

Article

Assessing the Bioenergy Potential of Peanut Shell Waste: High Heating Rate Combustion Behavior and Thermodynamic Analysis

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Abstract

This study provides a comprehensive analysis of peanut shell (PnS) combustion behavior using combined physicochemical characterization and non-isothermal thermogravimetric kinetics. To evaluate its potential as a sustainable solid biofuel, PnS was characterized for its proximate and ultimate composition, with its fiber structure analyzed via Van Soest methods and functional groups identified via FTIR spectroscopy. Thermogravimetric analysis (TGA) was performed at high heating rates (20, 40, 60, and 80 K min^{−1}) to investigate combustion stages under oxidative conditions. The results established PnS as a high-potential energy source, revealing a significant volatile matter content (65.30 wt%) and an exceptionally high heating value (20.87 MJ kg^{−1}), which surpasses many standard agricultural residues. The proximate analysis also indicated a moisture content of 9.61% and an ash content of 6.59%. TGA profiles displayed distinct decomposition stages, with the primary devolatilization occurring between 500 and 700 K. Kinetic analysis was conducted using six model-free methods: Friedman (FR), Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS), Starink (STK), Kissinger (K), and Vyazovkin (VY) and the Coats–Redfern model-fitting method. The apparent activation energy (E_a) was found to vary with conversion (α), reflecting the complex degradation of the lignocellulosic matrix (47.86% cellulose, 28.4% lignin). The activation energy values ranged from approximately 23 kJ mol^{−1} (VY method at low conversion) to 187 kJ mol^{−1} (FR method at $\alpha = 0.5$). Model-fitting analysis identified the three-dimensional diffusion (D3) model as the governing reaction mechanism. Thermodynamic analysis indicated positive enthalpy (ΔH : 70.7 – 181.8 kJ mol^{−1}) and Gibbs free energy (ΔG : 116.2 – 216.7 kJ mol^{−1}), with predominately negative entropy (ΔS), confirming the endothermic and non-spontaneous nature of the reaction activation.

Keywords: peanut shell; biomass combustion; TGA kinetics; thermodynamic parameters; solid biofuel; bioenergy; activation energy; lignocellulosic waste



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1. Introduction

The escalating global energy demand, coupled with the rapid depletion of fossil fuel reserves and associated environmental challenges such as greenhouse gas emissions and

climate change, has intensified the search for sustainable and renewable energy alternatives [1]. Biomass, derived from organic materials including agricultural residues, forestry wastes, and dedicated energy crops, emerges as a promising renewable resource due to its carbon-neutral nature, widespread availability, and potential to mitigate environmental impacts when utilized through thermochemical conversion processes like combustion, pyrolysis, and gasification [2,3]. Among these, combustion remains a dominant pathway for bioenergy production, offering direct heat and power generation while valorizing waste streams that would otherwise contribute to landfill burdens or open-field burning pollution [4,5].

Agricultural wastes, in particular, represent a significant untapped bioenergy potential, with global production exceeding billions of tons annually. Peanut (*Arachis hypogaea* L.) shell, a lignocellulosic byproduct from peanut processing, is generated in substantial quantities—estimated at over 10 million tons yearly worldwide, primarily in regions like China, India, and the United States [6,7]. Composed mainly of hemicellulose (14–20 wt%), cellulose (40–50 wt%), and lignin (25–30 wt%), PnS exhibits favorable fuel properties, including high volatile matter content (65–75 wt%) and higher heating values (HHV) ranging from 18 to 22 MJ kg^{−1}, making it suitable for thermal conversion [8,9]. However, its effective utilization requires a thorough understanding of combustion behavior, kinetic parameters, and thermodynamic feasibility to optimize process efficiency and minimize emissions [10,11].

Beyond direct bioenergy generation, the valorization of PnS waste has gained traction in the polymer industry. Prior research has established the utility of raw PnS powder as a reinforcing filler in recycled polypropylene composites [12]. More recently, Pączkowski et al. [13] demonstrated the chemical resistance and thermomechanical benefits of incorporating PnS into unsaturated polyester resins. Comprehensive reviews by Mandala et al. [14] and Guinati and Smith [15] have further mapped the potential of nutshell-derived fillers in enhancing the mechanical strength and thermal stability of sustainable biocomposites. However, optimizing these applications, particularly for the production of carbonized fillers or fire-retardant composites, requires a deep understanding of the biomass's thermal degradation and charring behavior. Therefore, investigating the combustion kinetics of PnS is not only vital for energy recovery but also provides essential data for predicting the thermal performance of PnS-based polymer materials.

Extensive literature has explored the thermochemical conversion of PnS, predominantly focusing on pyrolysis. Recent studies have utilized various kinetic approaches, including artificial neural networks [16], model-free methods [9,17], and Gaussian deconvolution [18], to characterize the decomposition stages. Reported activation energies vary significantly (115–257 kJ mol^{−1}) depending on the specific method and pseudo-components analyzed [19,20]. While valuable, these studies focus on inert atmospheres and low heating rates (≤ 20 K min^{−1}), leaving gaps in understanding oxidative combustion behavior.

Fewer studies address PnS combustion in oxidative environments, which is critical for practical bioenergy applications. Jerzak et al. (2016) [21] investigated PnS combustion in a bubbling fluidized bed, confirming its high reactivity and two-stage decomposition profile corresponding to holocellulose and lignin oxidation. Xu et al. (2020) [10] compared pyrolysis and combustion behaviors, noting four stages in air (dehydration, hemicellulose/cellulose cracking, lignin/volatiles decomposition, and fixed carbon pyrolysis) versus three in N₂, with E_a values stabilizing around 100 kJ mol^{−1} at mid-conversions. Nie et al. (2022) [22] examined co-combustion with wood sawdust, identifying three phases and E_a ranging 23.6–400.9 kJ mol^{−1}, with the best mechanism identified as Avrami–Erofeev nucleation. Their follow-up study (Nie et al., 2025) [23] demonstrated that pelletization enhances combustion performance, reducing E_a by 20–38% compared to powder form.

Most recently, Lei et al. (2024) [24] focused solely on PnS combustion at low heating rates ($10\text{--}30\text{ K min}^{-1}$), reporting E_a of $93\text{--}109\text{ kJ mol}^{-1}$ (FWO) and $89\text{--}103\text{ kJ mol}^{-1}$ (KAS), with thermodynamic parameters indicating an endothermic, non-spontaneous process. General biomass studies support these findings; Liu et al. (2021) [25] analyzed self-heating biomass particles, noting unstable bonds in hemicellulose leading to lower E_a , while Chen et al. (2014) [26] highlighted heating rate effects on kinetics in bamboo pyrolysis. Cai et al. (2018) [27] compared tea leaves' combustion via TG-FTIR (reporting E_a $205\text{--}209\text{ kJ mol}^{-1}$), while Yiga et al. (2023) [28] studied rice husk kinetics (E_a $95\text{--}101\text{ kJ mol}^{-1}$), offering comparisons for agricultural residues.

Despite these insights, gaps persist in combustion studies at high heating rates ($>30\text{ K min}^{-1}$), which better simulate the rapid thermal gradients characteristic of industrial fluidized bed boilers. While recent advances such as Mishra and Vinu (2024) [29] and Shagali et al. (2023) [30] have begun to explore higher rates and synergistic effects, a comprehensive kinetic and thermodynamic dataset for peanut shells at rates up to 80 K min^{-1} is lacking.

Building on our prior investigations into citrus and tropical fruit peels, where we characterized lemon peel (LP) combustion with four stages, E_a averaging 126 kJ mol^{-1} , and a diffusion-controlled mechanism Ismail et al., 2025a [31]; orange peel (OP) with three stages and E_a $64\text{--}309\text{ kJ mol}^{-1}$ Mousa et al., 2025 [32]; and mango peel (MP) with three stages, E_a $\sim 111\text{ kJ mol}^{-1}$ Ismail et al., 2025b [33], this study extends the framework to PnS. We aim to provide a detailed analysis of PnS combustion at heating rates of $20, 40, 60$, and 80 K min^{-1} using TGA, employing six model-free kinetic methods (FR, FWO, KAS, STK, K, VY) and the Coats–Redfern model-fitting method, alongside thermodynamic evaluations to assess its bioenergy potential.

