $F_4$ | $(1 - a)^{-3} - 1$ | $(1/3)(1 - a)^{4}$ | Chemical reaction |
| $G_1$ | $1 - (1 - a)^{2}$ | $[2(1 - a)]^{-1}$ | Chemical reaction |
| $G_2$ | $1 - (1 - a)^{3}$ | $[3(1 - a)^{2}]^{-1}$ | Chemical reaction |
| $G_3$ | $1 - (1 - a)^{4}$ | $[4(1 - a)]^{-1}$ | Chemical reaction |
| 2. Acceleratory rate equations | | | |
| $P_{3/2}$ | $a^{3/2}$ | $(2/3)a^{1/2}$ | Nucleation (power law) |
| $P_{1/2}$ | $a^{1/2}$ | $2a^{1/2}$ | Nucleation (power law) |
| $P_{3/4}$ | $a^{1/4}$ | $3a^{1/2}$ | Nucleation (power law) |
| | | $4a^{1/4}$ | Nucleation (power law) |
| $P_2$ | $a^{2}$ | $(1/2)a^{1}$ | Nucleation (exponential law) |
| $E_1$ | $lna$ | $\alpha$ | Nucleation (exponential law) |
| $E_2$ | $lna^2$ | $\alpha/2$ | Nucleation (exponential law) |
| 3. Sigmoidal rate equations or random nucleation and subsequent growth | | | |
| $A_1, F_1$ | $-ln(1 - a)$ | $1 - a$ | Random nucleation/first order (Mampel) |
| $A_{2/3}$ | $[-ln(1 - a)]^{3/4}$ | $(2/3)(1 - a)[-ln(1 - a)]^{1/2}$ | Random nucleation (Avrami–Erofeev) |
| $A_{3/2}$ | $[-ln(1 - a)]^{3/2}$ | $(3/2)(1 - a)[-ln(1 - a)]^{1/3}$ | Random nucleation (Avrami–Erofeev) |
| $A_{3/4}$ | $[-ln(1 - a)]^{3/4}$ | $(3/4)(1 - a)[-ln(1 - a)]^{1/3}$ | Random nucleation (Avrami–Erofeev) |
| $A_{3/2}$ | $[-ln(1 - a)]^{3/3}$ | $(5/2)(1 - a)[-ln(1 - a)]^{1/3}$ | Random nucleation (Avrami–Erofeev) |
| $A_3$ | $[-ln(1 - a)]^{1/3}$ | $2(1 - a)[-ln(1 - a)]^{1/2}$ | Random nucleation (Avrami–Erofeev) |
| $A_4$ | $[-ln(1 - a)]^{1/2}$ | $(1/2)(1 - a)[-ln(1 - a)]^{1/3}$ | Random nucleation (Avrami–Erofeev) |
| $A_{1/3}$ | $[-ln(1 - a)]^{1/4}$ | $(1/2)(1 - a)[-ln(1 - a)]^{1/4}$ | Random nucleation (Avrami–Erofeev) |
| $A_{1/3}$ | $[-ln(1 - a)]^{1/5}$ | $(1/2)(1 - a)[-ln(1 - a)]^{1/3}$ | Random nucleation (Avrami–Erofeev) |
| $A_{1/3}$ | $ln[a/(1 - a)]$ | $\alpha/(1 - a)$ | Random nucleation (Avrami–Erofeev) |
| $B_1$ | $ln[a/(1 - a)]$ | $\alpha/(1 - a)$ | Random nucleation (Avrami–Erofeev) |
| 4. Deceleratory rate equations (phase boundary reaction) | | | |
| $R_1, F_{1/3}$ | $\alpha$ | $1$ | Contracting disk |
| $R_2, F_{1/2}$ | $1 - (1 - a)^{1/2}$ | $2(1 - a)^{1/2}$ | Contracting cylinder |
| $R_3, F_{3/2}$ | $1 - (1 - a)^{1/3}$ | $3(1 - a)^{2/3}$ | Contracting sphere |
| 5. Deceleratory rate equations (equations based on the diffusion mechanism) | | | |
| $D_1$ | $a^2$ | $1/(2\alpha)$ | One-dimensional diffusion |
| $D_2$ | $\alpha + (1 - a)ln(1 - a)$ | $[-ln(1 - a)]^{-1}$ | Three-dimensional diffusion |
| $D_3$ | $[1 - (1 - a)^{1/3}]^2$ | $(3/2)(1 - a)^{1/3}[1 - (1 - a)^{1/3}]^{-1}$ | Three-dimensional diffusion (Jander) |
| $D_4$ | $1 - (2/3)\alpha - (1 - a)^{1/3}$ | $(3/2)[(1 - a)^{1/3} - 1]^{-1}$ | Three-dimensional diffusion (Ginstling–Brounshtein) |
| $D_5$ | $[(1 - a)^{-1/3} - 1]^2$ | $(3/2)(1 - a)^{1/3}(1 - a)^{-1/3} - 1]^{-1}$ | Three-dimensional diffusion (Crank) |
| $D_6$ | $[(1 + a)^{1/3} - 1]^2$ | $(3/2)(1 + a)^{1/3}(1 + a)^{1/3} - 1]^{-1}$ | Three-dimensional diffusion |
| $D_7$ | $1 + (2/3)\alpha - (1 - a)^{1/3}$ | $(3/2)[(1 + a)^{1/3} - 1]^{-1}$ | Three-dimensional diffusion |
| $D_8$ | $[(1 + a)^{-1/3} - 1]^2$ | $(3/2)(1 + a)^{1/3}(1 + a)^{-1/3} - 1]^{-1}$ | Three-dimensional diffusion |

Adapted from Trache et al. [30]
The corresponding activation energy $E_{a\alpha}$ and the pre-exponential factor $A_{\alpha}$ can be found from the linear plots on the left-hand side of Equations (11) and (12) vs. $1/T_{a\alpha}$ at constant $\alpha$.

Because of simplified approximations in integral methods, Vyazovkin and Dollimore [33] developed the advanced nonlinear isoconversional method, using a revision of the method to express the temperature integral (Equation (13)). As the initial value for the optimization problem, the $E_{a\alpha}$ values determined with the FWO method were considered.

The integral temperature of the VYZ method, $p(u)$, can be solved by means of numerical integration or using the approximation proposed by Pérez-Maqueda and Criado [35], presented in Equation (14).

$$p(u) = \left[ \frac{e^{-u}}{u} \right] \left( \frac{u^7 + 70u^6 + 1886u^5 + 24920u^4 + 170136u^3 + 577584u^2 + 844560u + 357120}{u^8 + 72u^7 + 2024u^6 + 28560u^5 + 216720u^4 + 880320u^3 + 1794240u^2 + 1572480u + 403200} \right)$$ (14)

**Determination of the kinetic mechanism**

Prediction of the kinetic behavior of the reaction was important to investigate the thermal/pyrolysis decomposition reaction mechanism, $f(\alpha)$. Solid-state kinetic reactions can be mechanistically categorized as reaction order models, acceleratory rate equations (nucleation), sigmoidal rate equations or random nucleation and subsequent growth, deceleratory rate equations (phase boundary reaction or geometrical contraction), and equations based on diffusion (Table 1). A schematic illustration of the proposed mechanism controlling the solid-state reaction is available in Table S2—supplementary material. The most acceptable mechanism was determined using the master-plot method proposed by Criado [36] (Equation (15)), in which the master plot $z(\alpha)$ was obtained by multiplying the differential and integral forms of the mechanisms described in Table 1, taking $\alpha=0.5$ as reference. These mechanisms were analyzed assuming in this study the thermogravimetric information related to the heating rate of 20 °C min⁻¹.

$$\frac{z(\alpha)}{z(0.5)} = \frac{f(\alpha) \times g(\alpha)}{f(0.5) \times g(0.5)} = \left( \frac{T_{a\alpha}}{T_{0.5}} \right)^2 \left( \frac{\frac{da}{dT}}{\frac{da}{dT}} \right) \alpha (15)$$

where the right-hand side is known as the reduced conversion rate, calculated from the experimental data, and the left-hand side represents the theoretical master plot. The quality of correspondence of this information was evaluated through the root mean square error (RMSE) and coefficient of determination ($R^2$). The choice of model was based on the curves that presented the best fit to the experimental data.

