

Integrated Kinetic and Thermodynamic Evaluation of Corn Cob Derived Nanomaterials from Agro-Waste Using Thermogravimetric Analysis for Sustainable Energy Application

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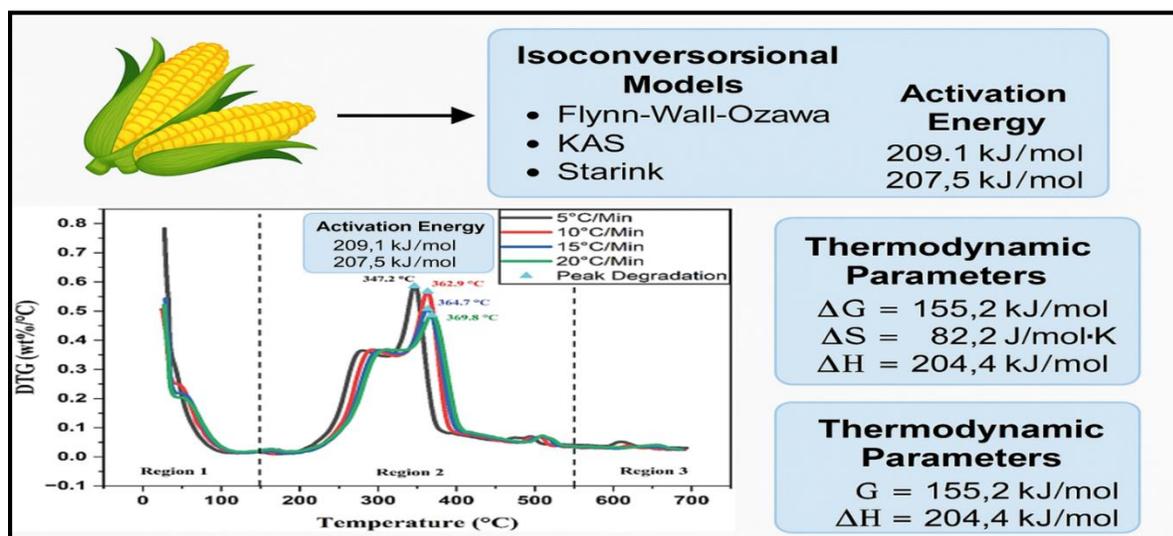
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Abstract: Corn cobs, an abundantly available agricultural residue, hold significant promise as a renewable feedstock for sustainable bio-energy production. This study provides a detailed investigation of their pyrolytic decomposition behavior, kinetic parameters, and thermodynamic characteristics using non-isothermal TGA (thermogravimetric analysis). Experiments were performed in an inert nitrogen atmosphere within a 25 - 700 °C temperature range, applying multiple (5, 10, 15, and 20 °C/min) heating rates. To determine the reaction kinetics, three well-established model-free iso-conversional approaches, KAS (Kissinger Akahira Sunose), FWO (Flynn Wall Ozawa), and Starink methods were utilized. The mean activation energies obtained were 209.1 kJ/mol (FWO), 207.5 kJ/mol (KAS), and 209.3 kJ/mol (Starink), each displaying strong correlation coefficients ($R^2 \approx 0.91 - 0.92$), validating the reliability of the kinetic modeling. Thermodynamic analysis using the KAS method revealed a ΔH (enthalpy change) of 204.4 kJ/mol, a ΔS (entropy change) of 82.2 J/mol·K, and a ΔG (Gibbs free energy change) of 155.2 kJ/mol. These findings indicate that corn cob pyrolysis is an endothermic and non-spontaneous process, reflecting the inherent energy requirements and thermal stability challenges during conversion. Nevertheless, the results highlight corn cobs as a viable and cost-effective biomass resource for thermochemical energy applications, offering substantial potential for sustainable fuel generation.

Keywords: Corn cob Nanomaterials, TGA, Kinetic Modeling, Thermodynamic Parameters, Agro-waste valorization, Biomass-derived Nanomaterials, Sustainable Energy.

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Graphical Abstract



1. Introduction

The growing global energy demand, coupled with the rapid depletion of fossil fuel resources and increasing environmental degradation, has intensified the pursuit of clean and sustainable energy alternatives. Traditional fossil fuels such as natural gas, coal, shale oil, petroleum, and bitumen have long been the backbone of power and thermal energy production. However, their combustion processes release harmful emissions, notably nitrogen oxides (NO_x) and sulfur oxides (SO_x), which significantly contribute to environmental issues like acid rain, smog formation, and ozone layer deterioration. Additionally, extended exposure to these pollutants is linked to serious health risks, including respiratory illnesses and cardiovascular diseases. Forecasts indicate that by 2050, only about 14 % of global oil reserves will be accessible for extraction [1], reinforcing the critical need to transition toward renewable, low-emission energy sources. Among the promising alternatives, biomass has emerged as a renewable and environmentally friendly energy source. It comprises organic material from both plant and animal origins, including crop residues, forestry by-products, aquatic plants, animal waste, sewage sludge, and certain industrial wastes [2, 3]. One of the major advantages of biomass is its carbon-neutral nature, attributed to the carbon dioxide uptake during plant photosynthesis, which is roughly equivalent to the amount released during combustion. Although biomass utilization may lead to the emission of some pollutants such as carbon monoxide (CO), volatile organic compounds (VOCs), and trace elements, the overall environmental burden is significantly less than that of fossil fuels [4, 5]. This makes biomass a compelling candidate for sustainable energy systems that aim to reduce greenhouse gas emissions and promote energy security.

