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Article

Combustion Characteristics, Kinetics and Thermodynamics of Peanut Shell for Its Bioenergy Valorization

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Abstract: To realize the utilization of peanut shell, this study investigates the combustion behavior, chemical kinetics, and thermodynamic parameters of peanut shell using TGA under atmospheric air. Results indicate that increasing the heating rate leads to higher ignition, burnout, and peak temperatures, as observed in the TG/DTG curves shifting to the right. Analysis of combustion performance parameters suggest that higher heating rates can enhance combustion performances. Kinetic analysis using two model-free methods, KAS and FWO, shows that the activation energy (E_a) ranges from 93.30 to 109.65 kJ/mol for FWO and 89.72 to 103.88 kJ/mol for KAS. The data fit well with coefficient of determination values (R^2) close to 1. Pre-exponential factors using FWO range from 2.19×10^6 to $8.06 \times 10^7 \text{ s}^{-1}$, and for KAS range from 9.72×10^5 to $2.25 \times 10^7 \text{ s}^{-1}$. Thermodynamic analysis indicates a low-energy barrier ($\leq \pm 6 \text{ kJ/mol}$) between activation energy and enthalpy changes, suggesting easy reaction initiation. Furthermore, variations in enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) upon conversion (α) suggest that peanut shell combustion is endothermic and non-spontaneous, with the generation of more homogeneous or well-ordered products as combustion progresses. These findings offer a theoretical basis and data support for the further utilization of agricultural biomass.

Keywords: combustion characteristics; kinetics and thermodynamics; thermogravimetric analysis; peanut shell

1. Introduction

Biomass is widely adopted as a renewable energy source with high sustainability. Its diverse sources include forestry, agriculture, organic waste, and livestock and poultry manure [1,2]. Through thermochemical conversions such as pyrolysis, gasification, and combustion, biomass can be transformed into valuable energy [3]. Notably, biomass is considered a carbon-neutral energy source, capable of achieving zero carbon emissions and mitigating greenhouse gas effects, particularly carbon dioxide [4,5]. With stringent requirements to reduce carbon emissions, China aims to run carbon reduction plans by 2030 and achieve carbon neutrality by 2060 [6,7]. To this end, the development of biomass energy is of significant importance. By reducing reliance on fossil fuels and addressing environmental concerns, biomass energy holds significant potential. Accordingly, numerous investigations have been conducted focusing on biomass energy to enhance global energy structures while meeting stringent carbon emission regulations.

Applications of biomass mainly include combustion directly or indirectly as fuel or the production of charcoal, bio-oil, tar, and gas by pyrolysis technology. The content of sulfur and nitrogen in biomass is low, and the emission of SO_x and NO_x in the combustion process is less, which has good emission characteristics. After combustion, there is less ash, and the generated ash contains a large amount of organic potassium salt, which can be used to recover and extract potash fertilizer, greatly reducing the site of ash stacking, and reducing the cost of ash disposal and resource waste

[8]. Therefore, based on the advantages of low cost, low risk and high efficiency of biomass, biomass power generation is one of the most promising utilization technologies, which can generate efficient and clean electric energy by direct combustion or gasification after simple treatment of collected biomass as raw materials. Promoting the deepening development of biomass energy will help increase the supply of high-quality energy, ease the pressure on domestic coal power generation, and play an important guiding role in improving the energy consumption structure and ecological environment.

Peanut shells represent a substantial agricultural waste in key peanut-producing nations like China, Vietnam, and Indonesia. China, as the world's largest peanut producer, produces 17 million tons of peanuts, accounting for more than 40% of the world's total production. The production of peanut shells is as high as 5 million tons, some of which are used as fuel, most of which are piled up or directly burned, wasting substantial resources [9]. Hence, exploring the utilization potential of peanut shells has become a hot research topic in recent years. In this context, understanding the combustion features and thermal characteristics of solid fuel in depth is crucial for designing combustion equipment on an industrial scale [10,11].