2. Materials and Methods

2.1. Sample Collection and Preparation

Peanut shells (*Arachis hypogaea* L.) were selected as the biomass feedstock for this investigation. The raw waste material was sourced from local agricultural markets in Cairo, Egypt. To ensure sample purity, the collected shells were initially washed with distilled water to remove dust, soil, and other surface impurities, followed by manual sorting to exclude damaged or non-representative pieces.

The cleaned shells were subjected to a two-step size reduction and drying process. First, the material was dried in a hot air oven (Mettler UN110, Büchenbach, Germany) at 310 K for 24 h to minimize initial moisture content. The dried shells were then pulverized using a high-speed laboratory mill (IKA MF 10 Basic, Staufen, Germany). To achieve a homogeneous powder suitable for kinetic analysis, the ground material was sieved using a mechanical shaker (ELE International, Milton Keynes, UK), isolating a particle size fraction of $0.34 \pm 0.05\text{ mm}$. The prepared PnS powder was stored in hermetically sealed glass containers at ambient temperature (298 K) to prevent moisture re-absorption prior to experimental use.

2.2. Physicochemical Characterization

2.2.1. Proximate Analysis

The thermal stability and compositional fractions of the PnS samples, specifically moisture, volatiles, and ash, were quantified using a thermogravimetric analyzer (TGA-2 Star System, Mettler Toledo, Greifensee, Switzerland). A sample mass of $\sim 10\text{ mg}$ was used for each run. The heating protocol consisted of three distinct phases: (1) Dehydration: Heating to 383 K and holding for 30 min under a nitrogen atmosphere (N_2) to determine moisture content; (2) Devolatilization: Ramping the temperature to 1173 K and holding

for 7 min under N₂ to measure volatile matter; and (3) Ashing: Switching the gas flow to oxygen (O₂) and maintaining the temperature at 823 K for 15 min to combust the remaining carbon. The fixed carbon (FC) percentage was subsequently derived using the mass balance described in Equation (1):

$$\text{FC}(\%) = 100 - (\text{Moisture} + \text{Volatile Matter} + \text{Ash}) \quad (1)$$

2.2.2. Ultimate Analysis

The elemental distribution (carbon, hydrogen, nitrogen, and sulphur) was analyzed using a Vario EL III CHNS elemental analyzer (Elementar, Langenselbold, Germany). Approximately 2 mg of the PnS powder was combusted at high temperature (1273 K) in a dynamic pure oxygen environment to ensure complete oxidation. The resulting gaseous products were separated and detected via thermal conductivity. The oxygen content was calculated by difference, assuming the total mass balance includes the ash content determined in the proximate analysis, as expressed in Equation (2):

$$\text{Oxygen}(\%) = 100 - (\text{C} + \text{H} + \text{N} + \text{S} + \text{Ash}) \quad (2)$$

2.2.3. Lignocellulosic Fiber Analysis

The macromolecular composition of the biomass was determined according to the standard Van Soest fractionation method using an automated fiber analyzer (ANKOM 2000, ANKOM Technology, Macedon, NY, USA). A 0.5 g aliquot of the PnS sample underwent a sequential chemical digestion process to isolate the fiber fractions. First, the sample was treated with a neutral detergent solution to obtain the Neutral Detergent Fiber (NDF). Subsequently, an acid detergent extraction was performed to yield the Acid Detergent Fiber (ADF). Finally, the residue was digested with 72% sulfuric acid (H₂SO₄) (Sigma-Aldrich, St. Louis, MO, USA) to isolate the Acid Detergent Lignin (ADL). The percentages of hemicellulose and cellulose were calculated based on the mass differences between these fractions, as detailed in Equation (3):

$$\text{Hemicellulose} = \text{NDF} - \text{ADFCellulose} = \text{ADF} - \text{ADL} \quad (3)$$

2.2.4. Higher Heating Value (HHV)

To assess the energy potential of the biomass, the Higher Heating Value (HHV) was measured using a plain oxygen bomb calorimeter (Model 1341EE, Parr Instrument Company, Moline, IL, USA). A pelletized PnS sample (0.5 g) was ignited within the vessel under a pressurized oxygen atmosphere (3 MPa). The system was calibrated using a benzoic acid standard, and all calorimetric tests were conducted in triplicate to ensure data reproducibility.

2.3. Spectroscopic and Morphological Analysis

2.3.1. Fourier Transform Infrared (FTIR) Spectroscopy

The surface functional groups of the peanut shell biomass were characterized using a JASCO FTIR-4100 type A spectrometer (Tokyo, Japan). The analysis was performed using the KBr pellet technique, where ~2 mg of PnS powder was homogenized with 200 mg of potassium bromide and compressed into a translucent disk. Spectra were acquired over a wavenumber range of 4000–400 cm^{−1} with a spectral resolution of 4 cm^{−1}, accumulating 32 scans per sample to improve the signal-to-noise ratio.

2.3.2. Scanning Electron Microscopy (SEM)

The surface topography and microstructural features of the PnS powder were visualized using a Field Emission Scanning Electron Microscope (JEOL JSM-7600F, JEOL Ltd., Akishima, Japan). Samples were secured onto aluminum stubs using conductive double-sided carbon tape and subsequently sputter-coated with a thin gold film to mitigate surface charging. Imaging was conducted using a secondary electron detector (SEI) at an accelerating voltage of 15.0 kV and a working distance (WD) of 8.0 mm. Micrographs were recorded at various magnifications (e.g., $\times 85$) to capture both the general particle distribution and specific surface porosities.

2.4. Thermogravimetric Analysis (Combustion Kinetics)

The combustion behavior of the peanut shells was investigated using a simultaneous TG–DSC analyzer (NETZSCH STA 449 F3 Jupiter, Selb, Germany). Approximately 10 mg of the sample was loaded into an alumina (Al_2O_3) crucible for each experiment. The combustion profile was monitored from 303 K to 1173 K under a synthetic air atmosphere (flow rate: 60 mL min^{-1} ; composition: 20% O_2 , 80% N_2). To evaluate the reaction kinetics, the experiments were performed at four distinct linear heating rates: 20, 40, 60, and 80 K min^{-1} . Heating rates were maintained using the high-speed furnace of the NETZSCH STA 449 F3 Jupiter[®], which is capable of linear heating rates up to 1000 K min^{-1} . The instrument's responsive PID controller, combined with the small sample mass, effectively dissipated the exothermic heat released during ignition (380–440 K), preventing thermal runaway and ensuring strict adherence to the programmed temperature profile. Both the mass loss (TG) and the rate of mass loss (DTG) were recorded continuously. All TGA runs were performed in triplicate to verify the consistency of the thermal degradation profiles.

2.5. Kinetic and Thermodynamic Modelling

To evaluate the combustion kinetics of peanut shells, the reaction rate was modeled as a function of temperature (T) and conversion (α) using the fundamental Arrhenius expression. The extent of conversion (α) was derived directly from the TGA mass loss profiles, defined as the ratio of the mass loss at a specific time to the total mass loss. In accordance with ICTAC recommendations for non-isothermal data, the apparent activation energy (E_a) was computed using a suite of six isoconversional models to ensure the reliability of the kinetic triplet (Table S1). These included one differential method (Friedman) and five integral methods (Flynn–Wall–Ozawa, Kissinger–Akahira–Sunose, Starink, Kissinger, and Vyazovkin).

Following the determination of E_a , the most probable reaction mechanism ($f(\alpha)$) was identified using the multivariate non-linear regression method (Coats–Redfern), testing against fifteen standard solid-state reaction models (including diffusion, nucleation, and geometrical contraction models) (Table S2). Finally, the thermodynamic parameters, enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS), were calculated to assess the bioenergy potential and spontaneity of the process. The detailed mathematical formulations, reaction mechanism functions, and specific equations for all applied methods are provided in the Supplementary Materials (Table S3, Equations (S11)–(S13)).