In numerous developing nations, especially those located in tropical and subtropical zones, biomass plays a vital role in meeting energy needs. For instance, Pakistan generated nearly 121 million tons of biomass in 2018, accounting for approximately 1.1 % of its total primary energy consumption. National energy strategies aim to expand this share to 5 % by 2030 [6]. Despite its widespread availability and renewability, raw biomass faces practical limitations when used directly as fuel. These include high moisture levels, low energy content, incomplete combustion, and significant ash residue, all of which hinder its efficiency. To overcome these limitations, advanced thermochemical conversion methods are essential for enhancing both energy yield and fuel quality. Among the various thermochemical conversion techniques, such as gasification,

combustion, and hydrothermal liquefaction, pyrolysis has attracted considerable attention as a promising method. This process entails the thermal decomposition of biomass in an oxygen-deficient environment, yielding a range of valuable products such as bio oil, biochar, and syngas [7, 8]. Pyrolysis offers multiple benefits, including fuels with higher energy density, improved combustion characteristics, and potential reuse of byproducts in energy or environmental applications. Nevertheless, to design and operate efficient pyrolysis systems, it is crucial to gain a detailed understanding of the biomass degradation process, which is governed by the material's thermal kinetics and thermodynamic behavior. TGA is a widely utilized technique to evaluate the thermal decomposition characteristics of biomass. By recording the mass loss of a sample over a range of temperatures or time under a controlled atmosphere, TGA reveals key information about degradation stages, thermal stability, and decomposition rates [9]. Based on this data, fundamental kinetic parameters including the activation energy (E), pre-exponential factor (A), and reaction order (n) can be extracted. These parameters are vital for simulating and optimizing pyrolysis reactions, as well as predicting fuel yields and system performance. Kinetic analysis techniques used in conjunction with TGA data can be broadly divided into two categories: model fitting and model-free (iso conversional) methods. Model fitting approaches rely on selecting a specific reaction mechanism to interpret the data. However, if the chosen model does not accurately represent the actual reaction pathway, the results can be misleading. On the other hand, iso conversional methods estimate the activation energy across various degrees of conversion and heating rates without assuming a predefined reaction model. This approach enhances the accuracy and reliability of the kinetic evaluation. Among the widely applied iso conversional methods are the FWO, KAS, and Starink models. These techniques offer robust tools for determining kinetic parameters, particularly activation energy, and are extensively used to characterize the thermal behavior of biomass during pyrolysis [10]. Through these methods, researchers can better understand the complexity of biomass degradation and develop more efficient thermochemical conversion systems tailored to specific feedstocks and energy applications. A variety of lignocellulosic biomass types have been effectively examined using model-free (iso conversional) kinetic approaches in recent years. For instance, thermal analysis of *Hyphaene thebaica* biomass revealed activation energy ranging from 118.15 to 142.81 kJ/mol, with variations arising from the choice of iso conversional model. These findings point toward a predominantly endothermic and irreversible decomposition mechanism [3]. Likewise, iso

conversional techniques have been successfully employed to study agricultural residues such as sawdust, rice husks, and wheat husks. These studies have yielded consistent kinetic triplets activation energy, reaction model, and pre-exponential factor with high correlation coefficients, validating the applicability of such methods for complex biomass systems [11, 12]. Collectively, these investigations confirm that iso conversional methods provide a reliable framework for understanding the multistep thermal degradation behavior of lignocellulosic materials. Despite considerable work on biomass pyrolysis, the thermal behavior of corn cobs remains relatively underexplored, especially in terms of kinetic and thermodynamic assessments using multiple iso conversion models. Corn (*Zea mays*), widely cultivated across the globe, produces significant amounts of agricultural waste, particularly corn cobs, which are frequently discarded or subjected to open burning. This practice contributes to environmental issues, whereas proper utilization can turn corn cobs into a valuable energy resource. Owing to their rich carbon content, low ash proportion, and high lignocellulosic fraction, corn cobs are considered promising candidates for thermochemical energy conversion processes. The effective valorization of corn cob waste via pyrolysis aligns well with circular economy objectives and supports environmental sustainability. Conducting detailed kinetic and thermodynamic analyses is essential to evaluate the suitability of corn cobs as a feedstock for biofuel production. Parameters such as activation energy (E_a), ΔH , ΔS , and ΔG are critical for assessing the feasibility, spontaneity, and energy requirements of the pyrolysis process. Accurate determination of these thermokinetic parameters enables the development of optimized, energy-efficient, and scalable pyrolysis systems for industrial use. However, current literature shows a noticeable gap, as few studies have utilized multiple iso-conversional models in accordance with ICTAC (International Confederation for Thermal Analysis and Calorimetry) standards to investigate corn cob pyrolysis. Bridging this research gap is essential for the broader implementation of biomass-based energy technologies. To contribute to this area of research, the current study investigates the pyrolysis behavior of corn cob biomass through TGA performed under non-isothermal conditions. The model-free iso-conversional methods FWO, KAS, and Starink are employed to estimate the activation energy and characterize the material's thermal degradation kinetics. In addition, key thermodynamic parameters are calculated to evaluate whether the pyrolysis reactions are endothermic or exothermic, as well as to determine the spontaneity and molecular disorder during transition states. The outcomes of this study aim to enhance the scientific understanding of the thermal