**Pre-exponential factor estimation**

After the determination of the kinetic mechanism that most fairly represented the thermal degradation of humins, the pre-exponential factor ($A_{\alpha}$) was estimated using the intercept obtained from the linear regressions of the linear methods presented in Equations (11) and (12). For the VYZ method, Equation (8) was linearized based on the information obtained from the thermogravimetric study for this method, and the ln($A_{\alpha}$) intercept was used as the initial value to estimate this parameter. By minimizing the RMSE (Equation (16), with $N=39$), parameter $A_{\alpha}$ was estimated by comparison of the experimental data of the conversion rate with the theoretical data obtained through Equation (8).

$$\text{RMSE} = \sqrt{\frac{\sum_{j=1}^{N} \left( \frac{\frac{da}{dT}}{\text{experimental}} - \frac{\frac{da}{dT}}{\text{theoretical}} \right)^2}{N}}$$ (16)

**Thermodynamic parameters**

The thermodynamic parameters were calculated using the fundamental theory of the activated complex [37]. The changes of enthalpy ($\Delta H$), Gibbs free energy ($\Delta G$), and entropy ($\Delta S$) were calculated by Equations (17)–(19).

$$\Delta H_{a} = E_{a\alpha} - RT_{a}$$ (17)

$$\Delta G_{a} = E_{a\alpha} + RT_{m} \ln \left( \frac{K_{p} T_{m}}{h A_{\alpha}} \right)$$ (18)

$$\Delta S_{a} = \frac{\Delta H_{a} - \Delta G_{a}}{T_{m}}$$ (19)

where $h$ is the Plank constant ($6.626 \times 10^{-34}$ m² kg s⁻¹), $K_p$ denotes Boltzmann constant ($1.381 \times 10^{-23}$ m² kg s⁻² K⁻¹), and $T_m$ is the maximum decomposition rate temperature.
Data processing and management

Experimental data were analyzed using the PAleontological STatistics (version 2.17c) and Microsoft Excel to perform the univariate statistical analysis and Tukey’s test at a significance level of $p < 0.05$. Thermoanalytical data, kinetic parameter estimation, and the one-step global single reaction modeling were carried out using Origin 8.1 (version v8. 0724) and Microsoft Excel. Vyazovkin’s optimization approach in Equation was solved using the Solver add-in of Microsoft Excel.

Results and Discussion

Purification

After the purification process, the yield of humins was 90.8 ± 0.7% for H-SCB and 95.7 ± 0.3% for H-RH. The results obtained in this work were similar to those reported by Song et al. [25] (92.5%), thus indicating that the process for extraction of humins from soils is applicable to the purification of humins synthesized in biorefineries. This extraction method, using NaOH, urea, DMSO, and $\text{H}_2\text{SO}_4$ as a catalyst, as described by Hoang et al. [40]. Despite the high yield, it is not possible to completely remove the impurities because some contaminants are adsorbed to the surface of the humins [39].

Physicochemical characteristics

The surface of humins consists of small, aggregated particles, with sizes between 1 and 6 µm for H-SCB and sizes between 1 and 10 µm for H-RH (Fig. 1a). These results are a characteristic aspect of humins and other carbonaceous solids, in addition to containing channels or micropores interconnecting the surfaces between particles [41]. This size range is smaller than that of humins obtained from lignocellulosic biomass using $\text{H}_2\text{SO}_4$ as a catalyst, as described by Hoang et al. [40]. On the other hand, the particle size is relatively larger than that reported by Björnerbäck and Hedin [41] for humins derived from 5-hydroxymethylfurfural, which presented a size between 1 and 100 nm and a less spherical shape. The spherical morphology of H-SCB and H-RH also resembles the spherical particles obtained from glucose, but with a larger particle size distribution [17].

The functional groups of humins were analyzed using FT-IR and the spectra obtained are shown in Fig. 1b. The spectra of both humins have similar transmittance patterns, but with different intensities, indicating that both humins had similar functional groups. The peak between 3420 and 3430 cm$^{-1}$ is explained by the presence of hydroxyl groups [11, 21], the peaks at 2920 cm$^{-1}$ and 2950 cm$^{-1}$ may indicate the presence of methyl and methylene structures [21, 42], and the peak at 1710 cm$^{-1}$ may belong to different groups such as aldehydes, ketones, and esters [11, 40, 43]. The peak observed between 1620 cm$^{-1}$ and 1600 cm$^{-1}$ may indicate the presence of amide groups [43]. The presence of furanic rings is observed at peaks between 1674 cm$^{-1}$ and 1500 cm$^{-1}$ for the C=O and C=C elongations [21, 40]. Finally, CO elongation is observed between peaks 1284 and 1110 cm$^{-1}$, representing alcohols and aliphatic ethers [21], while the peaks between 1000 and 800 cm$^{-1}$ are an indication of out-of-plan CH attributed to substituted furans [17].

The proximate and ultimate analyses and the HHV of H-SCB and H-RH are presented in Table 2. The moisture content (less than 5%) present in both humins is suitable for thermochemical processes involving the thermal decomposition of the material [44] because a higher moisture content can increase the sample dehydration step during the process and affect the yield of the formed products. Both humins have high volatile matter contents, thus helping in the regulation of thermal processes [18, 45]. In addition, the high volatile matter content makes these humins more suitable for the production of bio-liquids (e.g. pyrolysis biooil) and biogas [45], and could indicate a low porosity, good reactivity, and good combustion properties [46]. Despite the statistically significant differences obtained in the immediate analysis, the high volatile matter, fixed carbon, and low moisture contents of both humins characterize these materials as suitable for thermal degradation processes.

Elemental analysis is comparable with the existing literature on other humins synthesized from glucose [21] or in industrial processes [11, 19]. Both H-SCB and H-RH presented a high C (~60%) and O (~29%) content and low H content (~4.7%) compared to other carbonaceous materials such as the products of hydrothermal carbonization of rice husk [43], miscanthus [22], and brewer’s spent grains [46].

Despite the similar H/C and O/C atomic ratios (or degree of aromaticity and polarity) of both humins (Table 2), it is possible to conclude that H-RH presents more aliphatic bonds and oxygenated groups compared to H-SCB because H-RH presents sharper transmittance peaks in its FTIR spectrum (Fig. 1b). Also, the atomic ratios found for both H-SCB and H-RH indicate that they are more carbonaceous materials [46], making them comparable to lignite. The results are comparable to the atomic ratios obtained for humins synthesized from glucose [19, 21]. Moreover, the elemental composition of H-SCB and H-RH humins is slightly different
from the elemental composition of hexose-derived humins reported by van Zandvoort et al. [17]. This can be attributed to differences in the synthesis method or purification process. The humins obtained in this work present lower H/C and O/C atomic ratios than the humins formed from hexoses [17], thus indicating that fewer oxygenated groups and fewer aliphatic polymers/hydrocarbons containing C–H bonds are present in their structure compared to hexose-derived humins. van Zandvoort et al. [17] provided a similar analysis regarding the chemical structure of humins based on humins produced from xylose. The existence of structural differences of the investigated humins is observed through the empirical formulas $C_{1.00}H_{0.95}O_{0.37}$ and $C_{1.06}H_{0.97}O_{0.35}$ for H-SCB and H-RH, respectively. Therefore, both humins are recognized as having good potential for thermochemical processes.