3. Results and Discussion

3.1. Fundamental Properties of PnS

The physicochemical profile of the PnS feedstock is presented in Table 1. The proximate analysis indicates a volatile matter content of 65.30 wt%. While this is slightly lower than the very high values we previously observed for lemon peel (73.20 wt%) Ismail et al. (2025a) [31] and mango peel (70.64 wt%) Ismail et al. (2025b) [33], it remains sub-

stantial enough to ensure good ignition and reactivity during the gas-phase combustion stage. The moisture content was found to be 9.61 wt%, which is below the critical 10% threshold often recommended for the storage of solid biofuels to prevent biological degradation. The ash content of the PnS was measured at 6.59 wt%. This value places peanut shells in an intermediate position relative to our previous findings; it is higher than the 5.50 wt% found in orange peel but notably lower than the 7.55 wt% recorded for mango peel. While moderate, this ash content suggests that while PnS is a viable fuel, attention must be paid to potential slagging or fouling in industrial boilers, a common characteristic of agricultural residues.

Table 1. Physicochemical characteristics of peanut shell waste, including proximate, ultimate, and lignocellulosic fiber analysis.

Analysis/Property	Parameter	Value
Proximate Analysis		
	Moisture Content	9.61 ± 0.2
	Volatile Matter	65.30 ± 0.11
	Ash	6.59 ± 0.3
	Fixed Carbon	18.50 ± 0.10
Ultimate Analysis (dry basis)		
	Carbon (C)	43.50 ± 0.16
	Hydrogen (H)	6.73 ± 0.3
	Nitrogen (N)	0.85 ± 0.03
	Sulphur (S)	0.23 ± 0.04
	Oxygen (O)	48.69 ± 0.18
Heating Value (MJ kg^{-1})		20.87 ± 0.5
Fiber Fraction (dry basis)		
	Hemicellulose	14.5 ± 0.5
	Cellulose	47.86 ± 0.35
	Lignin	28.4 ± 0.11

The ultimate analysis reveals a carbon content of 43.50 wt% and an oxygen content of 48.69 wt%. This elemental composition yields a Higher Heating Value (HHV) of 20.87 MJ kg^{-1} . This energy density is highly competitive; it is comparable to the 21.9 MJ kg^{-1} we reported for mango peel and significantly higher than typical values for rice husk ($\sim 15 \text{ MJ kg}^{-1}$) or wheat straw ($\sim 17 \text{ MJ kg}^{-1}$). Importantly, the fuel is environmentally promising due to its low concentrations of nitrogen (0.85 wt%) and sulphur (0.23 wt%), which implies minimal generation of NO_x and SO_x pollutants during thermal conversion. Unlike the pectin-rich structure of citrus fruit peels, the fiber analysis of peanut shells confirms a highly lignocellulosic matrix. The sample is characterized by a high cellulose content (47.86%) and a significant lignin fraction (28.4%). This high lignin content, substantially higher than that found in fruit peels, is a critical factor for combustion kinetics. Lignin is the most thermally stable component of biomass; its abundance in PnS suggests that the combustion process will likely exhibit a prominent, high-temperature char oxidation stage and a potentially higher activation energy tail compared to hemicellulose-rich feedstocks.

3.2. Structural and Morphological Characterization

3.2.1. Surface Functional Groups (FTIR)

The FTIR spectrum of the PnS powder (Figure 1) exhibits a complex band pattern characteristic of a lignocellulosic matrix. The broad, high-intensity band centered at 3426 cm^{-1} is attributed to the O–H stretching vibrations of hydroxyl groups present

in cellulose, lignin, and adsorbed moisture. The distinct peaks at 2919 cm^{-1} and 2851 cm^{-1} correspond to the asymmetric and symmetric C–H stretching vibrations, respectively, arising from the aliphatic methylene ($-\text{CH}_2$) and methyl ($-\text{CH}_3$) groups in the polymer backbone. The region between 1800 and 1500 cm^{-1} provides insight into the fiber composition. The prominent peak observed at 1628 cm^{-1} is associated with the aromatic skeletal vibrations ($\text{C}=\text{C}$) of lignin and the absorbed water bending vibration. Notably, the $\text{C}=\text{O}$ stretching vibration characteristic of hemicellulose (typically $\sim 1730\text{ cm}^{-1}$) appears as a shoulder merged with the broader band at 1628 cm^{-1} , rather than a distinct peak. This overlapping is frequently observed in lignocellulosic biomass where high lignin content (28.4% in this study) or moisture interference masks the carbonyl signal. The lignocellulosic nature is further evidenced by the skeletal vibration near 1426 cm^{-1} and the characteristic guaiacyl ring breathing peak at 1261 cm^{-1} . The region around 1060 cm^{-1} is dominated by intense C–O and C–O–C stretching vibrations, confirming the high cellulosic content (47.86%) of the biomass. Finally, the band at 637 cm^{-1} is attributed to the out-of-plane bending vibrations of the aromatic ring C–H bonds.

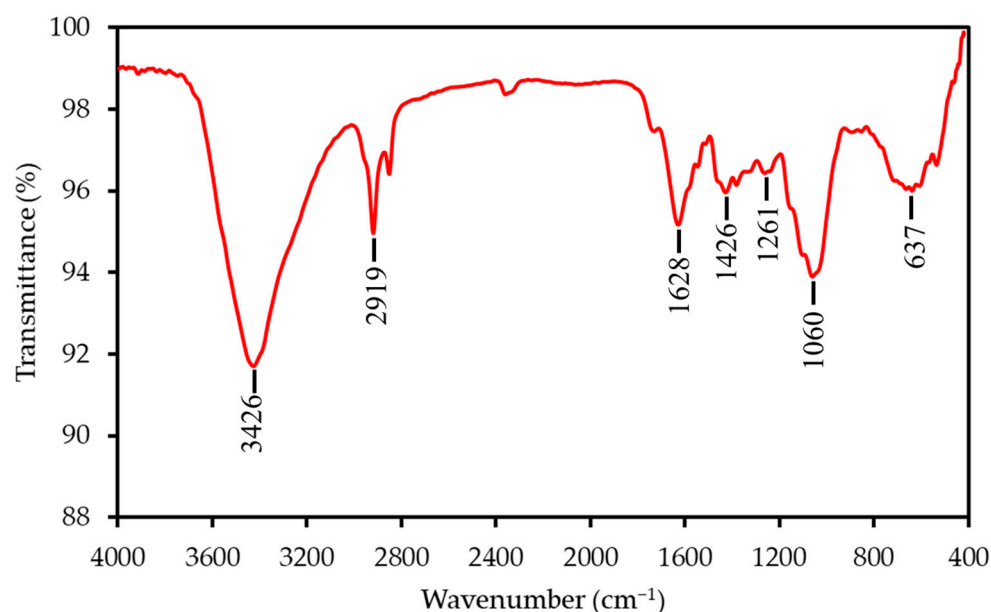


Figure 1. FTIR spectrum of peanut shell biomass powder showing the characteristic functional bands of the lignocellulosic matrix.

3.2.2. Morphology Feature (SEM)

The surface topography of the peanut shell particles was examined to understand the physical barriers to combustion. As shown in Figure 2, the material exhibits a highly heterogeneous morphology. The low-magnification overview (Figure 2a, $\times 100$) reveals particles with irregular, angular shapes and rough surfaces, a direct result of the mechanical pulverization process. Unlike the smoother texture often observed in pectin-rich fruit peels, these particles display a rigid, woody texture typical of high-lignin biomass. Closer inspection (Figure 2b, $\times 250$) reveals distinct fibrous bundles, confirming the strong presence of cellulose fibers shielded by a lignin matrix. At higher magnifications (Figure 2c, $\times 1000$), the surface roughness and layering become evident, providing a substantial surface area for reaction. Most critically for the combustion process, high-magnification imaging (Figure 2d, $\times 3000$) uncovers a network of surface cavities and pores. This porous microstructure is vital for bioenergy applications; it facilitates the mass transfer of oxygen into the particle interior and the outward diffusion of volatile gases during thermal decomposition. This physical evidence strongly supports the kinetic modeling results (discussed in Section 3.4),

which indicate that the reaction rate is governed by diffusion mechanisms through the porous char layer.

