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ISOCONVERSIONAL MODELING FOR DETERMINING PYROLYSIS KINETIC AND THERMODYNAMIC PARAMETERS OF BIOMASS RESIDUES

Mayara Gabi Moreira
University of Brasília, Mechanical Sciences Graduate Program, Laboratory of Energy and Environment, Brasilia-DF, 70910-900, Brazil
Mayaragabimoreira05@gmail.com

Giulia Cruz Lamas
University of Brasília, Mechanical Sciences Graduate Program, Laboratory of Energy and Environment, Brasilia-DF, 70910-900, Brazil
giuliac.lamas@gmail.com

Pedro Paulo Oliveira Rodrigues
University of Brasília, Mechanical Sciences Graduate Program, Laboratory of Energy and Environment, Brasilia-DF, 70910-900, Brazil
pedropaulo9334@gmail.com

Edgar A. Silveira
University of Brasília, Mechanical Sciences Graduate Program, Laboratory of Energy and Environment, Brasilia-DF, 70910-900, Brazil
edgar.silveira@unb.br

Abstract. Biomass is promising as a green energy vector. A thorough understanding of the kinetic of biomass and thermodynamic parameters is required for biomass conversion processes to operate under conditions of maximum efficiency. One of the techniques for obtaining this data is thermogravimetric experiments and isoconversional numerical methods, which allow obtaining these parameters without the need to assume a reaction model. Therefore, this work aims to perform and validate four numerical methods: Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa method (FWO), Starink, and Friedman. For this, a Python routine was developed. The data used were taken from the literature and referred to the pyrolysis of corn stalks. The activation energy values varied significantly with the conversion in the same way as the reference, with an average error of less than 0.5% for the results of the KAS, FWO, and Starink methods and an error of about 3% for the Friedman method. As for the pre-exponential factor, the results showed the same variation between 1011 and 1019 s–1. The errors of the KAS, FWO, and Starink methods were less than 0.2%, 0.1%, and 10% concerning enthalpy, Gibbs free energy and entropy, respectively. However, these errors were significantly higher for the Friedman method, reaching an average error of 117% for entropy. Thus, it is evident that the results of the first three methods were satisfactory and that the numerical routine was performed adequately. However, the Friedman method presents considerably discrepant values. In the literature, the results for this method are often divergent from the others. Therefore, numerical resolution of the KAS, FWO, and Starink methods is recommended to obtain the kinetic and thermodynamic parameters.

Keywords: *isoconversional methods, biomass, numerical resolution*

1. INTRODUCTION

The energy world demand heavily relies on fossil fuels, but Brazil stands out as a positive example for its renewable sources matrix. However, there is room for improvement, as several isolated cities in the country are not connected to the national electricity grid and rely on thermoelectric plants powered primarily by fossil fuels. Fortunately, Brazil possesses a wealth of biomass sources with the potential for significant energy recovery, offering a promising alternative fuel option.

Various methods have been developed for converting biomass, offering diverse energy outputs and valuable products (PURKAIT; HALDAR, 2021). Among these methods, pyrolysis is a promising approach for transforming biomass into bio-oil and pyrolysis char, which serve as valuable liquid and solid fuels, respectively (BRIDGWATER, 2012). Pyrolysis involves the thermal degradation of biomass in the absence of oxygen or oxygen-lean conditions. The knowledge of biomass pyrolysis kinetics plays a pivotal role in facilitating the design and optimization of biomass pyrolysis systems.

The primary objective of conducting a kinetic study is to elucidate the relationship between the rate of a process and temperature, which involves determining the Arrhenius parameters (activation energy and pre-exponential factor) and

understanding the underlying reaction mechanism or model. When investigating solid-state kinetics, thermal investigation is a commonly employed technique for kinetic analysis. However, the complexity of thermally driven processes in solids, characterized by multiple reactions, phase transitions, and mass and heat transport, presents challenges in accurately determining activation energies. Recognizing this complexity, the International Confederation for Thermal Analysis and Calorimetry (ICTAC) has demonstrated the suitability of isoconversional methods for analyzing multi-step processes in a Kinetic Project (BROWN et al., 2000).

Isoconversional methods are widely used to study the thermokinetic behavior of different materials. One of these methods, known as the Kissinger technique, can be employed to determine the pre-exponential factors once the activation energies of biomass pyrolysis have been measured (SAHA et al., 2021). Calculating activation energies and pre-exponential factors makes it possible to approximate key thermodynamic parameters such as Gibbs free energy, enthalpy, and entropy changes. These kinetic and thermodynamic characteristics provide valuable insights into the mechanisms of biomass pyrolysis while also aiding in evaluating conversion efficiency and developing biomass pyrolysis systems.