Methods for addressing the dynamic parameters of the combustion process are primarily categorized into model-fitting and model-free methods [12–14]. In the former method, kinetic parameters are calculated by assuming a model for each reaction and then finding the best fit of the data to the model. This method mainly adopts the method of a single heating rate, thus the kinetic parameters obtained are not applicable, and often cannot predict the reaction process under other heating rate conditions. This makes the model-fitting method under a single heating rate limited to some extent. The latter method, on the other hand, calculates the kinetic parameters at the same conversion from several pyrolysis curves with different heating rates. In this approach, variations in the activation energy with conversion rate can be determined using the iso-conversion rate method, which can reveal the nature of some seemingly simple reactions that are complex.

This paper aims to explore the thermochemical conversion of peanut shells during combustion. Through a combination of experimental analysis and theoretical approaches, thermogravimetric analysis is conducted to examine the combustion characteristics of peanut shell raw materials under atmospheric air. The study employs two model-free kinetic methods, namely the Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO) methods, to explore the combustion kinetics parameters. Additionally, a thermodynamic analysis is carried out. The findings of this study can offer valuable insights for the design, transformation, and operational optimization of combustion equipment, thereby facilitating the efficient and clean utilization of peanut shells..

2. Materials and Methods

2.1. Materials

The peanut shells utilized in this experimental investigation originated from Hubei province, China. These samples were grounded using a 150-mesh sieve. Subsequently, the finely ground samples were dried at 373 K for 24 hours.

The proximate analysis of the peanut shell was conducted following the GB/T 212–2008 standard. For the ultimate analysis, a CHNS/O analyzer was employed, which simultaneously detected the weight percentage of carbon, hydrogen, nitrogen, and sulfur in the samples. The weight percentage of oxygen was determined by the difference. Each experiment was repeated twice, and the average values were recorded. The results of the proximate and ultimate analyses of the peanut shell are summarized in Table 1. The significant volatile and fixed carbon content indicates the potential of peanut shells as a fuel source in thermochemical processes. The low nitrogen and sulfur content in the ultimate analysis is advantageous as it leads to lower emissions of toxic NO_x and SO_x during conversion processes, making peanut shells a promising alternative for bioenergy production regarding environmental sustainability and high volatility [15].

Table 1. Proximate and ultimate analyses of peanut shell.

Proximate analysis /%				Ultimate analysis /%				
Moisture	Fixed carbon	Volatiles	Ash	C	H	N	S	O
8.16	14.38	57.20	20.26	34.97	5.33	0.54	0.01	59.69

2.2. Experimental Procedures

Thermogravimetric testing was conducted using a thermogravimetric analyzer (TGA5500, Waters, USA). Each sample, weighing approximately 6 ± 0.5 mg, was placed in an alumina crucible. The samples were then heated at various rates: 10, 20, and 30 K/min, starting from room temperature and reaching 1073 K, under atmospheric air with a flow rate of 100 mL/min. The real-time change in mass loss was monitored throughout the entire process. To enhance accuracy, each test was performed in triplicate to minimize vibration errors.

2.3. Combustion Characteristic Parameters

To explore the oxidative decomposition of peanut shells, it is crucial to explore the characteristic temperature, characteristic time, and weight loss rate from the TG/DTG curve during the process.

2.3.1. Characteristic Temperature and Characteristic time

The ignition temperature (T_i) represents the minimum temperature at which the fuel ignites spontaneously without an external source. Typically, the ignition temperature is determined using the TG-DTG tangent method [16]. This method involves drawing a vertical line on the X-axis at the maximum peak of the DTG curve and intersecting the TG curve at a point. Subsequently, a tangent line is drawn on the TG curve after this point. When the tangent line intersects with a parallel line parallel to the X-axis, it indicates the point at which the TG begins to lose weight. The temperature corresponding to this point is the ignition temperature (T_i), and the time corresponding to reaching the ignition temperature is the ignition time (t_i).

The burnout temperature (T_b) represents the temperature at which the combustion of the sample ceases, indicating the difficulty of sample burnout. It is identified when the TG curve approaches a horizontal line and the DTG curve approaches 0, signifying that the fuel combustion is essentially complete. In this study, the burnout temperature is defined as the point where the weight loss at the terminal phase of the TG profile reaches 98% [17]. The time corresponding to reaching the burnout temperature is referred to as the burnout time (t_b).