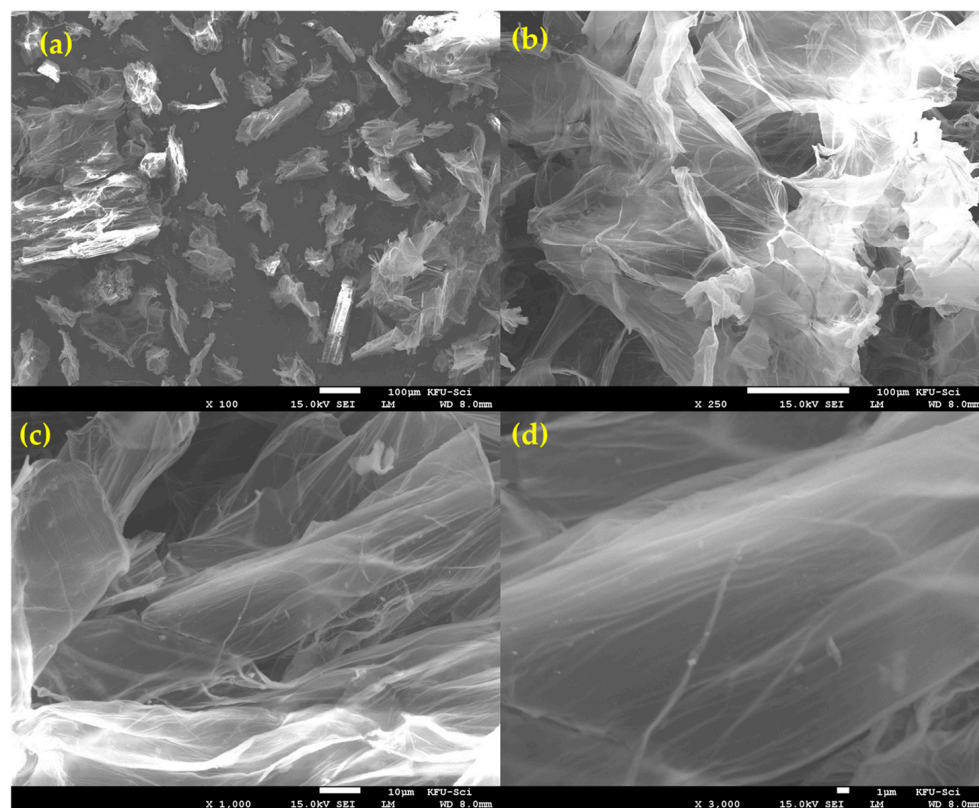


Figure 2. SEM micrographs of peanut shell particles at progressive magnifications: (a) $\times 100$: General overview showing irregular particle distribution and fragmentation; (b) $\times 250$: Fibrous bundles characteristic of the lignocellulosic matrix; (c) $\times 1000$: Detailed surface view revealing significant roughness and layering; and (d) $\times 3000$ revealing the porous microstructure that facilitates oxygen diffusion.

3.3. Combustion Characteristics via TGA

The suitability of PnS as a solid fuel is initially supported by its compositional analysis. With a high lignocellulose content (90.8%) and a moisture content (9.2%) below the critical 10% threshold, PnS is considered highly favorable for direct combustion applications [5]. The thermogravimetric (TG) and derivative thermogravimetric (DTG) profiles for PnS combustion at heating rates of 20, 40, 60, and 80 K min^{−1} are presented in Figure 3a,b. As anticipated, and consistent with extensive TGA literature, increasing the heating rate resulted in a consistent lateral shift in both TG and DTG curves toward higher temperatures. This phenomenon is attributed to thermal lag; at higher heating rates, the short residence time prevents the particle interior from reaching thermal equilibrium with the furnace immediately, thereby delaying downstream decomposition reactions. The DTG curves reveal that the combustion process occurs in two distinct stages of mass loss, the details of which are summarized in Table 2. Stage 1 (Dehydration): Occurring between 300 and 500 K, this stage corresponds to the evaporation of moisture and light volatiles, resulting in a mass loss of approximately 8–9%. Stage 2 (Main Combustion): The TG curve drops precipitously in the range of 460–720 K. This major devolatilization stage accounts for a mass loss of 50–61% and is attributed to the collective degradation and oxidation of the lignocellulosic components (hemicellulose, cellulose, and lignin). A noticeable trend in Table 2 is the increase in mass loss during this stage with increasing heating rates (rising from 50% at 20 K min^{−1} to 61% at 80 K min^{−1}). This phenomenon is attributed to the

competitive nature of thermal degradation reactions. Higher heating rates facilitate rapid volatilization, favoring the release of volatiles over the secondary cross-linking reactions that promote char formation. Consequently, this leads to a lower final char yield and a correspondingly higher percentage of mass loss in the devolatilization stage. Meanwhile, Jerzak et al. (2016) [21] noted that this main decomposition region could be chemically distinguished into two phases: cellulose/hemicellulose combustion (523–673 K) and lignin combustion (673–873 K).

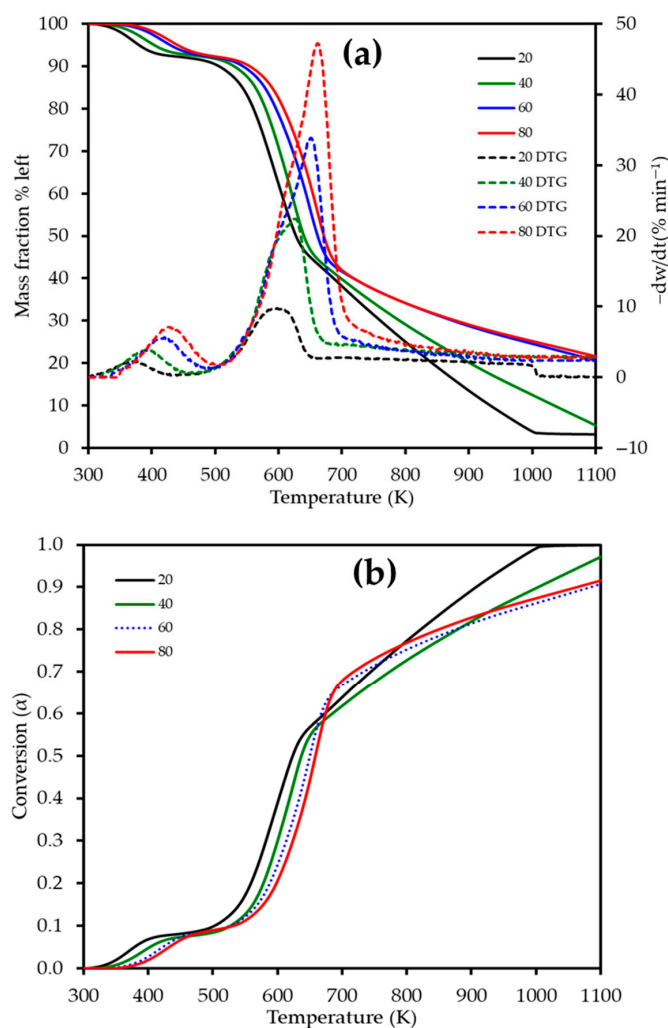


Figure 3. Thermal decomposition profiles of peanut shell combustion: (a) Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves for heating rates of 20, 40, 60, and 80 K min⁻¹; (b) Extent of conversion (α) as a function of temperature.

Table 2. Characteristic temperatures and mass loss percentages for the two primary combustion stages of peanut shells at varying heating rates.