Performing isoconversional computations often involves substantial numerical computing capabilities, encompassing tasks such as linear regression, integration or differentiation, and managing large experimental datasets. A significant challenge in thermokinetic analysis is the time-consuming nature of the process (RAMÍREZ et al., 2022). Thankfully, several programming languages are available to address numerical challenges, with Python standing out due to its intuitive language, user-friendly syntax, and interactive data manipulation and software development environment.

This study aimed to develop and validate the numerical resolution of four distinct methods: KAS, FWO, Starink, and Friedman. The additional kinetic and thermodynamic parameters were calculated with a parametric Python function by leveraging the activation energy data obtained from each method. The dataset utilized for this analysis was based on previous literature on corn stalk pyrolysis (GUO et al., 2022).

2. THEORETICAL KINETICS

According to the Arrhenius equation, the kinetics of the combustion reaction of lignocellulosic biomass, governed by a heterogeneous (solid-volatile-gas) conversion process, can be described (VYAZOVKIN et al., 2011). The decomposition rate can be evaluated using a general expression for biomass pyrolysis kinetics, represented mathematically by Eq. (1). The decomposition rate is evaluated by the general expression for biomass pyrolysis kinetics as a function of temperature (T) and conversion (α), which can be expressed mathematically by

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

Here the experimental conversion (α) was calculated with Eq. (2)

$$\alpha = \frac{m_i - m}{m_i - m_f}, \tag{2}$$

where m_i is the initial mass of the sample (mg), m is the sample mass (mg) at time t, and m_f is the final mass of the sample (mg). The $(d\alpha/dt)$ can be written as Eq. (3):

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = k(T) \, . f(\alpha), \tag{3}$$

where β represents the average heating rate (K. min^{-1}). The $k(T)$ can be defined following Eq. (4)

$$k(T) = A . e^{\frac{-E_\alpha}{RT}}, \tag{4}$$

where E_α (J. mol^{-1}) is the apparent activation energy, A (min^{-1}) is the pre-exponential factor, T is the temperature in K, and R is the gas constant (8.314 J mol^{-1} K^{-1}). Applying Eq. (4) to Eq. (3) results in Eq. (5)

$$\frac{d\alpha}{dt} = \beta \frac{d\alpha}{dT} = A . e^{\frac{-E_\alpha}{RT}} \, . f(\alpha) \tag{5}$$

The integrated reaction model, g(α), can be obtained after integrating Eq. (5) for temperature. The kinetics triplet (activation energy, pre-exponential factor, and reaction model) is typically determined using the differential or integral methods of Eq. (6).

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T} e^{\frac{-E_\alpha}{RT}}\, dT \tag{6}$$

2.1 Estimation of activation energy (E_α)

The KAS, FWO, and Starink were developed in their integral form, while the Friedman method was modeled in its differential form. The mathematical formulas for these techniques can be found in Table 1. These isoconversional methods enabled the estimation of E_α at different conversion values while circumventing the uncertainties associated with assuming a reaction model. Understanding other kinetic factors requires consideration of the reaction model. As per recommendation, the conversion range employed to determine the spread of activation energy was 10–90% (VYAZOVKIN et al., 2011).

Table 1. Description of the isoconversional methods, their mathematical expression, and related observations.

Method	Mathematical expression	Eq.	Observations	Ref.
KAS	$\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = \ln\left(\frac{A_\alpha R}{g(\alpha)E_\alpha}\right) - \left(\frac{E_\alpha}{RT_{\alpha,i}}\right)$	7	Where β_i is the heating rate. The Eα can be calculated from the slope of the fit line drawn between $\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)$ versus $-\left(\frac{1}{RT_{\alpha,i}}\right)$.	Akahira and Sunose, 1971 (KISSINGER, 1956)
FWO	$\ln(\beta_i) = \ln\left(\frac{A_\alpha E_\alpha}{g(\alpha)R}\right) - 5{,}331 - 1{,}052\left(\frac{E_\alpha}{RT_{\alpha,i}}\right)$	8	Based on Doyle's approximation. The Eα can be determined from the slope of the fit line drawn between $ln(\beta_i)$ versus $-\left(\frac{1{,}052}{RT_{\alpha,i}}\right)$.	(FLYNN; WALL, 1965)(OZAWA, 1965)
Starink	$\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1,92}}\right) = \ln\left(\frac{A_\alpha R^{1,92}}{g(\alpha)E_\alpha^{0,92}}\right) - 0{,}312 - 1{,}0008\left(\frac{E_\alpha}{RT_{\alpha,i}}\right)$	9	Based on KAS and FWO methods. The Eα can be calculated from the slope of the fit line drawn between $\ln\left(\frac{\beta_i}{T_{\alpha,i}^{1,92}}\right)$ versus $-\left(\frac{1{,}0008}{RT_{\alpha,i}}\right)$.	(STARINK, 1996)
Friedman	$\ln\left[\beta_i\left(\frac{d\alpha}{dt}\right)_{\alpha,i}\right] = \ln[A_\alpha . f(\alpha)] - \left(\frac{E_\alpha}{RT_{\alpha,i}}\right)$	10	The E_α can be calculated from the slope of the fit line drawn between $\ln\left[\beta_i\left(\frac{d\alpha}{dt}\right)_{\alpha,i}\right]$ versus $-\left(\frac{1}{RT_{\alpha,i}}\right)$.	(FRIEDMAN, 1964)