The HHV of H-SCB (22.45 MJ kg$^{-1}$) was expected to be higher compared to H-RH (24.70 MJ kg$^{-1}$) because a
Thermal/pyrolysis behavior analysis

Thermogravimetric analyses were conducted in an N2 atmosphere using three heating rates to study the thermal decomposition of humins. Figure 2a and b shows the normalized mass loss (W) and normalized DTG (dW/dt) curves for H-SCB and H-RH. The investigation of species released during the mass loss stage of both humins is shown in Fig. 2c and d. The thermal/pyrolysis decomposition of these humins can be divided into a dehydration process followed by pyrolysis, the latter being classified according to the transitions that occur in the process. Based on the DTG curves (Fig. 2a and b), the decomposition patterns under N2 can be classified into three regions. The first one is almost identical for both humins, characterizing the sample's dehydration process. In the DTG curves, the water loss of the samples is observed through a peak between the beginning of the process and 150 °C and evidenced by peaks in the mass spectrum at m/z = 17 and m/z = 18 (Fig. 2c and d). At this stage, it is possible to observe a loss of mass for H-SCB (Fig. 2a) of approximately 2.8% and for H-RH (Fig. 2b) of approximately 4.6% for all heating rates. The behaviors observed in the mass loss and DTG profiles are similar between the different heating rates. From Fig. 2d, the release of CO2 (m/z = 48) and sulfur compounds (m/z = 44) for H-RH is observed. The primary pyrolysis process is visualized in the degradation process presented in Fig. 2a and b in which there is a significant reduction in sample mass between 300 °C and 600 °C. During this step, the H-SCB and H-RH lost approximately 26.49% and 21.43% in mass, respectively, around 400 °C, caused by the release of volatile compounds and structural changes. Compared to the DTG curve for H-SCB, the DTG curve for H-RH has a shoulder next to the main peak caused by the existence of other compounds formed during the biorefining process (such as 5-hydroxymethylfurfural) which were not removed during the extraction process [19] or by the breaking of unstable structures in these humins [21]. It can be inferred that, in this step, there is mainly the release of compounds containing sulfur (m/z = 48 and m/z = 64), hydrocarbons (m/z = 12), and CO2 (m/z = 44).

The secondary decomposition stage occurs in the temperature range between 600 and 800 °C, in which reactions such as dehydration and decarboxylation occur, with the decomposition of its structure at the same time [20]. Some condensation reactions and recombination of the formed fragments are possible [20] due to the slow degradation of non-carbonaceous and non-biodegradable residues and by the degradation of high molecular weight molecules into aromatic compounds and formation of solid waste; thus, the final biochar yield is about 42.37% for H-SCB and 40.50% for H-RH. Yields were lower than those of humins that were obtained from glucose [19, 21], suggesting that the thermal decomposition of H-SCB and H-RH tends to devolatilization instead of carbonization and consequently to a higher yield of gaseous and liquid products. On the other hand, the yields were close to those obtained in the pyrolysis of industrially obtained humins (44%) reported by Agarwal et al. [19], which have a high volatile content. Therefore, these conclusions highlight the results obtained through the immediate analysis of H-SCB and H-RH, which indicated the tendency for biogas production because of the high volatile matter content (57% and 54%, respectively).

There was an increase in biochar yield by increasing the heating rate, mostly observed in H-RH sample. This phenomenon was also observed by Olszewski et al. [46] and, according to the authors, lower heating rates, as used in slow pyrolysis, increase the residence time of volatiles within the particles, resulting in a higher yield of biochar due to cracking, polymerization, and condensation reactions. The signals obtained in the mass spectrum of the two samples possibly reflect the statement made by the authors because there is the presence of peaks referring to hydrocarbons and CO2 (m/z = 12 and m/z = 44) at the end of the heating process for H-RH while there is only the presence of peaks referring to water loss in the process for H-SCB (m/z = 18).

Table 2 Proximate and ultimate analysis and higher heating value of H-SCB and H-RH

| Parameters                        | H-SCB          | H-RH          |
|----------------------------------|----------------|---------------|
| Proximate analysis (%, dry basis*)|                |               |
| Moisture                         | 4.78 ± 0.40 a  | 4.32 ± 0.60 a |
| Volatile Matter *                 | 57.00 ± 1.06 a | 54.19 ± 0.97 b|
| Fixed Carbon *                    | 38.68 ± 1.37 a | 40.15 ± 0.68 a|
| Ash *                            | 4.32 ± 0.31 a  | 5.65 ± 0.30 b |
| Ultimate analysis (%, dry basis)  |                |               |
| C                                | 60.61 ± 0.90 a | 60.84 ± 0.25 a|
| H                                | 4.84 ± 0.04 a  | 4.67 ± 0.06 b |
| O                                | 29.55 ± 0.53 a | 28.10 ± 0.50 b|
| H/C                             | 0.94 ± 0.02 a  | 0.91 ± 0.01 a |
| O/C                             | 0.37 ± 0.01 a  | 0.35 ± 0.01 a |
| HHV (MJ kg−1)                    | 22.45          | 24.70         |

Groups followed by the same letter (overwritten) are not significantly different at p < 0.05 by ANOVA and complemented by Tukey’s test. The deviation in HHV was less than 1%

*Data expressed on a dry basis
corroborating the earlier statement that humins have different structures.

The secondary thermal decomposition step is represented by a less accentuated mass loss when compared to the primary thermal/pyrolysis decomposition (Fig. 2a and b). On the other hand, when comparing the H-SCB and H-RH profiles, the behavior between these thermogravimetric profiles is different. There is a decrease in the speed of degradation only after 700 °C and there is also a shoulder between 600 °C and 800 °C caused by the degradation of residual lignin from the biomass (which was not fully solubilized after the purification step).

The effect of the heating rate is visible in the DTG profiles because, with its increase, the peaks shift slightly to the right. This behavior is a consequence of the limitations of mass and heat transfer phenomena that cause temperature gradients among the surface and the interior of the sample and its particle [22]. Similarly, the increase in heating rates has significant effects on the release of volatile compounds, causing their increase. The DTG profiles indicated that thermal decomposition with the highest heating rate provides a higher decomposition rate and larger decomposition temperature ranges. Thus, it is likely that fast heating could impose a faster decomposition rate.
Isoconversional kinetic study

The activation energy

The thermal/pyrolysis decomposition kinetics of humins were calculated using the integral isoconversional methods. For the determination of the activation energy ($E_{a\alpha}$), conversions between 0.150 and 0.800 and a step equal to 0.025 were adopted as the study interval, covering the interval with determination factors greater than 0.7.

The linear fits of the STK and FWO methods in the studied conversion interval are shown in Fig. 3. The activation energy calculated for each method varying the conversion is shown in Table 3. The linear integral methods present a uniform behavior (Fig. 3), which is an expected result of these methods because they are directly based on the reaction rate data. As can be seen from Table 3, there is a low variation in the activation energy for H-SCB from the beginning of the studied conversion interval up to $\alpha=0.450$, for all studied methods, between 5.70 to 6.30 kJ mol$^{-1}$ approximately. The conversion of 0.425 corresponds to a temperature close to 400 °C, which corresponds to the peak observed in the DTG related to the maximum decomposition of organic matter and release of volatile components. Therefore, the primary thermal decomposition step occurs stably and with an activation energy between 165 and 175 kJ mol$^{-1}$. After a conversion of 0.425, there is an increase in the activation energy for the FWO, STK, and VYZ methods. This trend was also observed by Wang et al. [21] in the pyrolysis of humins derived from glucose and xylose. Sobek and Werle [47] stated that the increase in activation energy observed was the result of highly endothermic carbonization reactions, comprising the interval of secondary pyrolysis and biochar formation. Furthermore, Sangregorio et al. [24] stated that this behavior was due to the increased mobility of long-chain compounds that promoted the reactivation of chemical reactions.