The initial release temperature of volatile matter (T_v) is defined as the temperature corresponding to a mass loss rate of 0.1 mg/min [18]. The peak temperature (T_m) refers to the temperature of the maximum weight loss peak in the DTG curve during the combustion process. The time corresponding to reaching the peak temperature is t_m . $\Delta T_{1/2}$ represents the temperature interval at half the value of the peak weight loss rate in both the descending and rising parts of the DTG peak, while $\Delta t_{1/2}$ represents the time interval at half the value of the peak weight loss rate.

2.3.2. Weight Loss Rate

The maximum combustion rate (v_{\max}) refers to the highest weight loss rate of the fuel during combustion, indicating the intensity of the fuel combustion reaction. A higher maximum combustion rate suggests a more vigorous release of volatile matter, leading to a faster weight loss rate after ignition, typically associated with a lower corresponding temperature. Meanwhile, v_{mean} represents the average weight loss rate of the sample throughout the entire combustion process, from the ignition temperature to the burnout temperature. A higher v_{mean} value indicates a more intense overall combustion process.

2.3.3. Combustion Performance Parameters

To assess the combustion characteristics of peanut shells, several parameters were utilized in this study: volatile matter release (D_v), ignition index (D_i), burnout index (D_b), combustion intensity (H_i), combustion stability index (D_{si}), and comprehensive combustibility (S). These parameters are defined in terms of characteristic temperature, characteristic time, and weight loss rate. Relevant expressions of combustion performance parameters are described as follows [19–21]:

$$D_v = \frac{-v_{\max}}{T_m \times T_v \times \Delta T_{1/2}} \quad (1)$$

$$D_i = \frac{-v_{\max}}{t_m \times t_i} \quad (2)$$

$$D_b = \frac{-v_{\max}}{t_m \times t_b \times \Delta t_{1/2}} \quad (3)$$

$$H_f = 10^{-3} \times T_m \times \ln \left(\frac{\Delta T_{1/2}}{-v_{\max}} \right) \quad (4)$$

$$D_{si} = 8.5875 \times 10^7 \times \frac{-v_{\max}}{T_m \times T_i} \quad (5)$$

$$S = \frac{(-v_{\max}) \times (-v_{\text{mean}})}{T_i^2 \times T_b} \quad (6)$$

2.4. Kinetic Method

The kinetics analysis plays a crucial role in understanding the reaction process of biomass. As recommended by the Kinetics Committee of the International Confederation for Thermal Analysis and Calorimetry [22], this article employs model-free methods like FWO and KAS to compute the kinetic parameters. The solid-gas reaction rate is defined as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (7)$$

where α represents the conversion degree, t denotes the combustion time, $k(T)$ stands for the reaction rate constant, and $f(\alpha)$ represents the differential expression of the reaction model. The α during the combustion process can be obtained from thermogravimetric analysis data, as follows:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (8)$$

where m_0 , m_t , and m_∞ are the initial, instant, and residual mass of biomass during the combustion process, respectively. Based on the Arrhenius law, $k(T)$ can be obtained using the following expression:

$$k(T) = A \exp \left(-\frac{E_a}{RT} \right) \quad (9)$$

where T represents the combustion temperature, A is the pre-exponential factor, E_a is the activation energy, and R represents the universal gas constant. Combining Equations (7) and (9) at a given constant ($\beta = dT/dt$), and rearranging yields Equation (10):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp \left(-\frac{E_a}{RT} \right) f(\alpha) \quad (10)$$

The integral form of $f(\alpha)$ can be presented as:

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{-\frac{E_a}{RT}} dT \quad (11)$$

2.4.1. FWO method

The FWO approach utilizes Doyle's approximation for temperature integration and is formulated as Equation (12) [23,24]. It is worth noting that E_a can be determined from the gradient $-1.052E_a/R$ of the regression lines.

$$\ln \beta = \ln \frac{AE_a}{g(\alpha)R} - 5.331 - 1.052 \frac{E_a}{RT} \quad (12)$$

2.4.2. KAS method

The KAS technique is expressed by Equation (13) [25]. E_a can be derived from the slope $-E_a/R$ of the regression lines.

$$\ln \frac{\beta}{T^2} = \ln \frac{AE_a}{g(\alpha)R} - \frac{E_a}{RT} \quad (13)$$