2.2 Estimation of pre-exponential factor (A_α)

Due to the limitations of the isoconversional method in providing physically interpretable values within a narrow conversion range, it may not be the preferred approach for determining the value of A_α (SAHA et al., 2021). Consequently, researchers often turn to the ASTM E698-18 standard method, based on the Kissinger equation, as it provides a more reliable alternative. Eq. (11) represents the equation used in the ASTM E698-18 standard method.

$$A_\alpha = \frac{\beta\, E_{\alpha,i}\, e^{\left(\frac{E_{\alpha,i}}{RT_{m,i}}\right)}}{R\, T_{m,i}^2} \tag{11}$$

where $T_{m,}$ is the temperature determined by the derivative curve (DTG) for each value of β to correlate to the maximum mass loss in the TG curve.

2.3 Estimation of thermodynamic properties

To enable the transition of a process from thermochemical conversion to industrial-scale implementation, it is essential to evaluate thermodynamic properties such as ΔG (Gibbs free energy), ΔH (enthalpy), and ΔS (entropy) through their calculations. These properties can be predicted by the equations derived from activated complex theory to the kinetic

parameter data. The following equations illustrate the relationship between kinetic parameters and thermodynamic properties:

$$\Delta G = E_\alpha + RT_m ln\left(\frac{k_b\, T_m}{h\, A}\right) \tag{12}$$

$$\Delta H = E_\alpha - RT \tag{13}$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \tag{14}$$

where k_b (1.381 E–23 J.K^{-1}) and h (6.626 E–34 J.K^{-1}) represent the Boltzmann and Plank constants, respectively.

3. METHOD OF DESIGN AND MODEL VALIDATION

3.1 Model

A parametric model was developed to numerically solve the isoconversional and thermodynamic equations, allowing for the determination of both the kinetics and thermodynamic properties. The model was implemented using Python 3 programming language on the Google Compute Engine platform. The code structure (Figure 1) was organized into three main sections: data reading, manipulation, and organization of the experimental data; computational resolution of the isoconversional methods; and the resolution of Eq. (11) to (14).

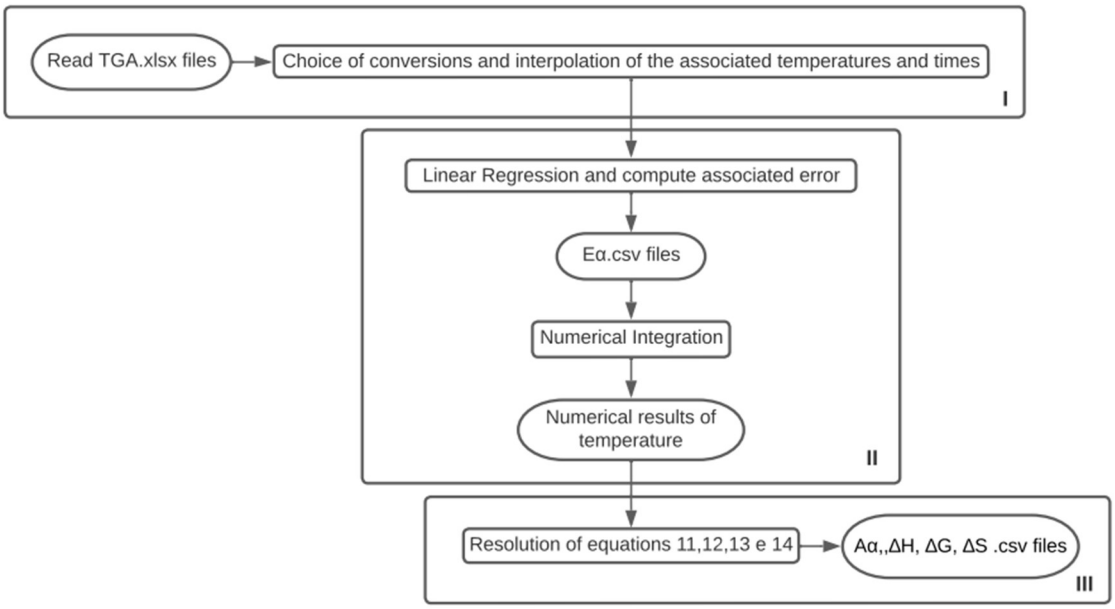

Figure 1. The framework of isoconversional kinetic modeling and thermodynamic properties determination.