Heating Rate (K min ⁻¹)	1st Reaction			2nd Reaction		
	T Range, T _{peak} (K)	Weight Loss%	Process	T Range, T _{peak} (K)	Weight Loss%	Process
20	300–430, 360	8.0	dehydration	460–650, 600	50.0	Hemicellulose, cellulose, and lignin degradation
40	340–460, 390	8.0		500–660, 630	50.0	
60	350–490, 430	9.0		520–700, 650	58.0	
80	360–500, 440	9.0		530–720, 660	61.0	

This two-stage decomposition profile for PnS stands in contrast to the four-stage profile we previously reported for lemon peel [31], and the three-stage profile observed for mango peel [33]. Above 720 K (corresponding to a conversion of $\alpha > 0.7$ in Figure 3b), the TG curves exhibit a slow, almost horizontal decline. This “creeping” behavior represents the slow oxidation of the remaining char and fixed carbon. It is observed that at the lowest heating rate of 20 K min^{-1} , the TG curve reaches a stable plateau after 1000 K, indicating that the char oxidation process was completed within the experimental timeframe. In contrast, at higher heating rates, the reaction is kinetically delayed due to thermal lag, resulting in incomplete burnout at the same temperature. Similar phenomena have been observed and justified by Xu et al. (2020) [10], who noted that the final stages of char burnout can be prolonged and less distinct. Consequently, to ensure the accuracy of the kinetic modeling, all calculations for kinetic parameters in this study were exclusively restricted to the active conversion range of 0.1 to 0.5, where the primary combustion reactions occur.

Our findings regarding the overlapping decomposition of components are supported by Nie et al. (2022) [22], who emphasized the complexity of the second phase of reaction in biomass combustion. Furthermore, the initiation of this stage is driven by the breakdown of hemicellulose, which fractures in the presence of air prior to cellulose due to its unstable chemical bonds, as highlighted by Liu et al. (2021) [25]. While Xu et al. (2020) [10] previously reported a 5.27% mass loss for the first stage and identified distinct cracking phases for hemicellulose and cellulose in their specific sample, the high heating rates (up to 80 K min^{-1}) explored in this study reveal an intensified, merged thermal behavior. This distinct two-stage behavior under high heating rates highlights the novelty of these findings for industrial thermal processing applications.

To further quantify the combustion performance, the Combustion Index (S) was evaluated. The S index is a comprehensive indicator of fuel reactivity, defined as $S = (R_{\max} \times R_{\text{mean}}) / (T_i^2 \times T_b)$, where $R_{\max}$ and R_{mean} are the maximum and mean mass loss rates, and T_i and T_b are the ignition and burnout temperatures, respectively. A higher S value indicates more vigorous combustion. As shown in Figure 4, the combustion index increases progressively with the heating rate. This confirms that higher heating rates enhance the overall reactivity and oxidation intensity of the peanut shells, improving the efficiency of the combustion process.

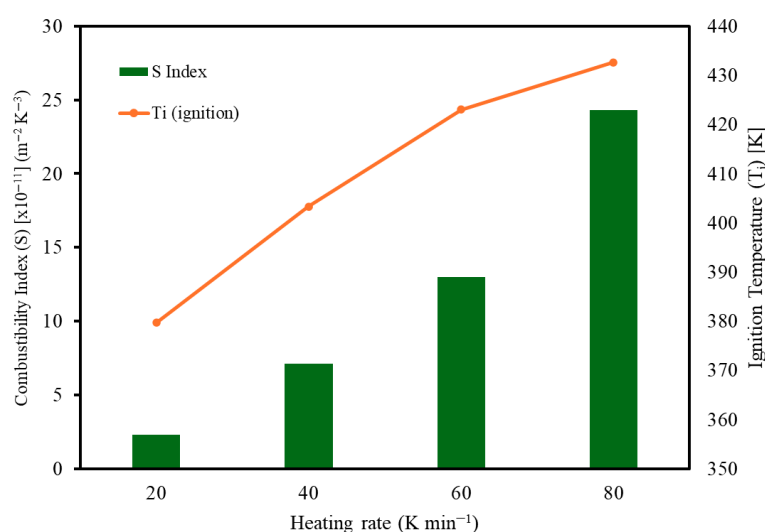


Figure 4. Effect of heating rate on the combustion index (S) and ignition Temperature of peanut shell, illustrating enhanced reactivity and delayed ignition at higher heating rates.

3.4. Kinetic Modelling of Peanut Shell Combustion

3.4.1. Activation Energies from Model-Free Methods

To quantify the energy barriers governing the combustion process, the apparent activation energy E_a was evaluated as a function of conversion using six model-free isoconversional methods. As justified in Section 3.3, the calculations for E_a were confined to the conversion range of $\alpha = 0.1$ –0.5. This restriction was necessary to exclude the “creeping” reaction tail observed at higher temperatures, ensuring that the kinetic parameters reflect the primary devolatilization and oxidation reactions rather than the slow, diffusion-limited burnout of residual char. These isoconversional methods are widely endorsed by the ICTAC committee for analyzing complex solid-state kinetics because they avoid the assumption of a specific reaction model. The linear regression plots derived from the experimental TGA data are illustrated in Figure 5, showing high coefficients of determination $R^2 > 0.95$ for the selected range. The resulting E_a values are listed in Table 3 and visualized in Figure 6.

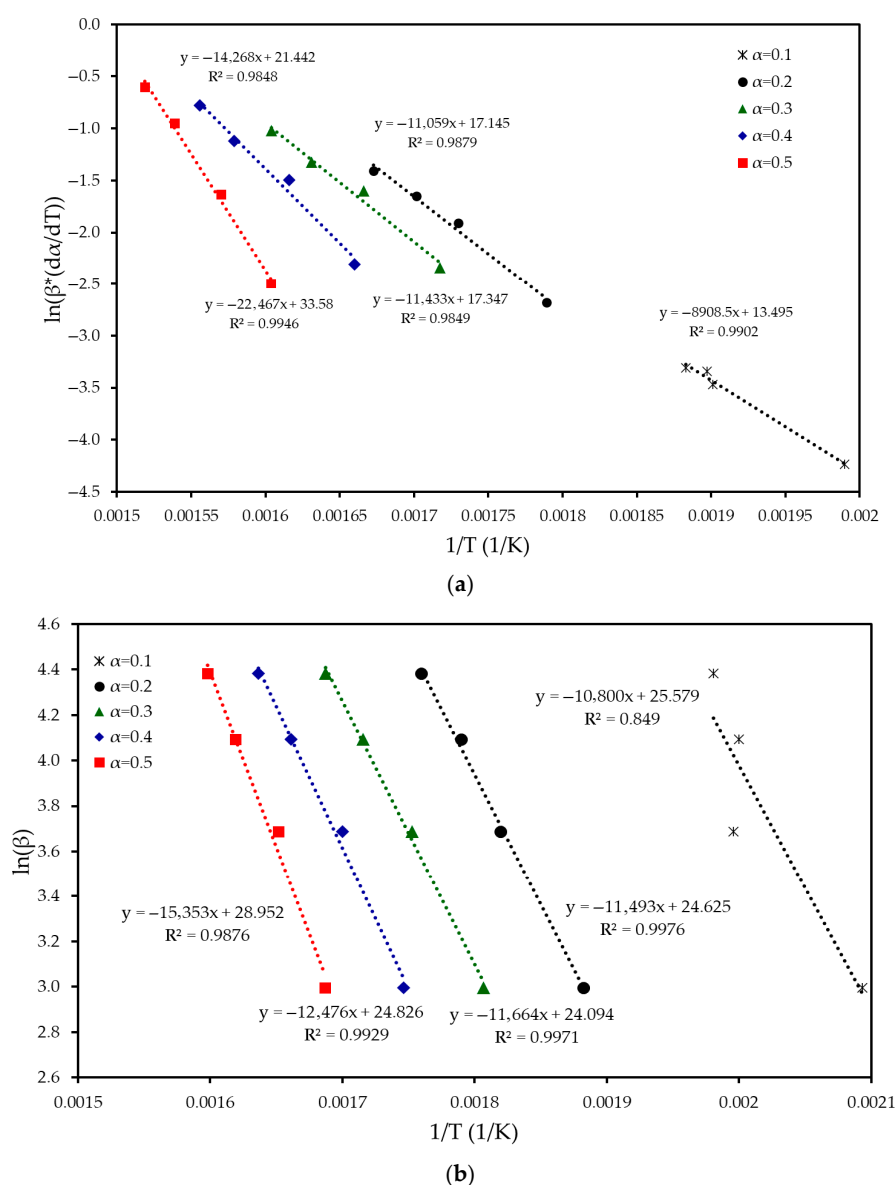


Figure 5. Cont.