2.5. Thermodynamic Method

Based on E_a computed using the FWO and KAS methods, the pre-exponential factor A , as well as thermodynamic parameters like change in enthalpy (ΔH), change in Gibbs free energy (ΔG), and change in entropy (ΔS) at a specific heating rate, can be determined as follows [26,27]:

$$A = \frac{\beta E_a \exp\left(\frac{E_a}{RT_m}\right)}{RT_m^2} \quad (14)$$

$$\Delta H = E_a - RT \quad (15)$$

$$\Delta G = E_a - RT_m \ln\left(\frac{K_B RT_m}{hA}\right) \quad (16)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \quad (17)$$

In these equations, $k_B=1.381 \times 10^{-23}$ J/K represents the Boltzmann constant, and $h=6.626 \times 10^{-34}$ J/s is the Planck's constant.

3. Results and Discussion

3.1. Thermogravimetric Analysis

Figure 1 illustrates the TG and DTG profiles of peanut shells from room temperature to 1073 K at three different heating rates. Focusing on the TG and DTG curves obtained at a heating rate of 20 K/min, distinct combustion stages are evident. Initially, there is a stage corresponding to water evaporation (ambient to 440 K), primarily involving the release of bound water within peanut shells. This stage is characterized by a minor decrease in the TG curve and a low weight loss rate, constituting approximately 7.68% of the total weight loss, closely aligning with the water content indicated in Table 1. The subsequent stage, spanning from 440 K to 832 K, represents the main combustion phase, exhibiting the highest weight loss rate and accounting for 72.39% of the total weight loss. Notably, this stage is marked by a significant decline in weight on the TG curve, accompanied by two distinct peaks on the DTG curve. The first peak corresponds to the combustion of volatile components, occurring at approximately 584.60 K. These weight losses primarily result from the thermal degradation and combustion of volatile substances such as hemicelluloses, celluloses, and certain lignin components [28]. The second peak corresponds to the combustion of residual volatiles and fixed carbon, with the weight loss peak occurring at 705.31 K. This stage mainly involves the combustion of lignin and fixed carbon, where the latter cannot combust until the volatile matter has been consumed, and the temperature is sufficiently elevated [29]. The maximum combustion rate is observed at the first DTG peak. The final stage, ranging from 832 K to 1073 K, is the burnout phase, during which both the TG and DTG curves stabilize, and there is no further change in sample mass. After the combustion process, the residual mass amounts to 19.93%.

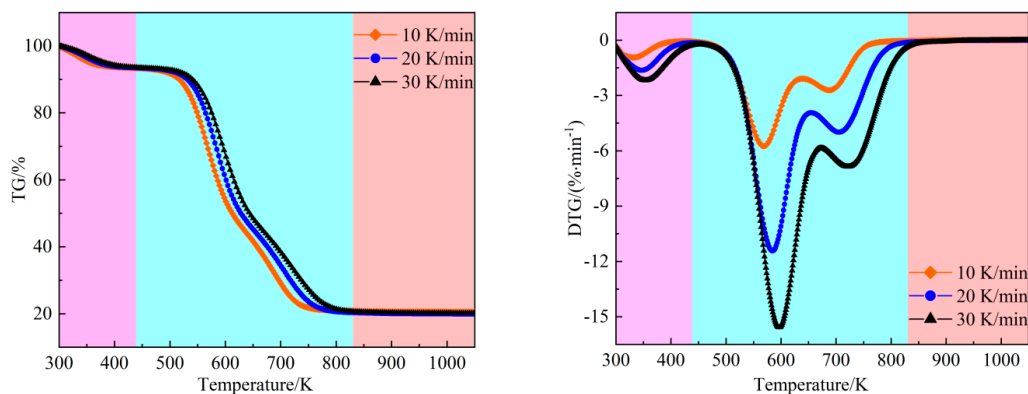


Figure 1. TG and DTG curves of the combustion process for peanut shell.

Table 2 presents the combustion stages and their associated weight losses throughout the entire combustion process at various heating rates. It indicates that the heating rate has minimal impact on the weight loss during stage II and the final residual at the end of the combustion. However, with an increase in heating rate, both the onset temperature of the main combustion stage and the temperature corresponding to the weight loss peak gradually rise. This observation may be attributed to the shorter residence time associated with higher heating rates, which impedes effective heat transfer. Consequently, a larger temperature differential between the surface and interior of the sample is observed, resulting in an upward shift of the overall DTG curve towards higher temperatures.