To ensure user-friendly usability, a simplified structure was implemented for the model. The first part of the code involves reading the experimental results obtained from thermogravimetric analysis (TGA). The code requires a list of file paths, which should be arranged in ascending order based on the heating rate. The raw data must be in .xlsx format and organized with temperature values in Kelvin, conversion values in decimal form, and time values in seconds, each in a separate column.

Upon running the code, the user is prompted to input the heating rates, sampling intervals, and the lower and upper limits of the conversion range. These parameters enable customization and flexibility for analysis. After reading the data, the code creates a vector containing the conversion values, and it performs interpolation to calculate the corresponding experimental temperature and time values. This interpolation step ensures precise data alignment for subsequent calculations. The model streamlines the input process by implementing this structure, allowing users to quickly provide

the required data and parameters. The interpolation step ensures accurate calculations by aligning the experimental values with the conversion values of interest.

The second part of the model involves creating vectors for each isoconversional method to linearize the corresponding equations. For example, for the Kissinger-Akahira-Sunose (KAS) method, vectors are created for $\ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)$ and $-\left(\frac{1}{RT_{\alpha,i}}\right)$, where β_i represents the heating rate and $T_{\alpha,i}$ is the temperature at a specific conversion α. These vectors are used to generate a scatter plot and a linear regression is performed to obtain the values of E_α (activation energy) and R^2 (coefficient of determination) for each α. Numerical integration is then carried out using these data to obtain a vector of temperatures. This section of the code utilizes various libraries including numpy (NUMPY COMMUNITY, 2022), pandas (MCKINNEY; PANDAS, 2022), scipy (SCIPY COMMUNITY, 2022), and matplotlib (HUNTER et al., 2019). These libraries provide essential functionalities for data manipulation, numerical calculations, and plotting. The calculated temperatures from the numerical resolution can be compared to the experimental results.

In the last part of the model, the differential thermogravimetric (DTG) curve is calculated using the experimental data. This calculation is performed to obtain T_m, a parameter used in Eqs. (11–14). The solutions to these equations are then computed to determine various thermodynamic properties. To export the results, the code generates a .csv file containing the conversion values, E_α, and R^2. Additionally, separate .csv files are created for each heating rate, containing the conversion values, temperature isoconversional, A_α, ΔG, ΔH, and ΔS. These results are further organized based on the isoconversional method used.

3.2 Model's Validation

To validate the developed model described in Section 3.1, experimental data from nonisothermal thermogravimetric analysis (TGA) were acquired from previous literature (GUO et al., 2022). The experimental pyrolysis data consisted of TGA measurements performed at four different heating rates (4, 8, 16, and 32 K min^{-1}) for corn stalks. Each TGA test involved approximately 4 mg of biomass samples. Figure 2 illustrates the heating program used in the TGA experiments, providing insights into the temperature ramping during the analysis (GUO et al., 2022).

By comparing the results obtained from the present model with the experimental data provided by (GUO et al. (2022)), the validity and reliability of the model predictions were assessed. This comparison allowed for a comprehensive evaluation of the model performance in accurately estimating the kinetic and thermodynamic properties of corn stalk pyrolysis.

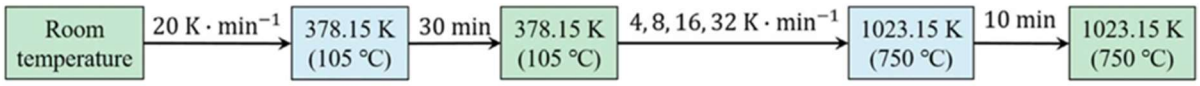

Figure 2. The heating program study of GUO et al., 2022 for kinetic tests.

4 RESULTS

4.1 Workflow

The numerical code reads the raw data containing temperatures in kelvin, conversion in decimal, and time in seconds. Then, the user determines the conversions for which the related parameters will be calculated. Naturally, the greater the number of conversions, the more results the code will have to calculate, consequently, the greater the computational cost. In this analysis, $\alpha_{inicial}$=0.05 and α_{final}=0.95 were chosen with a sampling step of $\Delta\alpha$=0.05. The computational costs referring to the use of memory, disk, and processing time for each method are shown in Table 2.

Regarding Table 2, the processing time stands out with considerably low values for all methods. The elapsed time for the Friedman method solution was more significant than the others. This happened because this method is the only one that needs to perform numerical integration of a non-linear ordinary differential equation to obtain the temperatures corresponding to each conversion, unlike the others (MISHRA et al., 2015).

Table 2. The computational cost of numerical resolution of the isocovensional and thermodynamic equations.