Similarly, it was observed for H-RH a variation between 3.89 and 4.5 kJ mol$^{-1}$ in the activation energy from the conversion of 0.175 to 0.300 for all methods, corresponding to the peak observed in the DTG between 354 and 370 °C related to the maximum decomposition of organic matter and release of volatile components, thus indicating that the primary thermal decomposition step also occurs stably. After this conversion interval, the activation energy increases in all methods until the conversion of 0.475, reaching a maximum between 234.79 and 237.28 kJ mol$^{-1}$. This conversion interval corresponds to the shoulder located close to the main peak. The decrease in the activation energy after the conversion of 0.525 is an indication of the decomposalition of thermally unstable structures and the reduction in the mobility of short-chain compounds due to diffusion limitations and increased viscosity [24]; this result was also observed by Bartocci et al. [48] for a lignin-rich process residue.

The results show the dependence of activation energy on the conversion is a strong indication that thermal/pyrolysis decomposition does not occur in a single step, but rather in...
Table 3 Activation energies ($E_a\alpha$, kJ mol$^{-1}$) obtained for the thermal/pyrolysis degradation of humins

| Method | STK | FWO | VYZ |
|--------|-----|-----|-----|
|        | H-SCB | H-RH | H-SCB | H-RH | H-SCB | H-RH |
| $\alpha$ | $E_a\alpha$ | $R^2$ | $E_a\alpha$ | $R^2$ | $E_a\alpha$ | $R^2$ |
| 0.150  | 166.12 | 0.99 | 163.11 | 0.90 | 164.63 | 0.99 | 162.44 | 0.89 | 166.09 | 0.99 | 163.61 | 0.99 |
| 0.175  | 165.00 | 0.99 | 175.99 | 0.96 | 163.30 | 0.99 | 175.68 | 0.96 | 164.76 | 0.99 | 176.93 | 0.98 |
| 0.200  | 167.25 | 1.00 | 179.25 | 0.98 | 165.53 | 1.00 | 178.89 | 0.98 | 167.01 | 0.99 | 180.16 | 0.98 |
| 0.225  | 169.04 | 1.00 | 181.46 | 0.99 | 167.28 | 1.00 | 181.03 | 0.99 | 168.77 | 0.99 | 182.32 | 0.98 |
| 0.250  | 169.39 | 1.00 | 180.79 | 0.99 | 167.54 | 1.00 | 180.16 | 0.99 | 169.04 | 0.99 | 181.45 | 0.98 |
| 0.275  | 164.82 | 1.00 | 179.63 | 0.99 | 162.63 | 1.00 | 178.80 | 0.99 | 164.09 | 0.99 | 180.09 | 0.98 |
| 0.300  | 164.45 | 1.00 | 180.49 | 0.99 | 162.15 | 1.00 | 179.57 | 0.99 | 163.60 | 0.99 | 180.87 | 0.98 |
| 0.325  | 166.65 | 1.00 | 185.78 | 0.99 | 164.38 | 1.00 | 185.00 | 0.99 | 165.85 | 0.99 | 186.33 | 0.98 |
| 0.350  | 171.27 | 1.00 | 189.42 | 0.99 | 169.16 | 1.00 | 188.70 | 0.99 | 170.67 | 0.99 | 190.05 | 0.98 |
| 0.375  | 172.73 | 1.00 | 197.24 | 0.99 | 170.61 | 1.00 | 196.79 | 0.99 | 172.14 | 0.99 | 198.19 | 0.98 |
| 0.400  | 172.16 | 1.00 | 207.32 | 0.99 | 169.94 | 1.00 | 207.26 | 0.99 | 171.46 | 0.99 | 208.71 | 0.98 |
| 0.425  | 171.30 | 1.00 | 218.13 | 0.99 | 168.96 | 0.99 | 218.49 | 0.99 | 170.47 | 0.99 | 219.98 | 0.98 |
| 0.450  | 175.91 | 1.00 | 228.57 | 1.00 | 173.75 | 1.00 | 229.34 | 1.00 | 175.30 | 0.99 | 230.86 | 0.98 |
| 0.475  | 184.51 | 0.99 | 234.79 | 1.00 | 182.72 | 0.99 | 235.74 | 1.00 | 184.34 | 0.99 | 237.28 | 0.98 |
| 0.500  | 188.74 | 1.00 | 233.40 | 1.00 | 187.08 | 0.99 | 234.13 | 1.00 | 188.74 | 0.99 | 235.68 | 0.98 |
| 0.525  | 199.82 | 0.99 | 232.96 | 1.00 | 198.66 | 0.99 | 233.53 | 1.00 | 200.39 | 0.99 | 235.09 | 0.98 |
| 0.550  | 210.70 | 0.99 | 228.24 | 1.00 | 210.02 | 0.99 | 228.42 | 1.00 | 211.81 | 0.99 | 229.99 | 0.98 |
| 0.575  | 224.70 | 0.98 | 222.26 | 1.00 | 224.66 | 0.97 | 221.99 | 1.00 | 226.49 | 0.99 | 232.55 | 0.98 |
| 0.600  | 235.69 | 0.96 | 215.70 | 1.00 | 236.12 | 0.96 | 214.93 | 1.00 | 237.97 | 0.99 | 216.46 | 0.98 |
| 0.625  | 242.75 | 0.95 | 206.28 | 1.00 | 243.43 | 0.95 | 204.84 | 1.00 | 245.31 | 0.99 | 206.32 | 0.98 |
| 0.650  | 249.85 | 0.96 | 190.42 | 1.00 | 250.77 | 0.95 | 187.97 | 1.00 | 252.66 | 0.99 | 189.28 | 0.98 |
| 0.675  | 255.77 | 0.95 | 169.31 | 1.00 | 256.87 | 0.95 | 165.57 | 1.00 | 258.78 | 0.99 | 166.52 | 0.98 |
| 0.700  | 270.46 | 0.94 | 148.27 | 1.00 | 272.18 | 0.94 | 143.22 | 1.00 | 274.11 | 0.99 | 143.61 | 0.98 |
| 0.725  | 289.75 | 0.89 | 130.79 | 1.00 | 292.31 | 0.89 | 124.62 | 1.00 | 294.24 | 0.99 | 124.37 | 0.98 |
| 0.750  | 295.57 | 0.87 | 116.01 | 1.00 | 298.23 | 0.86 | 108.85 | 0.99 | 300.19 | 1.00 | 107.98 | 0.98 |
| 0.775  | 312.12 | 0.77 | 104.71 | 0.99 | 315.40 | 0.75 | 96.74 | 0.99 | 317.38 | 1.00 | 95.44 | 0.98 |
| 0.800  | 324.12 | 0.73 | 95.259 | 0.99 | 327.75 | 0.72 | 86.58 | 0.99 | 329.76 | 1.00 | 84.99 | 0.98 |

Average 210.39 ± 51.78 185.02 ± 39.19 210.14 ± 53.68 183.31 ± 41.76 211.53 ± 53.89 184.30 ± 42.59
multiple steps, which is in agreement with previous results from Vyazovkin et al. [34]. Such behavior has also been observed in other works referring to the thermal decomposition of other residues such as rice husks [43] and brewer’s spent grains [46].

The average kinetic parameters (Table 3) have the same order of magnitude and their differences can be explained by the way the methods are structured, that is, FWO and STK use simplifications in their constructions while VYZ is solved through optimization procedures. The behavior observed for the two humins indicates the occurrence of at least two reactions occurring in sequence [48].

H-SCB humins have higher average activation energy (≈210 kJ mol⁻¹) compared to H-RH (≈185 kJ mol⁻¹). This fact demonstrates that these humins are more thermally stable. The activation energy obtained is higher, but comparable to those reported in the literature for humins synthesized from xylose and glucose (150 kJ mol⁻¹ and 163 kJ mol⁻¹, respectively [21]). The difference can be explained by the biomass source used for the synthesis of humins, the biorefining, and the purification processes.

**Elucidating the kinetic mechanism** The master-plot curves (Fig. 4) were determined by using the mean activation energy from the isoconversional methods with thermoanalytical data (da/dt kinetic curves and temperature profiles) at 20 °C min⁻¹. The reaction mechanism was established based on the best experimental fit to the functions in Table 1 according to the RMSE and R² values. The VYZ method is the method that best describes the pyrolysis of the studied humins considering the R² obtained (mean R² of 0.992 and 0.977 for H-SCB and H-RH, respectively, presented in Table 3) and for being the method that presents greater accuracy compared to integral methods. Table 4 presents the RMSE and R² found for all the mechanism functions from Table 1 for the VYZ method. Selected reaction models for the VYZ method (marked with a “*” in Table 4) are plotted in Fig. 4.