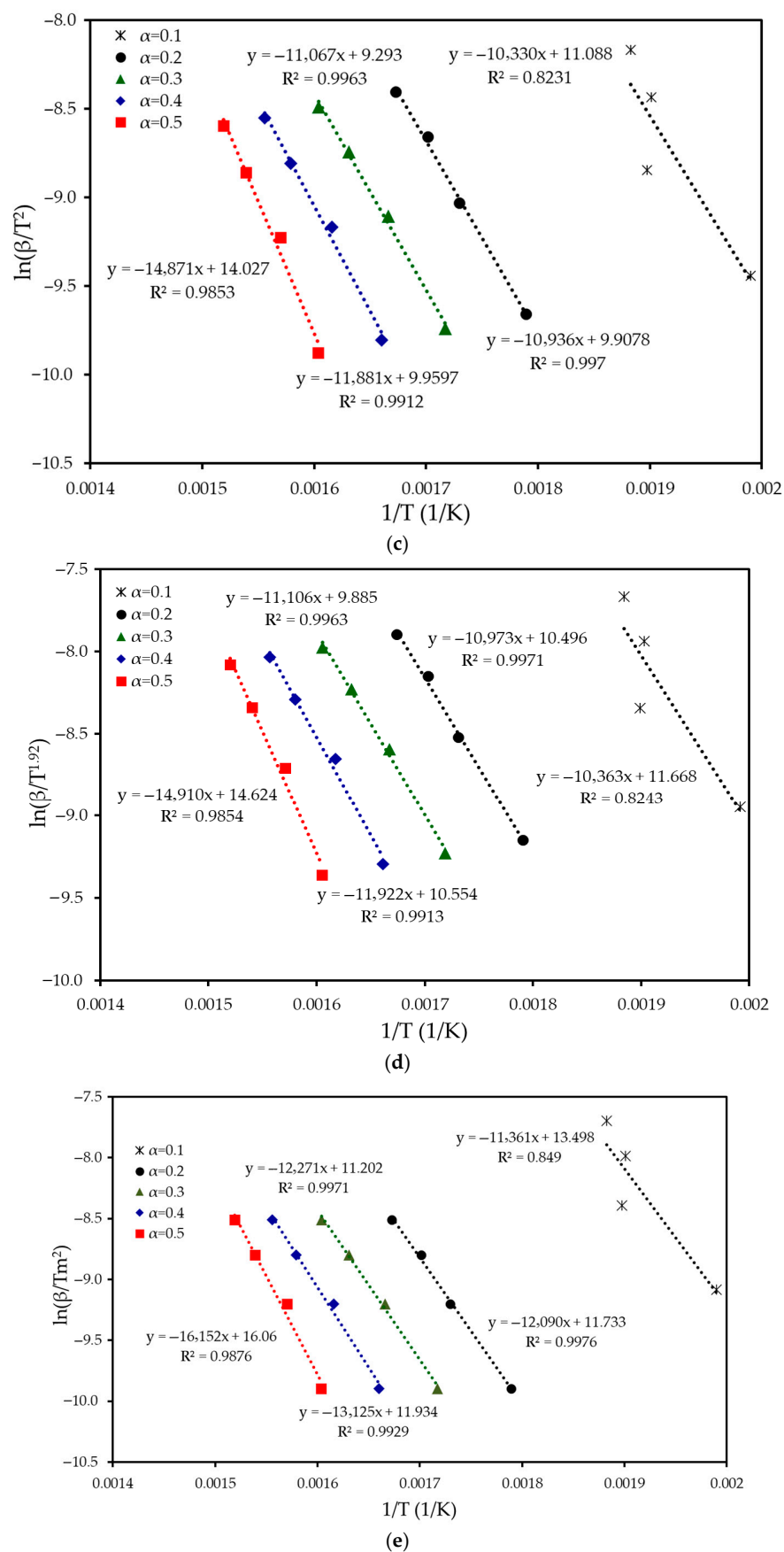
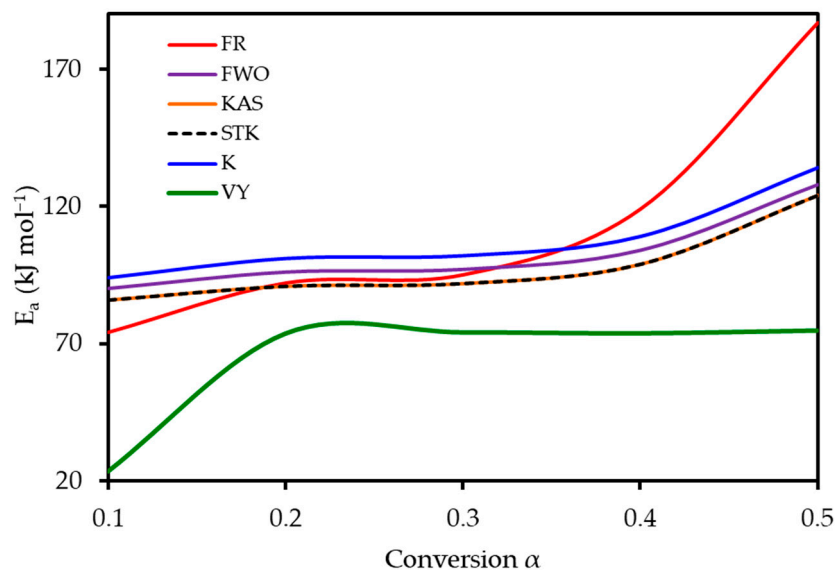


Figure 5. Linear regression plots for the kinetic analysis of peanut shell combustion using five model-free methods: (a) FR, (b) FWO, (c) KAS, (d) STK, and (e) K.

Table 3. Apparent activation energy (E_a) and correlation coefficients (R^2) for peanut shell combustion calculated at conversion levels $\alpha = 0.1$ – 0.5 using six model-free methods.

Conversion	FR		FWO		KAS		STK		K		VY		Average	
	E (kJ/mol)	R^2	E (kJ/mol)	R^2	E (kJ/mol)	R^2	E (kJ/mol)	R^2	E (kJ/mol)	R^2	E (kJ/mol)	R^2	E (kJ/mol)	R^2
0.1	74	0.9902	90	0.849	86	0.8231	86	0.8243	94	0.849	23	NA *	76	0.86712
0.2	92	0.9879	96	0.9976	91	0.997	91	0.9971	101	0.9976	74	NA	91	0.99544
0.3	95	0.9849	97	0.9971	92	0.9963	92	0.9963	102	0.9971	74	NA	92	0.99434
0.4	119	0.9848	104	0.9929	99	0.9912	99	0.9913	109	0.9929	74	NA	101	0.99062
0.5	187	0.9946	128	0.9876	124	0.9853	124	0.9854	134	0.9876	75	NA	129	0.9881
Average	113	0.9885	103	0.9648	98.4	0.9586	98.4	0.9589	108	0.9648	64	NA	98	0.9671

* NA: R^2 is not applicable as the Vyazovkin method is a non-linear isoconversional method that does not rely on linear regression.

**Figure 6.** Evolution of apparent activation energy (E_a) as a function of conversion (α) determined using six isoconversional methods (FR, FWO, KAS, STK, K, and VY).

The results indicate that the combustion of peanut shells is a complex multi-step process where E_a varies with conversion. The process initiates with a relatively low average activation energy of $\sim 76 \text{ kJ mol}^{-1}$ at $\alpha = 0.1$. This low barrier corresponds to the rupture of weak chemical bonds, such as those in hemicellulose and amorphous structures, which require less energy to break. As the conversion progresses $\alpha > 0.3$, the E_a steadily rises, reaching an average of $\sim 129 \text{ kJ mol}^{-1}$ at $\alpha = 0.5$. This increasing trend reflects the shift in reaction dominance toward the thermal decomposition of the more stable crystalline cellulose and lignin components [34].