conversion mechanisms of corn cob biomass and support its development as a promising renewable feedstock for sustainable energy systems.

2. Materials and methods

2.1 Biomass Collection and Preparation

Corn cob residues were sourced from local agricultural fields in Vehari, Punjab, Pakistan. The biomass was initially air-dried under sunlight for approximately six hours to reduce its natural moisture content. After drying, the material was mechanically milled and passed through a standard sieve to obtain a uniform particle size of approximately 0.5 mm. The processed sample was immediately sealed in airtight, moisture-proof polyethylene bags to avoid rehydration before subsequent analyses.

2.2 Thermogravimetric Analysis

Thermal degradation studies were carried out using an SDT Q600 V20.9 Build 20 thermal analyzer (TA Instruments, USA). Non-isothermal TGA was performed at a 25 - 700 °C temperature range for four distinct linear heating rates (5, 10, 15, and 20 °C/min). Approximately 2.5 mg of pre-conditioned corn cob powder was precisely weighed and placed in an alumina crucible mounted on the DSC-TGA microbalance. High-purity nitrogen (99.99 %) was continuously supplied at a flow rate of 200 mL/min to maintain an inert atmosphere and prevent oxidative degradation during the pyrolysis process.

2.3 Physicochemical Characterization

Proximate analysis of the biomass was conducted in accordance with ASTM standard methods: E872 for volatile matter, D1102 for ash content, and E871-82 for moisture determination. Fixed carbon content was determined by difference. Ultimate analysis was performed using a PerkinElmer CHNS elemental analyzer to quantify nitrogen (N), hydrogen (H), sulfur (S), and carbon (C) contents, while oxygen was estimated by difference. The HHV (higher heating value) of the biomass was determined using a Parr 6200 oxygen bomb calorimeter. Each analysis was carried out in triplicate, and the mean values were reported to ensure accuracy and reproducibility.

2.4 Kinetic Modeling

To thoroughly analyze the pyrolytic kinetics of corn cob biomass, three widely accepted model-free iso-conversional approaches were employed: FWO, KAS, and Starink methods. These approaches estimate the apparent activation energy (E_a) across different conversion levels (α)

without assuming a predefined reaction mechanism, thus providing a more reliable representation of the multi-step and complex nature of biomass thermal degradation.

The biomass of thermal decomposition can be described by the general rate expression:

$$\frac{d\alpha}{dt} = kf(\alpha)$$

(1)

Where α is the fractional conversion, k is the temperature-dependent rate constant, t is the reaction time, and $f(\alpha)$ represents the reaction model function. The fractional conversion is defined as:

$$\alpha = \frac{m_i - m_t}{m_i - m_f}$$

(2)

Where m_i , m_f , and m_t are the initial, final masses, and instantaneous, and of the sample, respectively. The rate constant k is temperature-dependent and follows the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}}$$

(3)

Where A is the pre-exponential factor, T is the absolute temperature (K), and R is the universal gas constant. The integral form of the KAS method is expressed as [13]:

$$g(\alpha) = \frac{ART^2}{\beta E_a} e^{-\frac{E_a}{RT}}$$

(4)

Taking the logarithm (natural) and rearranging gives:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AE_a}{Rg(\alpha)}\right) - \frac{E_a}{RT}$$

(5)

A plot of $\ln\left(\frac{\beta}{T^2}\right)$ against $1/T$ at constant conversion provides E_a from the slope:

$$g(\alpha) = \frac{A}{\beta} 0.00484e^{-\frac{E_a}{RT}}$$

(6)

Based on Doyle's approximation, the linearized expression is:

$$\ln(\beta) = \ln\left(\frac{AE}{Rg(\alpha)}\right) - 5.331 - 1.052\frac{E_a}{RT}$$

(7)

Here, E_a is determined from the slope of a plot of $\ln(\beta)$ versus $1/T$.

The Starink equation is expressed as:

$$\ln\left(\frac{\beta}{T^{1.92}}\right) = C_s - \frac{1.0008E_a}{RT} \quad (8)$$

Where C_s is a constant. The activation energy is obtained from the slope of a plot of $\ln(\beta/T^{1.92})$ versus $1/T$. This method has been reported to provide higher accuracy and robustness in the kinetic analysis of lignocellulosic biomasses [14].