The results showed that the thermal/pyrolysis decomposition of H-SCB obeyed the chemical reaction mechanisms (F₂, F₃, and F₄) because of the low RMSE (between 0.149 and 0.187) and R² greater than 0.800. Comparing the obtained curves in Fig. 4, the Avrami–Erofeev random nucleation (Aₙ models) and three-dimensional diffusion (D₃, D₄, and D₅) mechanisms showed greater numerical correspondence with the experimental data from the VYZ method up to a conversion of 0.300, while the mechanisms of second and third-order chemical reaction (F₂ and F₃, respectively) showed better correspondence up to a conversion of 0.500. It is noteworthy that the nucleation mechanisms described by exponential (E₁ and E₂) and chemical reaction (F₄) laws showed similar behavior after conversion of 0.500.

Similarly, the thermal/pyrolysis decomposition of H-RH obeyed the chemical reaction mechanisms (F₃/2 and F₂) also because of the low RMSE (0.131 and 0.151, respectively) and R² greater than 0.800, in addition to the three-dimensional diffusion (D₃). It was observed that a phase boundary-controlled reaction described by a one-dimensional diffusion mechanism (D₁) exists up to a conversion of 0.500, followed by three-dimensional diffusion reactions (D₃), nucleation (E₁), and chemical reaction (F₃ and F₄) for conversion between 0.300 and 0.700. Finally, the final step of thermal decomposition can be represented by one-dimensional boundary layer reactions (R₁/F₀).

The diffusion mechanisms that described the pyrolysis of H-RH (such as the D₃ model presented in Equation) are characterized by deceleration kinetics, that is, the conversion reaches an upper limit at the beginning of the thermal/pyrolysis decomposition and then reduces as the conversion increases [34].
Chemical reaction mechanism or models based on the order of reaction (model \( F_2 \) presented in Equation) are also characterized by deceleration kinetics and are simpler and more practical [34]. In this model, the kinetic rate is directly proportional to the change in concentration of unreacted material raised to a given power [34]. It is frequently used in thermal analysis studies due to its simplicity.

Nucleation mechanism describes the formation of a new product phase at nucleation sites within the sample and can occur in one (\( E_1 \) model) or multiple steps (\( P_{1/2} \) model described in Equation (22)). Furthermore, when nucleation occurs in multiple stages, the nuclei are classified as germinated nuclei, where the product particles can revert to reactants, and growth nuclei, in which the reaction normally takes place.

The results observed are consistent with the phenomena that occur during pyrolysis and with reports referring to pyrolysis of algal biomass [49] or waste wood [47] and acid hydrolysis residue of miscanthus [22]. The pyrolysis process of humins was mostly associated with diffusion reactions (conversion interval between 0.15–0.30) because the reaction occurs between the solid phase and gas and in conversions near the end of the reaction when the formation of biochar occurs. At this stage, the reaction propagates from the external surface of the biochar to its interior [49]. The occurrence of nuclei growth reactions can be justified by the occurrence of defects in the structure of humins that act as nucleation sites [49].

Especially, the fact that more than one kinetic mechanism can represent the studied processes corroborates the hypothesis pointed out in the previous sections that pyrolysis is a complex process that occurs in multiple stages. Thus, it becomes necessary to consider a multiple reactions approach, that is, considering that the thermal/pyrolysis decomposition of humins is characterized by overlapping reactions (parallel independent and consecutive reactions), which will be developed in further studies for a better description of the thermal degradation of humins.

### Estimating the pre-exponential factor

Based on the kinetic model that best described the thermal decomposition of humins, the pre-exponential factor (\( A_\alpha \)) was determined by minimizing Equation using the selected heating rates and the conversion range between 0.150 and 0.800. As a result, pre-exponential factors equal to \( 2.343 \times 10^{13} \text{ min}^{-1} \) for H-SCB and \( 7.467 \times 10^{10} \text{ min}^{-1} \) for H-RH were obtained. The pre-exponential factor found for the one-step global single reaction of H-SCB and H-RH

\[
f(\alpha) = \frac{3}{2} (1 - \alpha)^{4/3} \left[ (1 - \alpha)^{-1/3} - 1 \right]^{-1}
\]

\[
f(\alpha) = (1 - \alpha)^2
\]

\[
f(\alpha) = 2\alpha^{1/2}
\]

Table 4 Root mean squared error (RMSE) and coefficient of determination (\( R^2 \)) between theoretical and experimental master plots. Mechanism marked with an “*” is plotted in Fig. 4

| Mechanism  | H-SCB RMSE | H-SCB \( R^2 \) | H-RH RMSE | H-RH \( R^2 \) | Mechanism  | H-SCB RMSE | H-SCB \( R^2 \) | H-RH RMSE | H-RH \( R^2 \) | Mechanism  | H-SCB RMSE | H-SCB \( R^2 \) | H-RH RMSE | H-RH \( R^2 \) |
|------------|--------|-------------|--------|-------------|------------|--------|-------------|--------|-------------|------------|--------|-------------|--------|-------------|
| \( F_{1/3} \) | 0.446 | 0.004 | 0.244 | 0.426 | \( D_2 \) | 0.457 | 0.007 | 0.252 | 0.416 | \( E_2 \) | 0.825 | 0.023 | 0.893 | 0.342 |
| \( F_{3/4} \) | 0.343 | 0.202 | 0.167 | 0.551 | \( D_3 \) | 0.362 | 0.011 | 0.179 | 0.526 | \( A_1 \) | 0.295 | 0.090 | 0.142 | 0.623 |
| \( F_{3/2} \) | 0.220 | 0.629 | 0.131 | 0.857 | \( D_1 \) | 0.588 | 0.053 | 0.369 | 0.316 | \( A_2 \) | 0.295 | 0.090 | 0.142 | 0.623 |
| \( F_{2} \) | 0.172 | 0.821 | 0.151 | 0.807 | \( D_4 \) | 0.242 | 0.262 | 0.129 | 0.854 | \( A_3 \) | 0.295 | 0.090 | 0.142 | 0.623 |
| \( F_{3} \) | 0.149 | 0.947 | 0.211 | 0.200 | \( D_6 \) | 0.591 | 0.052 | 0.373 | 0.316 | \( A_4 \) | 0.295 | 0.090 | 0.142 | 0.623 |
| \( F_{4} \) | 0.187 | 0.836 | 0.268 | 0.031 | \( D_7 \) | 0.578 | 0.048 | 0.361 | 0.323 | \( A_{1/2} \) | 0.295 | 0.090 | 0.142 | 0.623 |
| \( G_1 \) | 1.088 | 0.208 | 0.849 | 0.172 | \( D_8 \) | 0.635 | 0.066 | 0.416 | 0.294 | \( A_{3/2} \) | 0.295 | 0.090 | 0.142 | 0.623 |
| \( G_2 \) | 2.278 | 0.316 | 2.033 | 0.101 | \( P_{2/3} \) | 0.553 | 0.040 | 0.336 | 0.338 | \( A_{3/4} \) | 0.295 | 0.090 | 0.142 | 0.623 |
| \( G_3 \) | 5.058 | 0.350 | 4.816 | 0.072 | \( P_{1/2} \) | 0.553 | 0.040 | 0.336 | 0.338 | \( A_{5/2} \) | 0.295 | 0.090 | 0.142 | 0.623 |
| \( R_{1/F_0} \) | 0.553 | 0.040 | 0.336 | 0.338 | \( P_{1/3} \) | 0.553 | 0.040 | 0.336 | 0.338 | \( A_{1/2} \) | 0.295 | 0.090 | 0.142 | 0.623 |
| \( R_{2/F_1/2} \) | 0.402 | 0.000 | 0.208 | 0.475 | \( P_{1/4} \) | 0.553 | 0.040 | 0.336 | 0.338 | \( A_{1/3} \) | 0.295 | 0.090 | 0.142 | 0.623 |
| \( R_{2/F_2/3} \) | 0.362 | 0.011 | 0.179 | 0.526 | \( P_2 \) | 0.553 | 0.040 | 0.336 | 0.338 | \( A_{1/4} \) | 0.295 | 0.090 | 0.142 | 0.623 |
| \( D_4 \) | 1.527 | 0.239 | 1.292 | 0.135 | \( E_1 \) | 0.213 | 0.698 | 0.263 | 0.112 | \( B_1 \) | - | - | - | - |

* Mechanisms that described the thermal decomposition of H-SCB

§ Mechanisms that described the thermal decomposition of H-RH
indicates that fewer molecular collisions are required for the generation of active complexes [44].