The six kinetic methods produced results that can be categorized into two distinct trends: 1. Integral Methods (FWO, KAS, STK, K): These methods yielded highly consistent and overlapping E_a profiles. For instance, the KAS and STK methods produced nearly identical ranges (86 – 124 kJ mol^{-1}), and the FWO method showed a similar trend (90 – 128 kJ mol^{-1}). This consistency is expected as these methods share similar integral derivations. 2. Differential (FR) and Non-Linear (VY) Methods: The differential Friedman (FR) method displayed higher sensitivity to local reaction rates, resulting in a broader E_a range (74 – 187 kJ mol^{-1}). Conversely, the Vyazovkin (VY) method yielded significantly lower values (23 – 75 kJ mol^{-1}).

Despite these methodological variances, the average activation energy across all methods was found to be 98 kJ mol^{-1} . This finding is in excellent agreement with Nie et al. (2022) [22], who reported an average E_a of $\sim 93.21 \text{ kJ mol}^{-1}$ for peanut shell combustion. Interestingly, Nie et al., 2022 observed that while E_a increased initially, it decreased at higher

conversions $\alpha > 0.2$, a phenomenon they attributed to volatilization in the porous media enhancing oxygen diffusion [22]. Our results align more closely with Xu et al. (2020) [10], who used FWO and DAEM models to analyze PnS combustion and observed a gradually increasing E_a trend within the 0.1–0.65 conversion range, with values stabilizing around 100 kJ mol^{-1} . This behavior of a slow rising trend is characteristic of the complex, overlapping decomposition of the lignocellulosic matrix.

3.4.2. Validation of Kinetic Parameters: The Kinetic Compensation Effect

To verify the reliability of the calculated kinetic parameters, the Kinetic Compensation Effect (KCE) was evaluated. The KCE posits a linear relationship between the natural logarithm of the pre-exponential factor, $\ln A$, and the activation energy (E_a) for a reaction series, described by the equation $\ln A_i = a + bE_{a,i}$. The existence of this linearity serves as a quality check, ensuring that the variations in E_a and $\ln A$ are physically coupled and not artifacts of the calculation method. As illustrated in Figure 7, the plot of $\ln A$ versus E_a for the Friedman method yields a distinct straight line with a high coefficient of determination $R^2 = 0.99$. This strong linearity confirms the kinetic compensation effect, suggesting that the reaction mechanism remains fundamentally consistent across the conversion range analyzed, $\alpha = 0.1$ – 0.5 , despite the observed increase in activation energy.

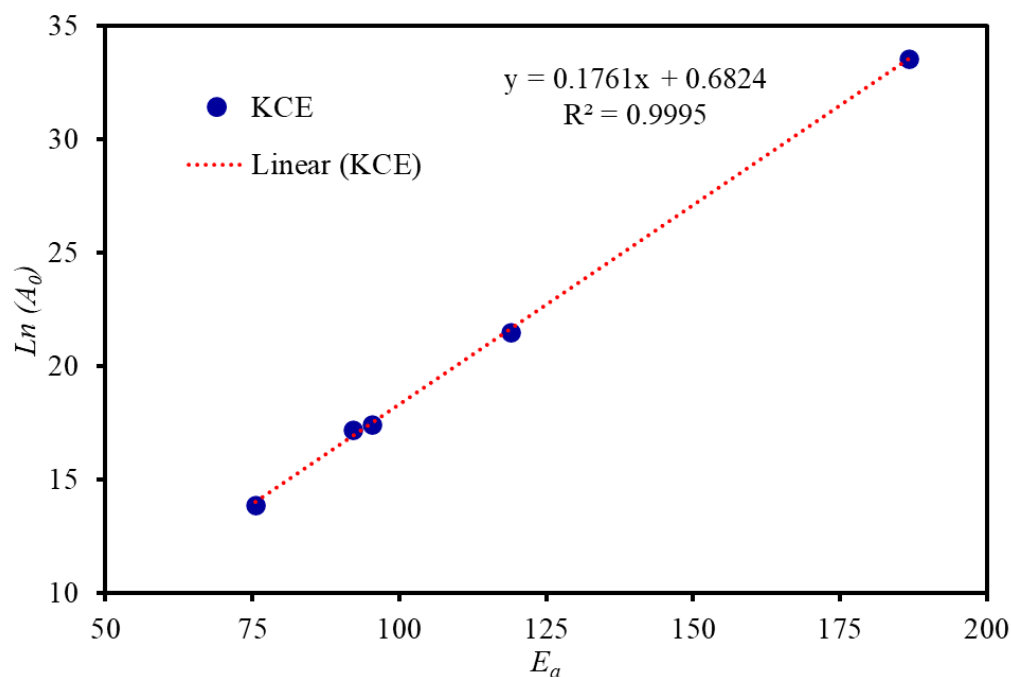


Figure 7. Validation of the kinetic compensation effect: Linear correlation ($R^2 = 0.9995$) between the natural logarithm of the pre-exponential factor ($\ln A$) and activation energy (E_a) derived from the Friedman method.

3.4.3. Reaction Mechanism and Kinetic Parameters from CR Method

To determine the most suitable solid-state reaction mechanism governing PnS combustion, the Coats–Redfern (CR) model-fitting method was employed. The kinetic data were fitted to sixteen standard solid-state reaction models at all heating rates (Table S4). The resulting kinetic triplets (E_a , $\ln A$, and correlation coefficient R^2) were evaluated. Across the active combustion stage, the Three-Dimensional Diffusion model (D3, Jander equation) consistently provided the best statistical fit to the experimental data, yielding the highest correlation coefficients ($R^2 > 0.99$). This result indicates that the oxidation rate of peanut shells is governed by a diffusion-controlled mechanism $\left(f(\alpha) = \left[1.5 \left(1 - (1 - \alpha)^{1/3} \right)^{-1} (1 - \alpha)^{2/3} \right] \right)$.

In this regime, the reaction rate is limited by the transport of oxygen through the porous char layer formed during the devolatilization of lignin and cellulose. This finding aligns with the SEM observations (Figure 2), which revealed a porous microstructure capable of inhibiting gas diffusion at high conversion rates. This identification of a diffusion mechanism is consistent with our previous work on lemon peel [31] and mango peel [33], suggesting that high-lignin agro-wastes generally follow a D3 mechanism under oxidative conditions. However, this contrasts with the findings of Nie et al. (2022) [22], who reported that the best mechanism fitting among 42 combustion models was the Avrami–Erofeev equation (Nucleation model, A4), likely due to differences in particle size or heating rates utilized in their specific study.

3.5. Thermodynamic Assessment of Combustion

To further study the feasibility and energy dynamics of PnS combustion, pre-exponential factors (A_0) and the thermodynamic parameters, including activation enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS), were calculated depending on the kinetic parameters from different model-free methods, and compiled in Table 4. A_0 is calculated for each model-free method using the three-dimensional diffusion model (D3) for $g(\alpha)$. It was observed that as conversion increased from 0.1 to 0.5, the values of A_0 for the five model-free methods showed an increasing trend. This reflects the intensifying molecular collision frequency as the reaction interface penetrates the porous structure.

Table 4. Calculated pre-exponential factors (A_0) and thermodynamic parameters (ΔH , ΔG , and ΔS) for peanut shell combustion as a function of conversion.