2.5 Determination of Thermodynamic Parameter

Thermodynamic quantities such as enthalpy change (ΔH), entropy change (ΔS), and Gibbs free energy (ΔG) were calculated to further understand the energy requirements, spontaneity, and disorder associated with the pyrolysis reactions. These parameters are crucial for assessing the feasibility of converting biomass into energy-rich products [15].

The parameters were evaluated using the following expressions:

$$\Delta H = E_a - RT \quad (9)$$

$$\Delta S = R * \ln\left(\frac{Ah}{KT}\right) \quad (10)$$

$$\Delta G = \Delta H - T\Delta S \quad (11)$$

Where A is the pre-exponential factor, E_a is the activation energy, k is Boltzmann's constant (1.38×10^{-23} J/L), h is Planck's constant (6.63×10^{-34} J.s), R is the universal gas constant, and T is the absolute temperature (K). ΔH represents the net energy absorbed or released during bond dissociation, ΔS indicates the changes in molecular disorder during transition states, and ΔG reflects the spontaneity of the reaction. A negative ΔG value signifies a thermodynamically favorable (spontaneous) process, whereas positive values indicate non-spontaneity under the specified conditions.

3. Results and discussion

3.1 Physicochemical characterization of corn cob biomass

The ultimate and proximate analyses of the corn cob biomass are summarized in **Table 1**. The low moisture content (3.46 wt% %) indicates minimal energy loss during the drying stage, which is advantageous for thermochemical conversion processes. A moderate ash fraction (4.68 wt% %) suggests reduced risk of fouling, slagging, and particulate emissions during combustion or pyrolysis, thereby improving system efficiency and operational stability. The high volatile matter content (70.83 wt% %) demonstrates the strong potential of corn cobs to undergo rapid

devolatilization, producing a substantial fraction of condensable vapors and light gases essential for bio-oil and syngas generation. The fixed carbon content (21.03 wt% %) contributes significantly to the calorific value of the feedstock, making it suitable for sustained char formation and enhanced energy recovery. From the ultimate analysis, the relatively high carbon concentration (47.94 wt% %) and low sulfur content (0.01 wt% %) indicate the potential for high-quality biofuels with reduced SO_x emissions, supporting environmentally friendly energy production. The calculated HHV of 17.37 MJ/kg is within the range reported for other lignocellulosic residues, further validating corn cobs as an efficient and sustainable feedstock for thermochemical bioenergy applications.

Table 1: Physicochemical characteristics of corn cob biomass

Order	Ultimate analysis (wt%)		Proximate analysis (wt%)		HHV (MJ/kg)
1	C	47.94	Moisture	3.46	17.37
2	H	5.46	Volatile matter	70.83	
3	N	2.14	Ash	4.68	
4	S	0.01	Fixed Carbon	21.03	
5	O	44.46			

3.2 Thermal decomposition behavior (TGA and DTG analysis)

TGA of the corn cob biomass was conducted at four different heating rates (5, 10, 15, and 20 °C/min) to examine its thermal decomposition behavior. The TGA and DTG (derivative thermogravimetric) profiles are presented in **Figures 1A and 1B**, respectively. The weight loss trend revealed a three-stage decomposition pattern typical of lignocellulosic biomasses:

Drying Stage (0 - 150 °C): This region corresponds to the evaporation of inherent moisture and light volatiles, accounting for approximately 10 – 13 % of total weight loss. The low energy requirement at this stage indicates minimal preprocessing energy demand.

Active Pyrolysis Stage (150 - 550 °C): This zone exhibits the most rapid mass loss, attributed to the decomposition of cellulose, hemicellulose, and part of the lignin fraction. The major release of volatiles such as CO₂, CO, NO_x, and H₂ occurs in this temperature range. The sharp decline in weight percentage indicates high reactivity and favorable kinetics for biofuel production.

Carbonization Stage (550 - 700 °C): A gradual mass loss is observed in this final stage, representing the slow degradation of lignin and char formation. The lower decomposition rate is

attributed to the higher thermal stability of lignin and the progressive conversion of residual carbonaceous material.

The DTG profiles (**Figure 1B**) highlight a prominent peak within the active pyrolysis region, corresponding to the maximum degradation rates of 369.8 °C, 364.7 °C, 362.9 °C, and 347.2 °C for rates of heating 20, 15, 10, and 5 °C/min, respectively. The observed shift of peak temperatures towards higher values with increasing heating rates is consistent with kinetic compensation effects and has been similarly reported for other biomass residues, including *Camellia oleifera* shells, *Hyphaene thebaica* shells, and chestnut shells [14, 16-19]. The prolonged tailing of the DTG curve beyond 500 °C is associated with the gradual degradation of lignin, which has a complex, cross-linked aromatic structure resistant to thermal decomposition. These findings align with the thermal degradation patterns reported for other lignocellulosic materials, confirming the suitability of corn cobs for pyrolytic fuel production.