**Thermodynamic parameters**

The feasibility of the process was also evaluated through thermodynamic parameters. The mean activation energy values computed from the VYZ method were utilized to evaluate the thermodynamic parameters within a certain conversion range (0.150 < \( \alpha \) < 0.800).

The enthalpy change (\( \Delta H_\alpha \)) demonstrates the total energy consumption by humins in the thermal/pyrolysis decomposition for the formation of products. Positive enthalpy changes, such as those found for H-SCB and H-RH (Fig. 5a and d), demonstrate that the thermal decomposition is an endothermic process. It is observed that the \( \Delta H_\alpha \) for H-SCB slightly varies from the beginning of the process until the conversion of approximately 0.425, indicating that the primary pyrolysis step occurs stably. Then, there is an increase in \( \Delta H_\alpha \) after this conversion, showing that there is a greater need for energy to convert parts of the humins not yet reacted into activated complexes [49].

As for H-RH, there is an increase in \( \Delta H_\alpha \) up to the conversion of approximately 0.500 that indicates that more energy is needed to convert this humin into products, in addition to this process occurring in two or more stages, explained by the existence of the shoulder next to the major degradation peak or maximum decomposition rate. After a conversion of 0.500, there is a reduction in \( \Delta H_\alpha \) that indicates a decrease in the endothermic behavior of the process.

The small differences between activation energy and \( \Delta H_\alpha \) (~6 kJ mol\(^{-1}\)) demonstrate that the energy potential barrier required for the production of the activated complex to form the products is easily overcome [44], indicating that the formation of the products is favorable [44].
The entropy change ($\Delta S_\alpha$) shows the disorder of the system and how reactive the system is. In thermal degradation, $\Delta S_\alpha$ indicates that the thermochemical equilibrium was reached and a thermally stable product was formed [44]. In the comparison among the studied humins, it is inferred that H-SCB has greater reactivity compared to H-RH because it has higher $\Delta S_\alpha$ (Fig. 5b and e), suggesting that this material will take a shorter time to form the activated complex [44]. For both humins, it was observed that $\Delta S_\alpha$ decreases with increase in conversion (Fig. 5b and e), indicating a gradual drop in reactivity.

Finally, the Gibbs free energy change ($\Delta G_\alpha$) indicates the amount of energy supplied to a material during the thermal process. For both humins, the positive $\Delta G_\alpha$ (Fig. 5c and f) values observed during their decomposition reaction indicated that the process is not spontaneous. Analogously to what was observed in $\Delta H_\alpha$, the primary pyrolysis step of H-SCB occurs stably, requiring almost the same amount of energy, and after a conversion of 0.425, part of the energy supplied to the system was a surplus because the residual lignin was removed during the purification step. Additionally, the non-spontaneity associated with the pyrolysis of H-RH was clearly observed, as seen in Fig. 5f with the variation in $\Delta G_\alpha$, which was positive for any conversion. Nevertheless, it can be inferred that a greater amount of energy had to be supplied to the system for the process to occur [44] up to a conversion of 0.5; then, the decrease in $\Delta G_\alpha$ for conversions greater than 0.5 indicates that less energy was needed for the process to continue.

**Assessment of the one-step global single reaction and rate-limiting step**

Figure 6a and b presents the theoretical and experimental conversion rates obtained for the thermal decomposition of H-SCB and H-RH, assuming a global reaction model and three heating rates. Theoretical calculations were performed using the kinetic mechanism function established with the generalized master-plot method and kinetic parameters obtained from the VYZ method. Theoretical curves represent the experimental data well with a good fit, showing an RMSE in the order of $10^{-19}$ for H-SCB and $10^{-18}$ for H-RH.

The rate-limiting step is the one with the slowest reaction rate. The rate-limiting step is generally the step that requires the greatest activation energy or it is the transition state of highest free energy. In this work, parameters computed using the isocconversional methods helped to identify the change in the rate-limiting step of the overall pyrolysis mechanism. Then, the rate-limiting step and the variation of the reaction rate can be correlated with the extent of conversion. The terms $[A_\alpha f(\alpha)]$ and $exp[-E_\alpha/(RT)_\alpha]$ were evaluated using Equation (13), and the reaction rate was computed for each extent of conversion as the product of $[A_\alpha f(\alpha)]$ and $exp[-E_\alpha/(RT)_\alpha]$ [50]. Based on this method, the maximum rate reaction ($da/dT$) was observed in the conversion range of 0.425–0.475.

Using this methodology, it is not possible to determine the presence of a rate-limiting step for H-SCB (Fig. 6c) because the decrease in ($da/dT$) in conversions above
0.425 can be attributed to the decrease in $\exp\left[-E_a/(RT)\right]$, thus indicating that the decrease in the reaction rate occurs due to an energy factor [50]. On the other hand, for H-RH (Fig. 6d), it is possible to identify that the rate-limiting step occurs after a conversion of 0.475, caused by the decrease in both $(da/dT)$ and $[A_n f(\alpha)]$. The decrease in the reaction rate is caused by a change in the kinetic mechanism $(f(\alpha))$ or an entropic change $(A_n)$ [50]. This entropic change may be explained by a change in the configuration or a decrease in the efficiency of collisions [50].

The achieved results improve the understanding of the mechanisms of thermal/pyrolysis decomposition of humins from sugarcane bagasse and rice husks, in addition to serving as initial estimates for other processes that work with humins from other sources or carbonaceous materials.

**Conclusions**

This work showed that humins from a three-step biorefining of sugarcane bagasse (H-SCB) and rice husk (H-RH) have similar spherical morphology. The potential use of H-SCB and H-RH as solid fuels was confirmed by the high O/C and H/C atomic ratios and high carbon content. The pyrolysis behavior of the humins was divided into three stages: i) dehydration is the first reaction in humins pyrolysis; ii) severe mass loss due to the release of volatile organic compounds; and iii) formation of biochar. Isoconversional methods yielded comparable correlations between activation energy and conversion, and the obtained kinetic parameters were satisfactory and provided a good agreement with the one-step chemical reaction model used. The mechanisms that best described the decomposition of both humins were order-based models and three-dimensional diffusion, in addition to the nucleation mechanism for H-SCB and boundary layer reaction for H-RH. The reactivity of humins was evidenced by thermodynamic analysis, in which the pyrolysis of these materials is a spontaneous and endothermic process, and the formation of products is facilitated, with the thermal decomposition of H-SCB being more reactive compared to H-RH. As interest grows in the processing of biomass into levulinic acid, there will be greater production of humins. Therefore, the information presented in this work allows further research on the applications of by-products of biorefineries focused on the production of levulinic acid.

**Supplementary Information** The online version contains supplementary material available at https://doi.org/10.1007/s12155-022-10412-6.

**Acknowledgements** The authors would like to thank Centro de Equipamentos e Serviços Multisdisciplinares—CESM (Institute of Environmental, Chemical and Pharmaceutical Sciences at Federal University of São Paulo) for the support with TGA and the Laboratory of Recycling, Waste Treatment and Extraction—LAREX (Department of Chemical Engineering, Escola Politécnica of the University of São Paulo) for the support with TG-QMS.