Table 2. Combustion stages and weight losses at various heating rates.

Heating rates (K/min)	Stage I		Stage II			Stage III
	Water evaporation		Volatile and fixed carbon combustion			Burnout stage
	Temperature range(K)	Weight loss (%)	Temperature range (K)	T_m (K)	Weight loss (%)	Residual (%)
10	299.35–423.41	7.58	423.41–799.34	568.59	72.06	20.36
20	299.22–439.84	7.68	439.84–832.14	584.60	72.39	19.93
30	298.75–452.45	7.69	452.45–842.93	596.58	72.19	20.12

3.2. Combustion Characteristic Analysis

Table 3 provides detailed outcomes outlining the influence of heating rate on combustion characteristic parameters and performance parameters for a clearer comprehension of how variations in heating rate impact combustion behavior. It is observed that alterations in heating rate exert varying degrees of influence on these characteristics. As the heating rate rises, ignition and burnout temperatures increase, alongside the maximum combustion rate and its corresponding peak temperature. The elevation of the heating rate results in a noticeable delay in the combustion reaction of the sample, hindering ignition and prolonging burnout time. The elevation in ignition temperature can be attributed to the heightened heating rate, which increases the volatilization of fuel components and decreases the residual fuel content. Consequently, the combustion reaction shifts towards higher temperature ranges. Similarly, the rise in burnout temperature is a consequence of the increased heating rate, prolonging the incomplete volatilization analysis of the sample and delaying combustion, thereby increasing the sample's burnout temperature. Moreover, the escalation in maximum combustion rate and its corresponding peak temperature signifies a more vigorous combustion capacity per unit time with the heightened heating rate. However, as the heating rate increases, the heat transfer rate may not keep pace with temperature changes, resulting in a temperature differential between the sample's surface and interior [30]. This thermal lag exacerbates

the temperature gradient within the sample particles, leading to a noticeable thermal shock effect and an accelerated combustion reaction rate, thereby increasing the maximum peak temperature.

Table 3. Combustion parameters of peanut shells at three heating rates.

β (K·min ⁻¹)	T_i (K)	T_b (K)	T_m (K)	T_v (K)	v_{max} (%·min ⁻¹)	v_{mean} (%·min ⁻¹)	D_v (%·min ⁻¹ ·K ⁻³)	D_i (%·min ⁻¹ ·K ⁻³)	D_b (%·min ⁻¹ ·K ⁻⁴)	D_{si} (%·min ⁻¹ ·K ⁻³)	H_f (K)	S (% ² ·min ⁻¹ ·K ⁻³)
10	527.85	742.54	568.59	521.11	-5.7538	-3.055	2.47E-7	0.009	0.0006	1646.30	1.49	0.85E-7
20	540.10	772.98	584.60	520.45	-11.431	-5.733	4.82E-7	0.061	0.0081	3109.03	1.12	2.91E-7
30	550.32	793.45	596.58	519.84	-15.581	-8.165	5.68E-7	0.163	0.0291	4075.55	1.04	5.29E-7

D_i and D_b align with the findings regarding ignition temperature and burnout temperature. Higher values of D_b indicate enhanced ignition performance [31,32]. This suggests that as the heating rate increases, the flammability and burnout capabilities of the fuel improve. The heightened heating rate intensifies the volatilization analysis, leading to the formation of more pores within and on the surface of the coke. This phenomenon may induce the collapse of the coke structure, resulting in increased surface area conducive to oxygen transport to the interior of the coke and combustion of the coke surface, thereby enhancing combustion efficiency.