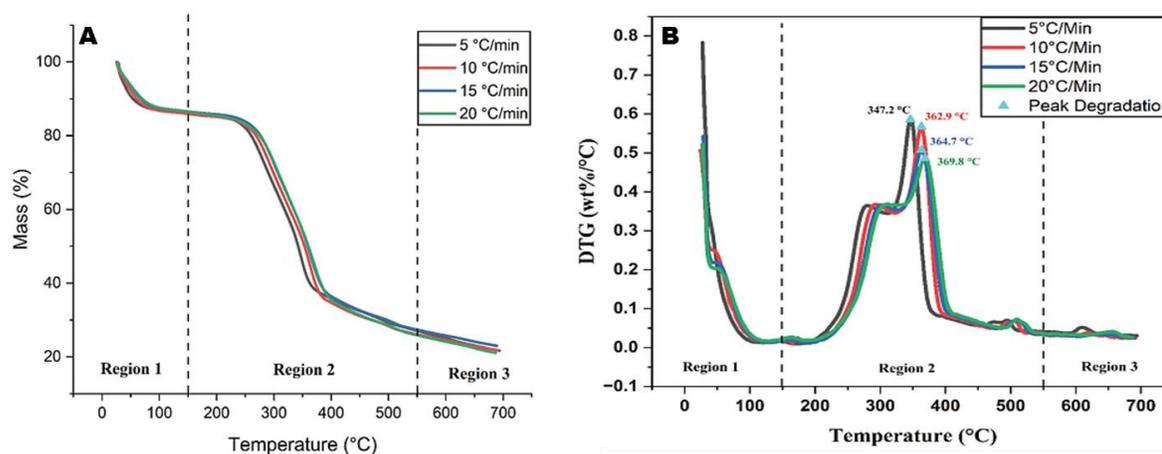


Figure 1: (A) TG curves of corn cob biomass at varying heating rates showing moisture loss (Region I), active pyrolysis (Region II), and lignin decomposition (Region III); (B) DTG curve showing decomposition peaks of major components.

The thermogravimetric (TG) analysis reveals a multi-stage thermal degradation pattern for corn cob biomass, which reflects its heterogeneous composition primarily consisting of hemicellulose, cellulose, and lignin [7]. These key components undergo distinct decomposition phases at different temperature ranges during pyrolysis. The TG curves demonstrate that as the heating rate increases, the peak decomposition temperatures shift to higher values, indicating the kinetic influence of heat transfer rates on biomass thermal breakdown. The initial weight loss in Region I (0 – 150 °C) corresponds to the evaporation of inherent moisture in biomass. Region II (150 –

550 °C) features the main devolatilization peak, primarily due to the thermal decomposition of cellulose, which releases a significant amount of volatiles. In Region III (550 – 700 °C), a slower degradation process occurs, associated with the thermal breakdown of lignin, which has a more complex and thermally stable aromatic structure. Lignin decomposes over a broader and higher temperature range compared to cellulose, which is reflected in its delayed degradation peak. The observed thermal degradation behaviors are consistent with findings reported for other lignocellulosic biomasses, such as those from *Camellia oleifera*, *Hyphaene thebaica*, and chestnut shells [14, 20]. The unique structural composition of these biomasses, primarily consisting of hemicellulose, cellulose, and lignin, dictates their thermal decomposition characteristics. A comparative analysis with other biomass materials further corroborates the idea that variations in the relative proportions of these components influence the thermal degradation profiles, confirming that the pyrolysis behavior is largely governed by the biomass's composition [12, 18].

3.3 Influence of heating rate on biomass decomposition

Thermogravimetric analysis revealed that increased heating rates resulted in elevated decomposition temperatures for corn cob biomass, a finding consistent with earlier studies [7, 20]. In the study, decomposition occurred within a temperature range of 347 – 370 °C, reflecting the heating rate impact on the pyrolysis process. According to Barchi et al. (2021), the thermogravimetric curve shifts towards higher temperatures as the rate of heating increases, though the overall shape of the curve remains unchanged [21]. The shift is attributed to thermal lag effects induced by rapid heating, which leads to a non-uniform temperature distribution within the biomass sample [17, 22]. Torres-García et al. (2020) further confirmed that while the heating rate primarily affects the position of the degradation curve, it accelerates the overall rate of decomposition without altering the profile of the thermal degradation process [23]. **Table 2** summarizes the influence of different heating rates on biomass mass loss. Region II, associated with volatile decomposition, displayed the highest weight loss, particularly due to the breakdown of cellulose. Notably, the maximum rate of mass loss (0.035 %/°C) was observed in Region III at the slowest heating rate (5 °C/min), underscoring that slower heating rates enhance the efficiency of thermal conversion [24]. This trend emphasizes the importance of optimizing heating conditions for biomass pyrolysis to improve overall energy recovery.