	KAS	FWO	STARINK	FRIEDMAN
RAM (GB)	0.9	1.3	1.4	1.4
Disco(GB)	23.4	23.4	23.4	23.4
Time (s)	3.487	3.787	2.581	4.393

4.2 Kinetic triplet assessment

4.2.1 Kinetics Parameters

The E_α values for the pyrolysis of corn stalks are plotted in Figure 3. As seen, E_α profiles for all isoconversional procedures are quite comparable. In this regard, the E_α profiles of corn stalks for the KAS, FWO, and Starink processes are nearly identical to the reference. There are certain approximations related to the temperature function because these methods are based on an integral form (JANKOVIĆ, 2008; MISHRA et al., 2015). However, compared to those derived using the other isoconversional approaches, the E_α profiles from the Friedman method are marginally different. The Friedman technique does not use an oversimplified approximation to evaluate the temperature function; it is based on the simple differential form of the kinetic rate law (MISHRA et al., 2015). Additionally, the Friedman technique is not restricted to the use of the linear variation of heating rate (CAI et al., 2018). The E_α varies strongly with conversion, gradually increasing from 181.3 to 213.8 kJ mol^{-1} in the conversion range between 0.05 and 0.85, then rapidly increasing to 265.5 kJ mol^{-1} in the conversion range 0.85–0.95.

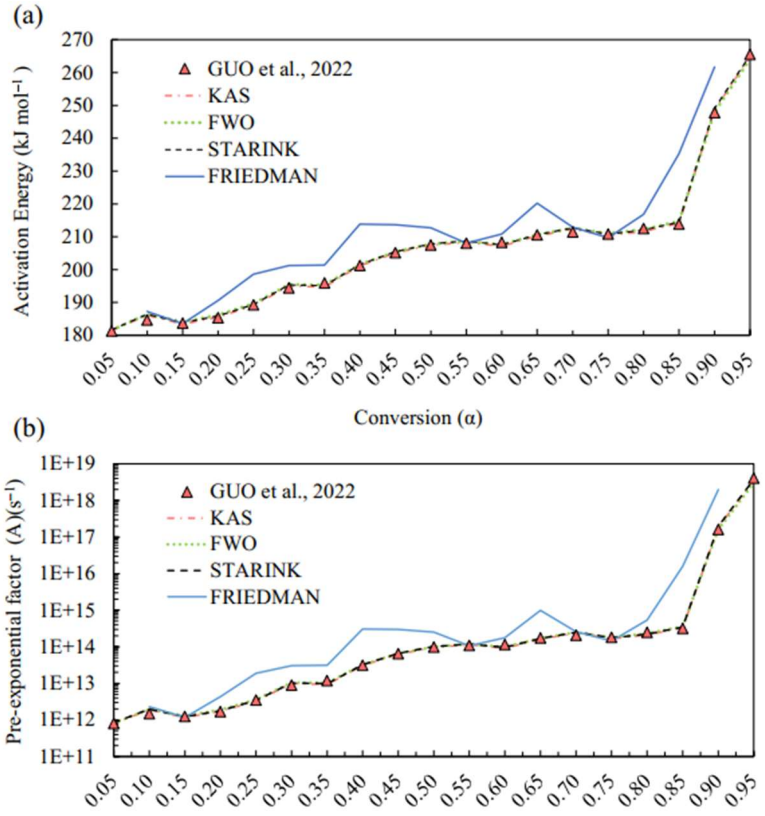

Figure 3. Experimental data from (GUO et al., 2022) and numerical prediction of (a) E_α and (b) pre-exponential factors for the pyrolysis of corn stalks considering the Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa method (FWO), Starink and Friedman isoconversional models.

Previous work developed an open-source module to solve the isoconversional methods and validated it by comparing its numerical result with literature regarding n-decane vaporization (RAMÍREZ et al., 2022). The authors obtained an average E_α of 49 kJ mol^{-1} and compared them with two literature references, which reported an average E_α of 47.4 kJ mol^{-1} (error of 3.37%) and 55 kJ mol^{-1} (error of –10.9%) (RAMÍREZ et al., 2022).

The present study obtained an average E_α of 206.09 kJ mol^{-1} for KAS, 206.45 kJ mol^{-1} for FWO, 206.48 kJ mol^{-1} for STARINK and 210.49 kJ mol^{-1} for Friedman. The difference was minimal for the KAS method and maximum for the Friedman method, as shown in Table 3. However, the errors presented were reduced concerning those presented by (RAMÍREZ et al., 2022), showing the quality of the model produced.

The pre-exponential factor and thermodynamic parameter values can then be computed from Eqs. (11) through (14) once the activation energies have been determined. Due to the dependence of Eq. (11) on the heating rate, Figure 3 displays the computed frequency factor values at an 8 K.min^{-1} heating rate, while Table 3 shows the errors.