**Author contribution** Julio César de Jesus Gariboti was involved in conceptualization, methodology (kinetic analysis), validation, formal analysis, data curation, writing - original draft; Marina Gontijo Souza Macedo helped in conceptualization, methodology (purification and physicochemical characteristics), data curation, writing - original draft; Vinicius Matheus Silva Macedo contributed to methodology (purification and physicochemical characteristics), Yesid Javier Rueda was involved in conceptualization, validation (kinetic analysis), writing- reviewing and editing; Emilia Savioli Lopes helped in methodology (production of agro-industrial acid hydrolysis residue); Jonathan Tenorio Vinhal contributed to methodology (TG-QMS analysis), validation, writing - original draft, Eliezer Ladeia Gomes was involved in conceptualization, validation, writing - original draft, supervision; Jorge Alberto Soares Tenório helped in validation, writing - reviewing and editing; Romilda Fernandez Felsibino contributed to validation, writing - original draft, supervision; Melina Savioli Lopes was involved in conceptualization, validation (thermodynamic analysis), writing- reviewing and editing; Laura Plazas Tovar helped in conceptualization, validation, writing - original draft, writing - reviewing and editing, resources, visualization, supervision, funding acquisition and project administration

**Funding** This work was supported by National Council for Scientific and Technological Development—CNPq [grants 408149/2018–3 and 162373/2020–1] and São Paulo Research Foundation—FAPESP [grants 2020/11347–5, 2015/17592–3, and 2015/20630–4].

**Data availability** E-supplementary information for this work can be found in e-version of this paper online.

**Declarations**

**Conflicts of interest** The authors declare that they have no conflict of interest.

**Ethics approval** Registers CEP N° 6389190320, 2804210420, and 5800140620 by Comitê de Ética em Pesquisa da Universidade Federal de São Paulo/Hospital São Paulo.

**Code availability** Not applicable.

**References**

1. Lopes ES, Leal Silva JF, Rivera EC, Gomes AP, Lopes MS, Maciel Filho R, Tovar LP (2020) Challenges to levulinic acid and humins valuation in the sugarcane bagasse biorefinery concept. Bioenerg Res 13(3):757–774. https://doi.org/10.1007/s12155-020-10124-9
2. Lopes ES, Gariboti JCJ, Feistel L, Rivera EC, Maciel Filho R, Tovar LP (2020) Acid Hydrolysis-based Sugarcane Bagasse Biorefining for Levulinic Acid Production: Dynamic Mechanistic Modeling Under Varying Operating Conditions. Chem Eng Trans 80:217–222. https://doi.org/10.3303/CET2080037
3. Lopes ES, Rivera EC, Gariboti JCJ, Feistel LHZ, Dutra JV, Maciel Filho R, Tovar LP (2020) Kinetic insights into the
lignocellulosic biomass-based levulinic acid production by a mechanistic model. Cellulose 27(10):5641–5663. https://doi.org/10.1007/s10570-020-03183-w

4. Fleig OP, Lopes ES, Rivera EC, Maciel Filho R, Tovar LP (2018) Concept of rice husk biofinery for levulinic acid production integrating three steps: Multi-response optimization, new perceptions and limitations. Process Biochem 65:146–156. https://doi.org/10.1016/j.procbio.2017.11.015

5. Leal Silva JF, Mariano AP, Maciel Filho R (2021) Less severe reaction conditions to produce levulinic acid with reduced humins formation at the expense of lower biomass conversion: Is it economically feasible? Fuel Commun 9:100029. https://doi.org/10.1016/j.fucomm.2021.100029

6. Kang S, Fu J, Zhang G (2018) From lignocellulosic biomass to levulinic acid: A review on acid-catalyzed hydrolysis. Renew Sustain Energy Rev 94:340–362. https://doi.org/10.1016/j.rser.2018.06.016

7. Shao Y, Lu W, Meng Y, Zhou D, Zhou Y, Shen D, Long Y (2021) The formation of 5-hydroxymethylfurfural and hydrochar during the valorization of biomass using a microwave hydrothermal method. Sci Total Environ 755:142499. https://doi.org/10.1016/j.scitotenv.2020.142499

8. Macedo MGS, Garibotti JCJ, Lopes ES, Gomes EL, Felisbino RF, Ardila YC, Tovar LP (2021) From sugarcane bagasse-derived humins towards porous materials with high-energy potential. 43rd Symposium on Biomaterials, Fuels and Chemicals, Virtual Conference

9. Muralidhara A, Tosi P, Mija A, Shirrazzuoli N, Len C, Engelen V, de Jong E, Marclair G (2018) Insights on thermal and fire hazards of humins in support of their sustainable use in advanced biofineries. ACS Sustainable Chem Eng 6(12):16692–16701. https://doi.org/10.1021/acs.suschemeng.8b03971

10. Higgins LJR, Brown AP, Harrington JP, Ross AB, Kaulich B, Higgins LJR, Brown AP, Harrington JP, Ross AB, Kaulich B, Higgins LJR, Brown AP, Harrington JP, Ross AB, Kaulich B (2020) Evidence for a core-shell structure of hydrothermal carbon. Carbon 161:423–431. https://doi.org/10.1016/j.carbon.2020.01.060

11. Tosi P, van Klink GPM, Celzard A, Fierrez V, Vincent L, de Jong E, Mija A (2018) Auto-crosslinked rigid foams derived from biofinery byproducts. Chemossuschem 11(6):2797–2809. https://doi.org/10.1002/cssc.201800778

12. Dinu R, Mija A (2019) Cross-linked polyfuran networks with elastomeric behaviour based on humins biofinery by-products. Green Chem 21(23):6277–6289. https://doi.org/10.1039/C9GC01813A

13. Yang J, Niu X, Wu H, Zhang H, Ao Z, Zhang S (2020) Valorization of humin as a glucose derivative to fabricate a porous carbon catalyst for esterification and hydroxyalkylation/alkylation. J Waste Manag 103:407–415. https://doi.org/10.1016/j.jwaspman.2020.01.004

14. Dinu R, Montes S, Orange F, Mija A (2021) Reprocessable humins thermosets and composites. Comp Sci Tech 207:108655. https://doi.org/10.1016/j.compscitech.2021.108655

15. Sun J, Cheng H, Zhang Y, Zhang Y, Lan X, Zhang Y, Xia Q, Ding D (2021) Catalytic hydrotreatment of humins into cyclic hydrocarbons over solid acid supported metal catalysts in cyclohexane. J Energy Chem 53:329–339. https://doi.org/10.1016/j.jechem.2020.05.034

16. Morone A, Apte M, Pandey RA (2015) Levulinic acid production from renewable waste resources: Bottlenecks, potential remedies, advancements and applications. Renew Sustain Energy Rev 51:548–565. https://doi.org/10.1016/j.rser.2015.06.032

17. van Zandvoort I, Wang Y, Rasrendra CB, van Eck ERH, Brujininx PCA, Heeres HJ, Weckhuysens BM (2013) Formation, molecular structure, and morphology of humins in biomass conversion: influence of feedstock and processing conditions. Chemosuschem 6(9):1745–1758. https://doi.org/10.1002/cssc.201300332

18. Magdziarz A, Wilk M, Wądryzak M (2020) Pyrolysis of hydrochar derived from biomass – Experimental investigation. Fuel 267:117246. https://doi.org/10.1016/j.fuel.2020.117246

19. Agarwal S, van Es D, Heeres HJ (2017) Catalytic pyrolysis of recalcitrant, insoluble humin byproducts from C6 sugar biofineries. J Anal Appl Pyrolysis 123:134–143. https://doi.org/10.1016/j.jaap.2016.12.014

20. Mija A, van der Waal JC, Pin J-M, Guigo N, de Jong E (2017) Humins as promising material for producing sustainable carbohydrate-derived building materials. Constr Build Mater 139:594–601. https://doi.org/10.1016/j.conbuildmat.2016.11.019