3.4 Kinetic analysis of corn cob pyrolysis

The E_a (activation energy) for corn cob biomass was calculated using three widely recognized iso-conversional methods: KAS, FWO, and Starink, based on thermogravimetric data obtained at different rates of heating. The KAS method was applied by plotting $\ln(\beta/T^2)$ versus $1000/T$, as shown in **Figure 2A**, following Equation (5). Similarly, the FWO method was used to plot $\ln(\beta)$ versus $1000/T$, based on Equation (7) and shown in **Figure 2B**. The starink method, employing Equation (8), utilized the plot of $\ln(\beta/T^{1.92})$ against $1000/T$, as depicted in **Figure 2C**. These iso conversional methods offer the significant advantage of estimating activation energy at constant conversion levels, without requiring assumptions about the reaction model. As highlighted by Sbirrazzuoli (2020), iso conversional methods provide valuable insight into the complex kinetics mechanisms of biomass byrolysis and help identify rate-limiting steps during thermal degradation [25]. **Figure 2D** illustrates the variation in activation energy with conversion fraction (α) across the FWO, KAS, and Starink methods. Although all three methods yielded consistent results, slight deviations were observed between the FWO model and the other two methods. Nevertheless, the overall agreement between the methods confirms the robustness and reliability of iso-conversional approaches for kinetic analysis of biomass pyrolysis.

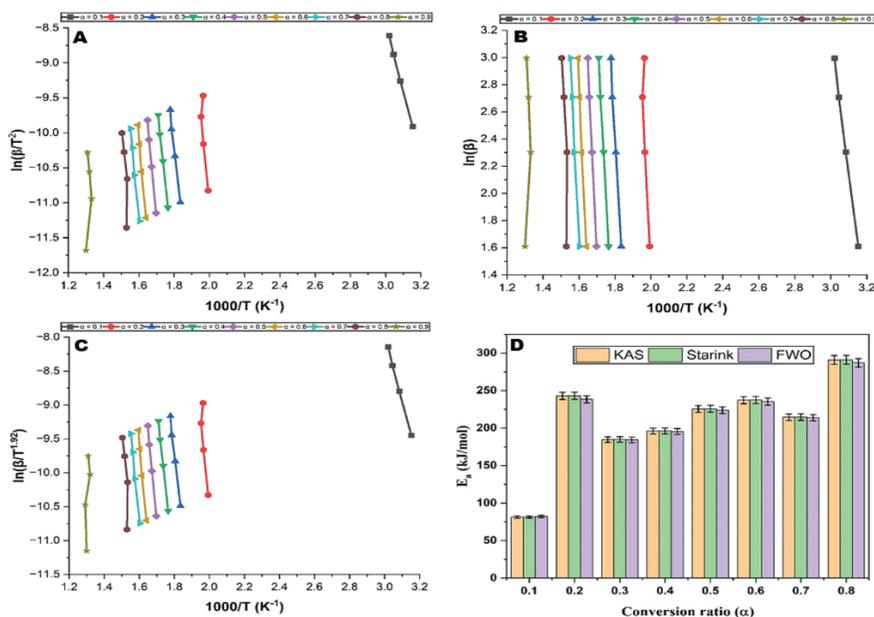


Figure 2: (A) KAS plots, (B) FWO plots, and (C) Starink plots for corn cob pyrolysis at different conversion ratios (α), illustrating the dependence of activation energy on the degree of conversion; (D) Variation of activation energy (E_a) with conversion ratio, highlighting the complex, multi-step nature of the thermal degradation process.

The average activation energies for corn cob pyrolysis, estimated using three widely applied iso-conversional methods, were found to be 209.3 kJ/mol (Starink), 207.5 kJ/mol (KAS), and 209.1 kJ/mol (FWO) (**Table 3**). The close agreement among these values reflects the robustness and reliability of these model-free approaches in capturing the complex kinetics of lignocellulosic biomass degradation. This consistency suggests that the thermal decomposition of corn cob follows similar energy requirements across the different analytical techniques, demonstrating minimal methodological bias. The coefficient of determination (R^2) values, also presented in **Table 3**, further support the strong correlation between experimental data and the calculated kinetic parameters, with most values approaching unity. Notably, the conversion interval of 0.3 - 0.7 displayed the highest linearity ($R^2 > 0.99$), indicating this range is particularly reliable for estimating kinetic triplets. Such findings align with ICTAC recommendations, which highlight mid-range conversions as the most representative for biomass thermal analysis [25]. Additionally, the effect of heating rate on mass loss across distinct thermal degradation zones is summarized in **Table 2**. Region II consistently showed the highest weight loss rate across all heating rates, reflecting the dominant role of cellulose decomposition during pyrolysis. Interestingly, the maximum rate of weight loss was observed at the lowest heating rate (5 °C/min) in Region III, corroborating earlier findings that slower heating enhances thermal conversion efficiency [24].

Table 2: Effect of heating rate on mass loss (%) across thermal degradation zones of corn cob biomass

Order	Heating rate (°C/min)	Region 1 loss rate (%/°C)	Region 2 loss rate (%/°C)	Region 3 loss rate (%/°C)
1	5	0.092	0.147	0.035
2	10	0.093	0.149	0.027
3	15	0.089	0.148	0.028
4	20	0.089	0.151	0.031

Table 3: Variation in corn cob activation energy (E_a) and correlation coefficients (R^2) determined using iso-conversional model-free methods.