The data at various heating rates can be used to determine that the calculated frequency factor values are pretty near. As a result, the heating rate has a negligible impact on the frequency factor value determined by the Kissinger approach.

The pre-exponential factor values determined using the Kissinger technique and the simulated values differ slightly. From Figure 3, it can be shown that the A_α values for the pyrolysis of all methods and reference fluctuate dramatically with α, ranging from 10^{11} to $10^{19} s^{-1}$ (GUO et al., 2022).

Table 3. Results comparison of (GUO et al., 2022) and numerical prediction of E_α and pre-exponential factors for the pyrolysis of corn stalks considering the Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa method (FWO), Starink and Friedman isoconversional models.

Conversion (α)	**KAS**		**FWO**		**STARINK**		**FRIEDMAN**	
	Error E_α	Error A_α	Error E_α	Error A_α	Error E_α	Error A_α	Error E_α	Error A_α
0.05	-0,03%	-0.91%	-0,15%	-3.19%	-0,21%	-5.42%	-	-
0.10	-0.75%	-29.22%	-0.92%	-34.09%	-0.94%	-35.22%	-1.41%	-58.57%
0.15	0.17%	5.67%	-0.17%	-4.12%	-0.02%	1.09%	0.11%	5.25%
0.20	-0.07%	-2.35%	-0.44%	-13.93%	-0.26%	-7.41%	-2.84%	-158.42%
0.25	0.15%	5.09%	-0.20%	-5.06%	-0.04%	0.35%	-4.93%	-447.15%
0.30	-0.27%	-10.22%	-0.52%	-18.13%	-0.46%	-15.73%	-3.51%	-243.70%
0.35	0.63%	20.33%	0.31%	12.29%	0.44%	16.25%	-2.77%	-166.50%
0.40	0.05%	1.88%	-0.16%	-4.14%	-0.14%	-3.13%	-6.27%	-894.19%
0.45	0.06%	2.08%	-0.11%	-2.20%	-0.13%	-2.94%	-4.15%	-368.09%
0.50	0.01%	0.43%	-0.14%	-3.45%	-0.17%	-4.71%	-2.54%	-158.05%
0.55	-0.12%	-4.88%	-0.30%	-9.81%	-0.31%	-10.35%	-0.01%	1.55%
0.60	0.54%	18.76%	0.30%	12.68%	0.35%	14.44%	-1.23%	-56.93%
0.65	0.18%	6.56%	-0.03%	1.01%	-0.01%	1.59%	-4.59%	-475.80%
0.70	-0.37%	-15.52%	-0.56%	-21.74%	-0.56%	-21.70%	-0.68%	-27.30%
0.75	0.20%	7.62%	-0.07%	-0.64%	0.01%	2.59%	0.51%	19.65%
0.80	0.42%	15.11%	0.13%	7.03%	0.23%	10.44%	-2.04%	-117.18%
0.85	-0.11%	-4.52%	-0.40%	-14.56%	-0.30%	-10.34%	-10.06%	-4951.79%
0.90	-0.35%	-17.41%	-0.06%	-0.14%	-0.52%	-23.62%	-5.60%	-1131.34%
0.95	0.28%	12.56%	0,55%	25.55%	0,11%	7.61%	-	-
Average	**0.03%**	**-**	**-0.15%**	**-**	**-0.16%**	**-**	**-3.06%**	**-**

Again, the three methods presented in an integrated form showed a good approximation between the data; only the Friedman method showed the greatest differences. This last method reached a maximum difference of -4951.79% at α=0.85, resulting in 2 orders of magnitude higher. This variation is significant, as the pre-exponential factor was calculated from the results of E_α. E_α was already bigger for Friedman's method, but when put in this formula, the difference between the A's is much more expressive. As in this formula, the activation energy appears by multiplying the other factors and appears as an exponent of e; this makes the results of A_α larger than the other methods.

4.3 Thermodynamics Parameters

Once the activation energies and the pre-exponential factor are known, thermodynamic parameter values can be calculated using Eqs. (12) through (14). As a result of the reliance of equations on the heating rate, Figure 4 shows the computed values for ΔH, ΔG, and ΔS with an 8 K.min^{-1} heating rate, while Table 4 presents the errors.

The value of ΔH reflects the total thermal output of the pyrolysis process and is the least amount of required energy by biomass for the process. As the pyrolysis process advances, the endothermicity of the reaction increases, as shown by the fact that the ΔH values for the pyrolysis of both methods and the reference grow with α (DU et al., 2021). The percentage difference between the results presented in Table 4 shows great proximity of the results, with a maximum difference of -9.48% for α=0.85 in the Friedman method.