Table 3 indicates that the initial devolatilization temperature exhibits minimal change, suggesting that the heating rate slightly affects the temperature at which volatiles begin to precipitate. However, it does impact the volatile matter release index (D_v), which signifies the release performance of volatile matter in the fuel. It is also found that as the heating rate increases, the volatile matter release index increases too. A higher D_v value indicates a more centralized combustion region of char residues and higher burnout performance [33]. The comprehensive combustibility S encompasses various characteristics, including ignition and burnout. Utilizing the combustion index enables an evaluation of relative combustibility, offering the ability to select the most suitable option for specific conditions and purposes. A high S value indicates a high combustion reactivity of the material [34]. The combustion stability index D_{si} is employed to reflect the combustion stability [35]. It is observed that both the comprehensive combustibility and combustion stability index exhibit an increasing trend with the rise in heating rate. This suggests that within the discussed heating rate range, increasing the heating rate can enhance its comprehensive combustion performance and improve the stability of high combustion. Conversely, the combustion intensity (H_f) decreases with the rising heating rate. H_f characterizes the rate and intensity of the combustion process, with a smaller value indicating more efficient combustion [36]. Overall, the heating rate exhibits a positive correlation with the comprehensive combustion characteristics. However, due to variations in the degree of influence of the heating rate on different combustion indices, excessively high heating rates may induce instability and fluctuations in the combustion process of the sample.

3.3. Kinetics Analysis

The model-free methods, which don't rely on specific mechanism functions, have been commonly used for estimating more reliable activation energies (E_a). The E_a values for the combustion of peanut shells were estimated considering the conversion (α). Utilizing Equations (12) and (13), kinetics with conversions ranging from 0.10 to 0.90 at intervals of 0.05 were computed. Figure 2 illustrates the results.

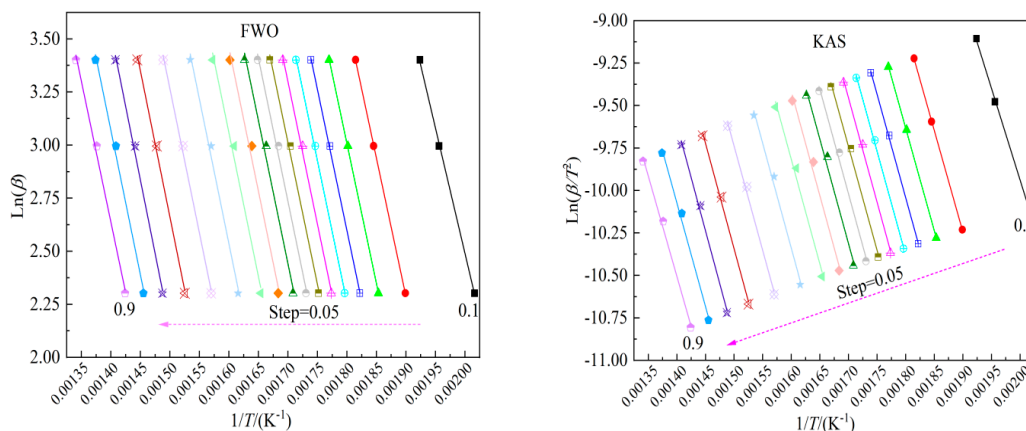


Figure 2. Combustion kinetics fitted by FWO and KAS methods.

Table 4 reveals that E_a varies from 93.30 to 109.65 kJ/mol and 89.72 to 103.88 kJ/mol, respectively, with average values of 105.60 kJ/mol and 100.93 kJ/mol for FWO and KAS methods. All correlations demonstrate statistical sufficiency, with R^2 values ranging from 0.9901 to 1.0, verifying the accuracy of the outcomes.

Table 4. Kinetic parameters obtained from the two model-free methods.

α	FWO			KAS		
	E_a /(kJ/mol)	A /(s ⁻¹)	R^2	E_a /(kJ/mol)	A /(s ⁻¹)	R^2
0.10	93.30	2.16E+06	0.9994	89.72	9.72E+05	0.9993
0.15	102.89	1.81E+07	0.9999	99.29	8.16E+06	0.9999
0.20	104.08	2.35E+07	0.9998	100.33	1.03E+07	0.9998
0.25	105.05	2.92E+07	1.0000	101.17	1.24E+07	0.9993
0.30	105.56	3.26E+07	0.9989	101.58	1.35E+07	0.9986
0.35	106.15	3.72E+07	0.9978	102.07	1.51E+07	0.9973
0.40	105.72	3.38E+07	0.9961	101.51	1.33E+07	0.9952
0.45	106.45	3.98E+07	0.9945	102.15	1.54E+07	0.9933
0.50	106.46	3.98E+07	0.9919	102.03	1.49E+07	0.9902
0.55	106.75	4.25E+07	0.9911	102.19	1.55E+07	0.9901
0.60	107.05	4.53E+07	0.9917	102.31	1.59E+07	0.9902
0.65	107.59	5.11E+07	0.9941	102.64	1.71E+07	0.9927
0.70	107.38	4.88E+07	0.9973	102.10	1.52E+07	0.9966
0.75	108.75	6.61E+07	0.9976	103.22	1.94E+07	0.9972
0.80	109.65	8.06E+07	0.9969	103.88	2.25E+07	0.9961
0.85	107.53	5.04E+07	0.9956	101.37	1.29E+07	0.9944
0.90	104.81	2.77E+07	0.9962	98.24	6.45E+06	0.9951
Average	105.60			100.93		