α	FR				FWO			
	A_0 min^{-1}	ΔH (kJ mol $^{-1}$)	ΔG (kJ mol $^{-1}$)	ΔS (kJ mol $^{-1}$ K $^{-1}$)	A_0 min^{-1}	ΔH (kJ mol $^{-1}$)	ΔG (kJ mol $^{-1}$)	ΔS (kJ mol $^{-1}$ K $^{-1}$)
0.1	1.79×10^4	70.67	140.37	−0.17425	3.17×10^9	86.67	116.19	−0.07378
0.2	1.55×10^6	86.76	175.56	−0.14095	2.74×10^9	90.76	140.38	−0.07876
0.3	3.24×10^6	89.76	174.69	−0.13481	2.76×10^9	91.76	141.35	−0.07872
0.4	3.01×10^8	113.76	174.96	−0.09713	8.88×10^9	98.76	142.23	−0.069
0.5	8.37×10^{13}	181.76	177.3	0.007086	8.18×10^{11}	122.76	142.54	−0.03139
α	KAS				STK			
	A_0 min^{-1}	ΔH (kJ mol $^{-1}$)	ΔG (kJ mol $^{-1}$)	ΔS (kJ mol $^{-1}$ K $^{-1}$)	A_0 min^{-1}	ΔH (kJ mol $^{-1}$)	ΔG (kJ mol $^{-1}$)	ΔS (kJ mol $^{-1}$ K $^{-1}$)
0.1	1.61×10^3	82.67	160.38	−0.19426	2.88×10^3	82.67	158.45	−0.18944
0.2	1.11×10^3	85.76	212.47	−0.20112	2.01×10^3	85.76	209.39	−0.19623
0.3	1.03×10^3	86.76	213.88	−0.20177	1.86×10^3	86.76	210.78	−0.19685
0.4	3.10×10^3	93.76	215.1	−0.1926	5.62×10^3	93.76	211.99	−0.18766
0.5	2.70×10^5	118.76	216.71	−0.15548	4.90×10^5	118.76	213.59	−0.15051
α	K							
	A_0 min^{-1}	ΔH (kJ mol $^{-1}$)	ΔG (kJ mol $^{-1}$)	ΔS (kJ mol $^{-1}$ K $^{-1}$)				
0.1	1.80×10^4	90.67	160.36	−0.17422				
0.2	6.91×10^3	95.76	212.91	−0.18594				
0.3	6.95×10^3	96.76	213.88	−0.1859				
0.4	2.24×10^4	103.76	214.76	−0.17618				
0.5	2.06×10^6	128.76	216.06	−0.13858				

ΔH is a measure of the energy difference between the reagent and the activated complex during a chemical reaction [2]. The calculated values for activation enthalpy (ΔH) are positive across the entire conversion range (0.1 – 0.5), confirming that PnS combustion is an endothermic process regarding the formation of the activated complex. Notably, ΔH exhibits a rising trend with conversion (e.g., increasing from ~70 to ~180 kJ mol $^{-1}$ for the FR method). This trend indicates that the energy barrier for complex formation rises as the

reaction progresses, reflecting the shift from degrading reactive hemicellulose/cellulose to the more recalcitrant lignin and fixed carbon structures. The difference between E_a and ΔH was found to be consistently small (in the range of $\sim 4 - 5 \text{ kJ mol}^{-1}$), which implies that only a modest additional energy barrier must be overcome to convert the activated complex into reaction products.

ΔG is usually investigated to judge the spontaneous nature, direction, and degree of reactions [11]. The Gibbs free energy (ΔG) was found to be positive for all methods across the entire conversion range ($116 - 220 \text{ kJ mol}^{-1}$), indicating that the reaction activation is non-spontaneous. Similarly to enthalpy, ΔG values increase with higher conversion. This increasing thermodynamic barrier signifies that sustaining the combustion of the remaining char requires a continuous and intensifying supply of external thermal energy, particularly during the later oxidation stages.

Finally, ΔS indicates the degree of disorder in the system [3]. The entropy (ΔS) values reveal a notable transition during the combustion process. At low to midlevels of conversion, the ΔS values are predominantly negative (e.g., $-0.17 \text{ kJ mol}^{-1} \text{ K}^{-1}$), suggesting that the activated complex is more structured and ordered than the initial reactants. However, a clear trend is observed where ΔS values become less negative (or even positive) as conversion increases. This shift suggests that as the biomass matrix disintegrates, the degrees of freedom in the activated complex increase, moving towards a less ordered state typical of advanced degradation and gasification. These findings regarding the thermodynamic nature of the process are consistent with trends reported in comparable biomass studies by Nie et al. (2022) [22] and Xu et al. (2020) [10].

3.6. Integrated Analysis and Implications for Biofuel Applications

This study confirms that PnS is a highly competitive solid biofuel, distinct in its properties from the fruit peels analyzed in our previous works. PnS exhibits an exceptionally high heating value ($\text{HHV} = 20.87 \text{ MJ kg}^{-1}$), which is comparable to Mango Peel (21.9 MJ kg^{-1}) and significantly higher than standard agricultural residues like rice husk ($\sim 15 \text{ MJ kg}^{-1}$). This high energy density, combined with a substantial volatile matter content (65.30 wt%), ensures efficient ignition and sustained combustion heat release. A critical advantage of PnS over Lemon Peel is its ash composition. While Lemon Peel presented a severe slagging risk due to extremely high ash content, PnS contains a moderate ash fraction (6.59 wt%). Although this is higher than the 5.50 wt% observed in Orange Peel, it is manageable for industrial boiler systems, provided that standard soot-blowing and ash removal protocols are in place. Furthermore, the ultimate analysis highlights PnS as an eco-friendly fuel; its low nitrogen (0.85 wt%) and sulphur (0.23 wt%) contents imply minimal NO_x and SO_x emissions, aligning with international environmental standards for clean energy. Theoretically, the combustion process is governed by a 3D-diffusion mechanism ($E_a \approx 98 \text{ kJ mol}^{-1}$). This suggests that for industrial applications, the particle size of pulverized PnS must be carefully optimized. Finer grinding may reduce the diffusion limitations identified by the D3 model, thereby enhancing combustion efficiency. Given its high energy content, moderate ash, and favorable kinetics, PnS is recommended for direct co-firing with coal or as a feedstock for densified fuel pellets.

4. Conclusions

This study provides a comprehensive kinetic and thermodynamic characterization of PnS combustion at high heating rates ($20\text{--}80 \text{ K min}^{-1}$). Unlike the four-stage decomposition observed in citrus peels, PnS combustion proceeds via two distinct stages: a dehydration phase followed by a major combined devolatilization of hemicellulose, cellulose, and lignin. The kinetic analysis using six model-free methods revealed an

average activation energy of 98 kJ mol^{-1} , with values increasing from $\sim 76 \text{ kJ mol}^{-1}$ at the start of conversion to $\sim 129 \text{ kJ mol}^{-1}$ at $\alpha = 0.5$. This progressive increase reflects the heterogeneous nature of the fuel, transitioning from easy-to-burn volatiles to recalcitrant lignin structures. The Coats–Redfern method confirmed that the reaction rate is limited by a three-dimensional diffusion (D3) mechanism, emphasizing the role of the porous char layer in regulating oxygen transfer. From an industrial perspective, PnS is verified as a superior biofuel candidate. It offers a high energy density (20.87 MJ kg^{-1}), low emissions potential ($S < 0.25\%$), and a manageable ash content (6.59%). These findings suggest that peanut shells are ideally suited for thermal power generation, provided that boiler designs account for the diffusion-limited combustion behavior at high temperatures. Future work will focus on the slagging indices of the ash to further refine boiler operating parameters.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym18050560/s1>, Table S1: Summary of model-free and model-fitting methods used for the kinetic analysis of PS combustion, including their corresponding equations and regression plots; Table S2: Fifteen of solid-state reaction mechanism; Table S3: Thermodynamic parameters, including ΔH , ΔG and ΔS for PS combustion were calculated using the following equation: [32]; Table S4: Kinetic parameters obtained by the CR method for PS combustion at four heating rates.

Author Contributions: Conceptualization, I.D. and M.A.I.; methodology, I.D., S.M. and M.A.I.; software, I.D., S.M. and A.A. (Abdullah Alshehab); validation, I.D. and S.M.; formal analysis, I.D. and A.A. (Abdulahman Almithn); investigation, M.A.I.; resources, M.A.I., A.A. (Abdulahman Almithn) and A.A. (Abdullah Alshehab); data curation, M.A.I.; writing—original draft preparation, I.D. and S.M.; writing—review and editing, I.D., S.M. and A.A. (Abdulahman Almithn); visualization, A.A. (Abdullah Alshehab) and S.M.; supervision, I.D. and A.A. (Abdullah Alshehab); project administration, I.D., M.A.I. and A.A. (Abdulahman Almithn); funding acquisition, I.D. All authors have read and agreed to the published version of the manuscript.

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