The G values are positive and somewhat influenced by conversion in the pyrolysis of corn stalks (GUO et al., 2022). This shows that the pyrolysis of the biomass sample is a process that requires energy from outside sources to be thermally degraded. The percentage difference between the results presented in Table 4 shows excellent proximity of the results, with a maximum difference of 0.25% for α=0.85 in the Friedman method.

ΔS is a state characteristic that denotes the degree of chaos in a reaction process (DU et al., 2021). While a high ΔS number indicates significant reactivity, a low ΔS value indicates increased reaction time. For the pyrolysis, the ΔS values for both approaches and the (GUO et al., 2022) findings move from negative to positive. This shows that the sample's pyrolysis reactivity increases as the pyrolysis reaction progresses. The ΔS is calculated by Eq.(14), which uses the subtraction of the results of ΔH and ΔG for its calculation. Because of this, the errors of the results of ΔS were more expressive than those of the other thermodynamic parameters. The most significant difference of the Friedman method was -2133% for α=0.45.

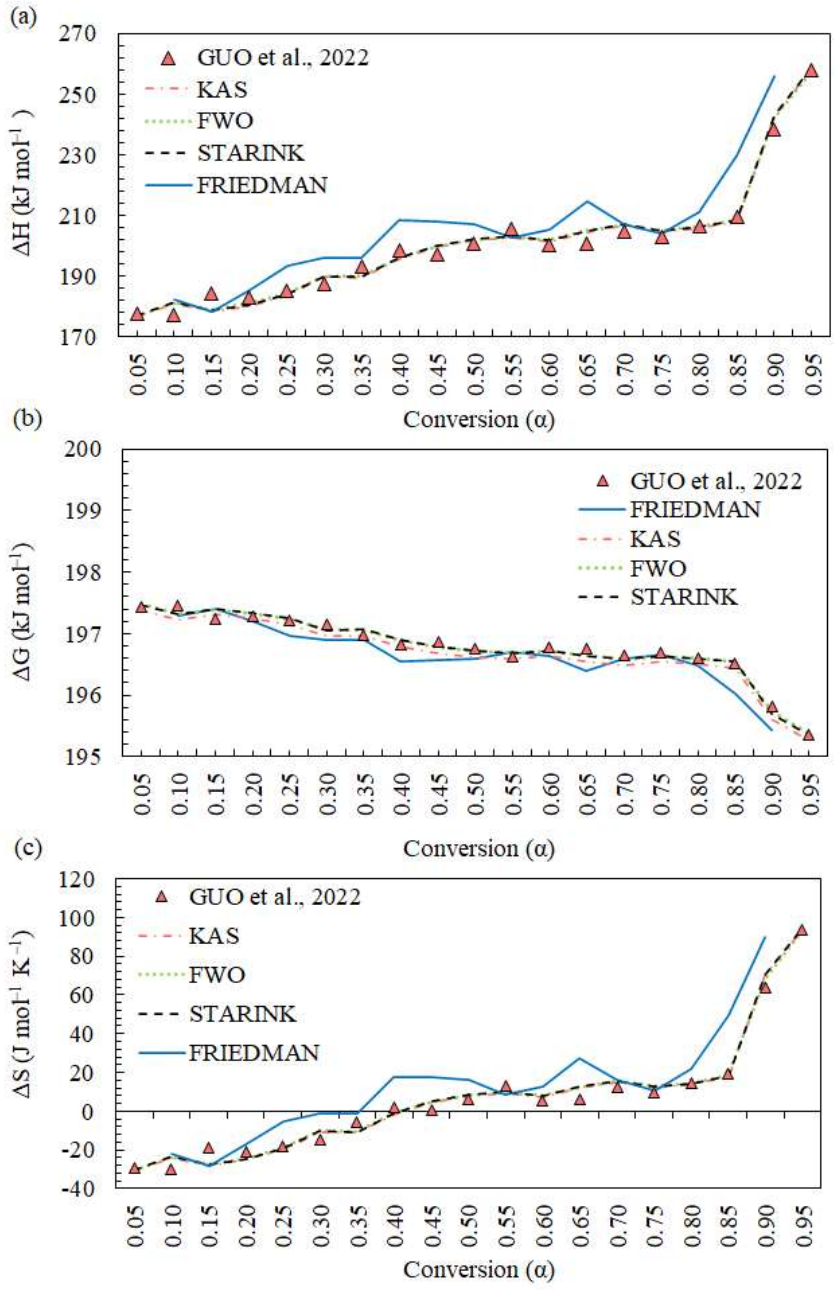

Figure 4. Experimental data from (GUO et al., 2022) and numerical prediction of (a) (b) ΔG, and (c) ΔS for the pyrolysis of corn stalks considering the Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa method (FWO), Starink and Friedman isoconversional models.

Table 4. Results comparison of experimental (GUO et al., 2022) and numerical prediction of ΔH, ΔG, and ΔS for the pyrolysis of corn stalks considering the Kissinger-Akahira-Sunose (KAS), Flynn-Wall-Ozawa method (FWO), Starink and Friedman isoconversional models.