Order	Conversion ratio (α)	Activation Energy (E_a)			R^2		
		KAS	STARINK	FWO	KAS	STARINK	FWO
1	0.1	81.15	81.30	82.26	0.9985	0.9985	0.9987
2	0.2	242.91	243.05	238.20	0.7321	0.7321	0.7453
3	0.3	184.62	184.83	184.23	0.9911	0.9911	0.9919
4	0.4	196.01	196.23	195.41	0.9975	0.9975	0.9977
5	0.5	225.56	225.78	223.86	0.9979	0.9979	0.9981
6	0.6	237.25	237.47	235.29	0.9927	0.9928	0.9933
7	0.7	214.43	214.67	213.84	0.9903	0.9904	0.9912
8	0.8	290.87	291.08	286.90	0.6402	0.6409	0.657
	Average	209.10	209.30	207.50	0.9175375	0.917725	0.92165

3.5 Thermodynamic Analysis

The thermodynamic parameters governing corn cob pyrolysis were evaluated using Eqs. (9 - 11) to determine the ΔH , ΔG , and ΔS at varying conversion ratios. The calculated trends based on the three iso-conversional model-free approaches are illustrated in **Figures 3A, 3B, and 3C**. The KAS model yielded average values of $\Delta H = 204.4$ kJ/mol, $\Delta G = 155.2$ kJ/mol, and $\Delta S = 82.2$ J/mol·K, while the Starink approach provided closely matching results ($\Delta H = 204.6$ kJ/mol, $\Delta G = 155.2$ kJ/mol, $\Delta S = 82.6$ J/mol·K). The FWO method produced slightly lower estimates, with $\Delta H = 202.8$ kJ/mol, $\Delta G = 155.1$ kJ/mol, and $\Delta S = 79.5$ J/mol·K. The high consistency across the three techniques underscores the reliability and robustness of the thermodynamic estimations for corn cob thermal conversion. ΔH reflects the net energy required for bond dissociation during devolatilization and subsequent formation of reaction intermediates. As illustrated in **Figure 3A**, ΔH values gradually increased with higher conversion ratios, signifying an endothermic reaction pathway that demands additional energy input at advanced stages of pyrolysis. This observation aligns with reported trends for other lignocellulosic feedstocks such as corn stalks and watermelon seed biomass [16, 26]. The ΔG describes the feasibility and spontaneity of the thermal degradation process. **Figure 3B** shows that ΔG increased progressively with conversion, suggesting that corn cob pyrolysis is a non-spontaneous, energy-driven process under the studied

conditions. Similar behavior has been observed in previous studies on various biomass species [17, 26, 27], highlighting the universal energy-intensive nature of biomass thermolysis reactions. ΔS , an indicator of disorder within the system, displayed a distinct shift from negative to positive values between $\alpha = 0.1$ and 0.2, followed by a continuous rise up to $\alpha = 0.9$ (**Figure 3C**). This trend reflects the transition from a more ordered to a progressively disordered state, coinciding with extensive devolatilization and bond scission events. The decline in ΔS observed beyond $\alpha = 0.9$ suggests reduced molecular randomness as the process approaches char formation. Reported ΔS values for other biomass types, such as chestnut shells (46.01 - 270.39 J/mol·K) and *Hyphaene thebaica* shells (-0.14 - 0.06 kJ/mol·K) [14, 17], demonstrate comparable thermodynamic behavior, confirming the general applicability of these findings to lignocellulosic feedstocks.

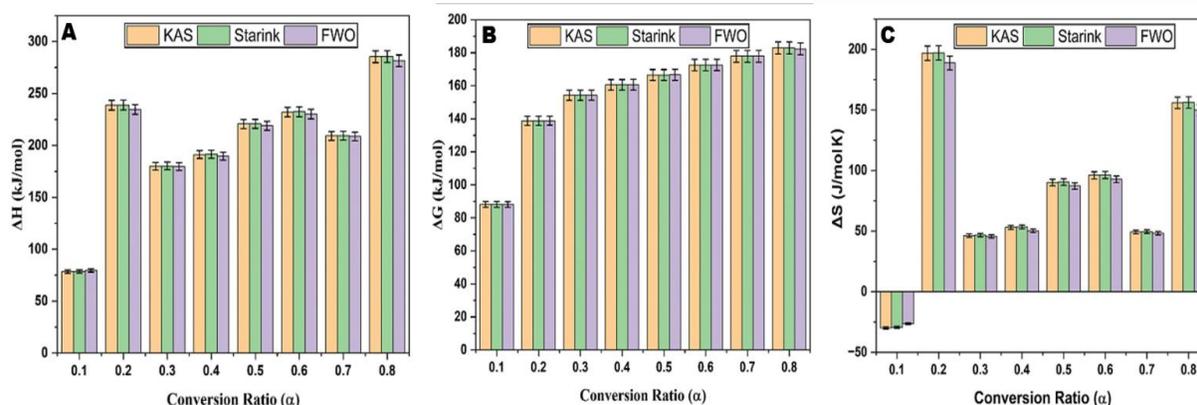


Figure 3: (A) Variation in ΔH , (B) ΔG , and (C) ΔS across different conversion ratios (α) during corn cob pyrolysis, illustrating the thermodynamic behavior of the system.