Figure 3 illustrates the variations of E_a against the conversion rate, indicating that both methods yield similar activation energy values, with slightly higher values obtained using the FWO method. These curves can be categorized into three stages: Initially, in the α range of 0.10 to 0.15, there is a slight increase in E_a values. For the KAS and FWO methods, E_a rises from 93.30 to 102.89 kJ/mol and 89.72

to 99.29 kJ/mol, respectively. The second region had a stable E_a , but a substantial decrease in the third region with a range of 0.80 to 0.90.

At the initial stage of the reaction, with the increase in temperature, the precipitation of volatile substances and the initial decomposition of hemicellulose and cellulose first occur. The initial decomposition requires a higher temperature and more heat to achieve its activation state, which leads to an increase in activation energy. With a further increase in temperature, the combustion process enters the main combustion stage of volatiles. At the same time, cellulose and lignin with high polymerization degree gradually transform into coke, the carbon structure tends to be orderly, the active site decreases, and the semi-coke formed on the surface of the reactants will increase the reaction difficulty inside the reactants, and the activation energy will further increase. However, the overall increase trend is relatively gentle with increase amplitude of 6.6% and 4.6% for FWO and KAS methods, respectively. E_a reaches its maximum value when α reaches 0.80. Then, the E_a gradually decreases, mainly in the combustion stage of fixed carbon. The porosity of semi-coke increases due to the volatilization and carbonization process, and the pre-pyrolysis, aerobic cracking and volatilization ignition processes can provide more heat, which improves the reaction activity of fixed carbon in the combustion stage, and thus the activation energy decreases.

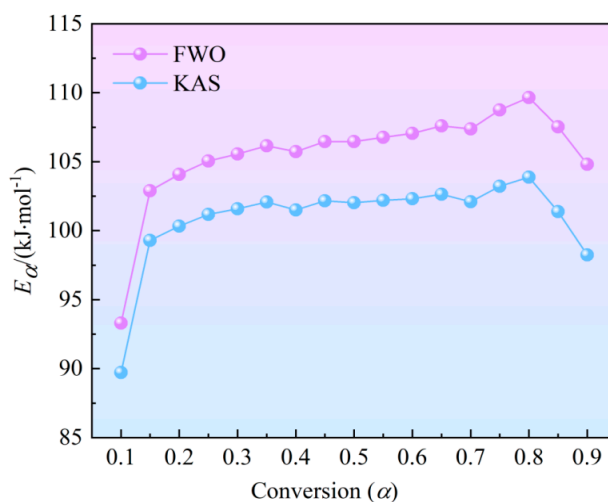


Figure 3. Distribution of activation energy (E_a) against conversion (α).

The parameter A is a crucial indicator of the sample's surface structure or the complexity of the combustion reaction [37]. A value lower than 10^9 s^{-1} suggests surface reactions, while A higher than 10^9 s^{-1} indicates simpler complexes with higher reactivity [38]. The results demonstrate that at a heating rate of 10 K/min, the parameter A calculated by the FWO and KAS methods ranges from 2.19×10^6 to $8.06 \times 10^7 \text{ s}^{-1}$ and from 9.72×10^5 to $2.25 \times 10^7 \text{ s}^{-1}$, respectively. All A values fall below 10^9 s^{-1} , suggesting that the combustion process of peanut shells primarily involves surface reactions associated with a closed complex. The trend of variation in the pre-exponential factor with conversion aligns with that of the activation energy.