Conversion (α)	KAS			FWO			STARINK			FRIEDMAN		
	Error ΔH	Error ΔG	Error ΔS	Error ΔH	Error ΔG	Error ΔS	Error ΔH	Error ΔG	Error ΔS	Error ΔH	Error ΔG	Error ΔS
0.05	0.75%	0.04%	-6%	0.62%	-0.02%	-6%	0.56%	-0.02%	-5%	-	-	-
0.10	2.12%	0.11%	20%	-2.29%	0.06%	21%	-2.32%	0.07%	21%	-2.80%	0.08%	26%
0.15	3.22%	-0.03%	-47%	2.89%	-0.08%	-42%	3.03%	-0.08%	-45%	3.15%	-0.09%	-46%
0.20	1.50%	0.01%	-19%	1.12%	-0.03%	-15%	1.30%	-0.04%	-17%	-1.31%	0.04%	18%
0.25	0.66%	0.04%	-9%	0.30%	-0.01%	-5%	0.46%	-0.02%	-7%	-4.55%	0.12%	71%
0.30	1.25%	0.09%	26%	-1.51%	0.04%	30%	-1.45%	0.04%	29%	-4.62%	0.12%	91%
0.35	1.95%	0.00%	-100%	1.63%	-0.04%	-85%	1.75%	-0.05%	-92%	-1.52%	0.04%	80%
0.40	1.31%	0.02%	166%	1.09%	-0.03%	144%	1.12%	-0.03%	148%	-5.12%	0.14%	-677%
0.45	1.13%	0.09%	-460%	-1.31%	0.04%	-506%	-1.33%	0.04%	-514%	-5.52%	0.15%	-2133%
0.50	0.53%	0.07%	-29%	-0.69%	0.02%	-34%	-0.72%	0.02%	-36%	-3.18%	0.09%	-158%
0.55	1.34%	0.02%	31%	1.17%	-0.03%	28%	1.15%	-0.03%	27%	1.44%	-0.04%	34%
0.60	0.64%	0.07%	-40%	-0.88%	0.03%	-51%	-0.83%	0.03%	-48%	-2.49%	0.07%	-144%
0.65	1.91%	0.11%	-101%	-2.12%	0.06%	-109%	-2.10%	0.06%	-108%	-6.91%	0.19%	-354%
0.70	0.88%	0.08%	-24%	-1.07%	0.03%	-28%	-1.07%	0.03%	-28%	-1.20%	0.04%	-31%
0.75	0.78%	0.08%	-27%	-1.07%	0.03%	-35%	-0.98%	0.03%	-32%	-0.47%	0.01%	-16%
0.80	0.25%	0.05%	4%	-0.04%	0.00%	-1%	0.05%	0.00%	1%	-2.30%	0.06%	-50%
0.85	0.68%	0.04%	10%	0.39%	-0.01%	6%	0.49%	-0.01%	8%	-9.48%	0.25%	-155%
0.90	1.7%	0.10%	-10%	-1.46%	0.04%	-8%	-1.95%	0.06%	-11%	-7.27%	0.20%	-42%
0.95	0.02%	0.05%	0%	0.31%	-0.01%	1%	-0.15%	0.01%	-1%	-	-	-
Average	**0.01%**	**0.06%**	**-3%**	**-0.17%**	**0.01%**	**-9%**	**-0.18%**	**0.01%**	**-10%**	**-2.20%**	**0.06%**	**-117%**

5 CONCLUSIONS

This article presents the design, development, and validation of a Python model for computing thermal kinetic triplet processes and thermodynamic characteristics. The model was developed with parametric equations and a simple language to enhance its usability. The activation energy was determined using four isoconversional methods, which were then utilized to calculate the other parameters.

The code has been implemented and is fully functional. To validate the model, previous literature on the pyrolysis of corn stalks was used. The results obtained from the model closely matched the expected behavior, with only minor differences observed. The parameters exhibited similar trends, and the differences between the model's predictions and the experimental data were relatively small.

The pre-exponential factor and entropy showed the most significant discrepancies among the parameters. This can be attributed to the fact that the activation energy is multiplied by the other factors and appears as an exponent of the base value, leading to a larger impact on the final result. This is particularly true for the pre-exponential factor. Similar justifications can be made for the differences observed in entropy calculations.

Furthermore, the Friedman method exhibited greater differences than the other isoconversional methods, utilizing a differential calculation approach. However, despite these differences, all the results consistently exhibited the same overall behavior, with relatively minor variations within the expected range. Overall, the model has proven to be a reliable tool for analyzing thermal processes and understanding their kinetic and thermodynamic characteristics.

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8 RESPONSIBILITY NOTICE

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