21. Wang S, Lin H, Zhao Y, Chen J, Zhou J (2016) Structural characterization and pyrolysis behavior of humin by-products from the acid-catalyzed conversion of C6 and C5 carbohydrates. J Anal Appl Pyrolysis 118:259–266. https://doi.org/10.1016/j.jaap.2016.02.009

22. Cortés AM, Bridgewater AV (2015) Kinetic study of the pyrolysis of miscanthus and its acid hydrolysis residue by thermogravimetric analysis. Fuel Process Technol 138:184–193. https://doi.org/10.1016/j.fuproc.2015.05.013

23. Shirrazzuoli N (2020) Interpretation and physical meaning of kinetic parameters obtained from isoconversional kinetic analysis of polymers. Polymers (Basel) 12(6):1280. https://doi.org/10.3390/polym12061280

24. Sangregorio A, Guigo N, Jong ED, Shirrazzuoli N (2019) Kinetics and chemorheological analysis of cross-linking reactions in humins. Polymers (Basel) 11(11):1804. https://doi.org/10.3390/polym11111804

25. Song G, Novotny E, Simpson A, Clapp CE, Hayes MHB (2008) Sequential exhaustive extraction of a Molissol soil, and characterizations of humic components, including humin, by solid and solution state NMR. Eur J Soil Sci 59:505–516. https://doi.org/10.1111/j.1365-2389.2007.01006.x

26. American Society for Testing and Materials (2017) ASTM D3173 / D3173M–17a, Standard test method for moisture in the analysis sample of coal and coke. American Society for Testing and Materials, West Conshohocken. https://doi.org/10.1520/D3173_D3173M-17A

27. American Society for Testing and Materials (2018) ASTM D3174–02, Standard test method for ash in the analysis sample of coal and coke from coal. American Society for Testing and Materials, West Conshohocken. https://doi.org/10.1520/D3174-12R18

28. American Society for Testing and Materials (2020) ASTM D3175–20, Standard test method for volatile matter in the analysis sample of coal and coke. American Society for Testing and Materials, West Conshohocken. https://doi.org/10.1520/D3175-20

29. Nhuochhen DR (2016) Prediction of carbon, hydrogen, and oxygen compositions of raw and torrefied biomass using proximate analysis. Fuel 180:348–356. https://doi.org/10.1016/j.fuel.2016.04.058

30. Trache D, Abdelaziz A, Siouani B (2016) A simple and linear isoconversional method to determine the pre-exponential factors and the mathematical reaction mechanism functions. J Therm Anal Calorim. https://doi.org/10.1007/s10973-016-5962-0

31. Flynn JH, Wall LA (1966) General treatment of the thermogravimetry of polymers. J Res Nat Bur Standards, Section A 70A(6):487–523. https://doi.org/10.6028/jres.070A.043

32. Starink MJ (2003) The determination of activation energy from isothermal decomposition measurements by isoconversional method. Thermochim Acta 404(1):163–176. https://doi.org/10.1016/S0040-6031(03)00144-8

33. Vyazovkin S, Dollimore D (1996) Linear and nonlinear procedures in isoconversional computations of the activation energy of nonsmooth reactions in solids. J Chem Inf Comp Sci 36(1):42–45. https://doi.org/10.1021/ci950062m

34. Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Shirrazzuoli N (2011) ICTAC kinetics committee
recommendations for performing kinetic computations on thermal analysis data. Thermochim Acta 520(1):1–19. https://doi.org/10.1016/j.tca.2011.03.034

35. Pérez-Maqueda LA, Criado JM (2000) The accuracy of Senu and Yang’s approximations to the Arrhenius integral. J Therm Anal Calorim 60(3):909–915. https://doi.org/10.1023/A:101015926340

36. Criado JM (1978) Kinetic analysis of DTG data from master curves. Thermochim Acta 24(1):186–189. https://doi.org/10.1016/0040-6033(78)85151-X

37. Eyring H (1935) The activated complex in chemical reactions. J Chem Phys 3:107. https://doi.org/10.1063/1.1749604

38. Sumerskii IV, Kruyov SM, Zarubin MY (2010) Humin-like substances formed under the conditions of industrial hydrolysis of wood. Russ J Appl Chem 83(2):320–327. https://doi.org/10.1134/S1070427210020266

39. Cheng Z, Everhart JL, Tsiolomelekis G, Nikolakis V, Saha B, Vlachos DG (2018) Structural analysis of humins formed in the Brønsted acid catalyzed dehydration of fructose. Green Chem 20(5):997–1006. https://doi.org/10.1039/C7GC03054A

40. Hoang TMC, van Eck ERH, Bula WP, Gardeniers JGE, Lefferts L, Seshan K (2015) Humins based by-products from biomass processing as a potential carbonaceous source for synthesis gas production. Green Chem 17(2):959–972. https://doi.org/10.1039/C4GC01324G

41. Björnerbäck F, Hedin N (2019) Microporous humins prepared from sugars and bio-based polymers in concentrated sulfuric acid. ACS Sustainable Chem Eng 7(1):1018–1027. https://doi.org/10.1021/acsuschemeng.8b04658

42. Alves ILF, Da Silva JCG, da Silva Filho VF, Alves RF, de Araujo Galdino WV, Andersen SLF, De Sena RF (2019) Determination of the bioenergy potential of brazilian pine-fruit shell via pyrolysis kinetics, thermodynamic study, and evolved gas analysis. Bioenerg Res 12(1):168–183. https://doi.org/10.1007/s12155-019-9964-1

43. Zhang S, Pi M, Su Y, Xu D, Xiong Y, Zhang H (2020) Physicochemical properties and pyrolysis behavior evaluations of hydrochar from co-hydrothermal treatment of rice straw and sewage sludge. Biomass Bioenergy 140:105664. https://doi.org/10.1016/j.biombioe.2020.105664

44. Shahid A, Ishfaq M, Ahmad MS, Malik S, Farooq M, Hui Z, Batawi AH, Shafi ME, Aloqbi AA, Gull M, Mehmoond MA (2019) Bioenergy potential of the residual microalgal biomass produced in city wastewater assessed through pyrolysis, kinetics and thermodynamics study to design algal biorefinery. Bioresour Technol 289:121701. https://doi.org/10.1016/j.biortech.2019.121701

45. Radojević M, Janković B, Jovanović V, Stojiljković D, Manić N (2018) Comparative pyrolysis kinetics of various biomasses based on model-free and DAEM approaches improved with numerical optimization procedure. PLoS ONE 13(10):e0206657. https://doi.org/10.1371/journal.pone.0206657

46. Olszewski MP, Arauzo PJ, Maziarka PA, Ronse F, Kruse A (2019) Pyrolysis kinetics of hydrochars produced from brewer’s spent grains. Catalysts 9(7):625. https://doi.org/10.3390/catal9070625

47. Sobek S, Werle S (2020) Kinetic modelling of waste wood devolatilization during pyrolysis based on thermogravimetric data and solar pyrolysis reactor performance. Fuel 261:116459. https://doi.org/10.1016/j.fuel.2019.116459

48. Bartocci P, Tschentscher R, Stensrød RE, Banabanera M, Fantozzi F (2019) Kinetic analysis of digestate slow pyrolysis with the application of the master-plots method and independent parallel reactions scheme. Molecules 24(9):1657. https://doi.org/10.3390/ molecules24091657

49. Vasudev V, Ku X, Lin J (2020) Pyrolysis of algal biomass: Determination of the kinetic triplet and thermodynamic analysis. Bioresour Technol 317:124007. https://doi.org/10.1016/j.biortech.2020.124007

50. Shibrazzuoli N (2019) Advanced isoconversional kinetic analysis for the elucidation of complex reaction mechanisms: a new method for the identification of rate-limiting steps. Molecules 24(9):1683. https://doi.org/10.3390/molecules24091683

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.