Moreover, the difference between the activation energy (E_a) and ΔH was consistently below 5 kJ/mol, indicating that only a small fraction of input energy is consumed in overcoming energy barriers other than bond dissociation. This low E_a ΔH disparity suggests that corn cobs possess a favorable energy profile for pyrolysis, outperforming other biomass residues such as chestnut and *Hyphaene thebaica* shells, which exhibit larger energy gaps [14, 17]. This result highlights the potential of corn cobs as an efficient and cost-effective feedstock for thermochemical energy applications.

3.6 Performance Evaluation

A comparative thermo-kinetic analysis of corn cob biomass against other commonly studied feedstocks is presented in **Table 4**. The results highlight the superior energetic and thermodynamic characteristics of corn cobs for pyrolysis-based energy recovery systems. Corn cob exhibited a high apparent activation energy ($E_a \approx 207.5 - 209.3$ kJ/mol), which reflects a robust thermal structure yet remains within a range that supports efficient thermal decomposition. Importantly, the process displayed a positive entropy change ($\Delta S \approx 79 - 83$ J/mol·K) and a moderate Gibbs free energy ($\Delta G \approx 155$ kJ/mol), signifying a favorable increase in molecular disorder and a lower energetic barrier to decomposition. Moreover, the difference between ΔH and E_a remained below 5 kJ/mol, indicating that most of the input energy is directly utilized for bond cleavage, enhancing energy efficiency during pyrolysis. In contrast, rice husks showed higher E_a values ($\sim 220 - 225$ kJ/mol) accompanied by negative entropy change ($\Delta S \approx -135$ J/mol·K) and elevated ΔG (~ 222 kJ/mol) [28]. These parameters suggest a more ordered, non-spontaneous degradation process, requiring greater energy input to initiate pyrolysis. Sugarcane bagasse demonstrated considerably lower E_a values (110 - 116 kJ/mol) [29], indicating easier thermal breakdown but with lower-energy density and reduced thermal resilience, making it less suitable for high-energy applications. Similarly, torrefied rice husks exhibited moderate activation energies ($\sim 150 - 162$ kJ/mol) [30], which, while improved over untreated biomass, still underperformed compared to corn cob in terms of energy potential and stability. The combined thermo-kinetic and thermodynamic profile of corn cob biomass demonstrates a favorable balance between activation resistance and energy yield. Its high E_a ensures controlled and sustained decomposition, while positive ΔS and moderate ΔG reflect efficient energy release and favorable molecular reordering during pyrolysis. These properties position corn cob as a reliable, energy-rich, and thermodynamically efficient feedstock for thermochemical bioenergy conversion technologies.

Table 4. Comparative pyrolysis kinetic and thermodynamic parameters of selected biomass feedstocks

Order	Biomass Feedstock	Ea (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol·K)	ΔG (kJ/mol)	Notes	Ref:
1	Corn Cob	207.5 - 209.3	~203 - 205	~79 - 83	~155	Consistent across FWO, KAS, Starink; ΔE_a $\Delta H < 5$ kJ/mol	this study
2	Rice Husks	220.06 - 224.85	~137	-135.25	222.38	Negative ΔS indicates lower disorder; a high ΔG barrier	[28]
3	Sugarcane Bagasse	110 - 116	---	---	---	Lower activation energy; easier degradation	[29]
4	Torrefied Rice Husks	~150 - 162	---	---	---	Lower Ea for treated biomass	[30]

4. Conclusion

This study provides a detailed thermodynamic evaluation and thermokinetic analysis of corn cob biomass, demonstrating its potential as a sustainable feedstock for bioenergy generation. Thermogravimetric analysis conducted at four heating rates (5, 10, 15, and 20 °C/min) revealed a distinct three-step degradation pathway: (i) initial dehydration (25 - 150 °C), (ii) major devolatilization driven by hemicellulose and cellulose breakdown (150 - 550 °C), and (iii) slow carbonization beyond 550 °C leading to char formation. The physicochemical profile of the biomass—characterized by high volatile matter (70.83 %), low ash content (4.68 %), minimal moisture (3.46 %), and substantial carbon content (46.98 %) supports its suitability for thermochemical energy conversion processes. Model-free iso-conversional methods (FWO, KAS, and Starink) consistently estimated the apparent activation energy in the range of 207.5–209.3 kJ/mol, reflecting a controlled yet energetically favorable decomposition behavior. Complementary thermodynamic analysis revealed $\Delta H \approx 204 - 205$ kJ/mol, $\Delta S \approx 79 - 83$ J/mol·K, and $\Delta G \approx 155$ kJ/mol, highlighting that pyrolysis is predominantly endothermic, non-spontaneous, and irreversible, requiring external energy input to initiate decomposition. The small difference between Ea and ΔH (<5 kJ/mol) further indicates efficient energy utilization with minimal energy loss during the transition state. Overall, the findings affirm that corn cobs possess the thermal stability, favorable reaction kinetics, and efficient energy conversion potential required for biofuel and bioenergy applications. Future research should focus on multi-step kinetic modeling, catalyst-assisted pyrolysis, and process optimization to enhance product

yields and enable large-scale deployment of corn cob biomass in advanced thermochemical energy recovery systems.

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