3.4. Thermodynamic Analysis

Estimating the thermodynamic parameters of combustion is crucial for designing combustion reactors on a large scale and selecting appropriate biofuels. ΔH , ΔG , and ΔS are presented in Table 5 at the heating rate of 10 K/min.

Table 5. Thermodynamic properties of wheat straw obtained using different methods.

α	FWO			KAS		
	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS J/(mol×K)	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS J/(mol×K)
0.10	89.18	166.66	-136.27	85.59	166.85	-142.91
0.15	98.51	166.20	-119.05	94.92	166.37	-125.67
0.20	99.60	166.15	-117.04	95.84	166.32	-123.96
0.25	100.48	166.10	-115.40	96.61	166.28	-122.53
0.30	100.93	166.08	-114.58	96.95	166.26	-121.90
0.35	101.46	166.05	-113.61	97.38	166.24	-121.10
0.40	100.97	166.07	-114.49	96.76	166.26	-122.24
0.45	101.65	166.04	-113.25	97.35	166.23	-121.15
0.50	101.60	166.04	-113.34	97.16	166.24	-121.49
0.55	101.82	166.03	-112.93	97.25	166.23	-121.33
0.60	102.02	166.01	-112.55	97.28	166.23	-121.25
0.65	102.45	165.99	-111.76	97.49	166.21	-120.87
0.70	102.08	166.00	-112.41	96.80	166.24	-122.12
0.75	103.30	165.94	-110.16	97.77	166.19	-120.33
0.80	104.06	165.90	-108.75	98.29	166.16	-119.37
0.85	101.81	165.99	-112.87	95.66	166.27	-124.19
0.90	98.97	166.11	-118.09	92.40	166.42	-130.18
Average	100.64	166.08	-115.09	95.97	166.29	-123.68

The reaction enthalpy (ΔH) signifies the energy exchange in a chemical reaction or the energy necessary for the thermal degradation of the feedstock. The variation trend concerning conversion (α) is depicted in Figure 4. The calculated ΔH values range from 89.18 to 104.06 kJ/mol and 158.74 to 446.68 kJ/mol, with average values of 85.59 and 98.29 kJ/mol, respectively. All ΔH values corresponding to different degrees of conversion are positive, indicating the occurrence of endothermic reactions throughout the combustion process. The difference between ΔH and E_a values, lower than ± 6 kJ/mol, reflects the potential energy barrier in the process for the formation of activated complexes [39].

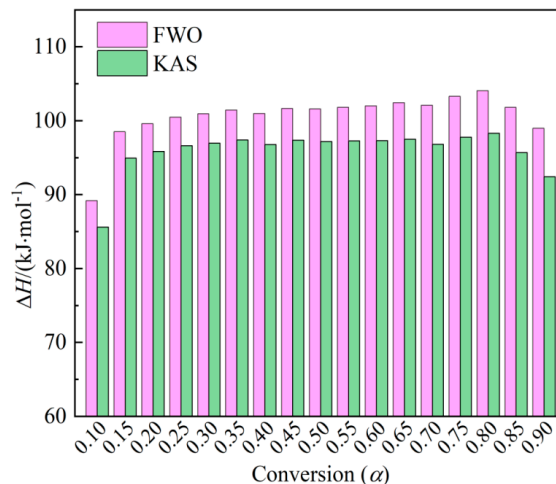


Figure 4. Variation trend of enthalpy (ΔH) upon conversion (α).

Gibbs free energy (ΔG) reflects the difficulty and direction of reactions and the total energy of the system, where a higher ΔG value indicates lower reaction favorability. Figure 5 illustrates the variations concerning conversion (α). The ΔG values calculated by the FWO and KAS methods range from 165.90 to 166.66 kJ/mol and 166.16 to 166.85 kJ/mol. The average values of ΔG for the thermal combustion of peanut shell are 166.08 kJ/mol for FWO and 166.29 kJ/mol for KAS, respectively. ΔG values at different conversions are all positive, suggesting non-spontaneous reactions in peanut shell combustion. Moreover, the values of ΔG vary within ± 1 kJ/mol corresponding to each conversion (α), indicating that the peanut shell maintains a stable energy output throughout the combustion process.

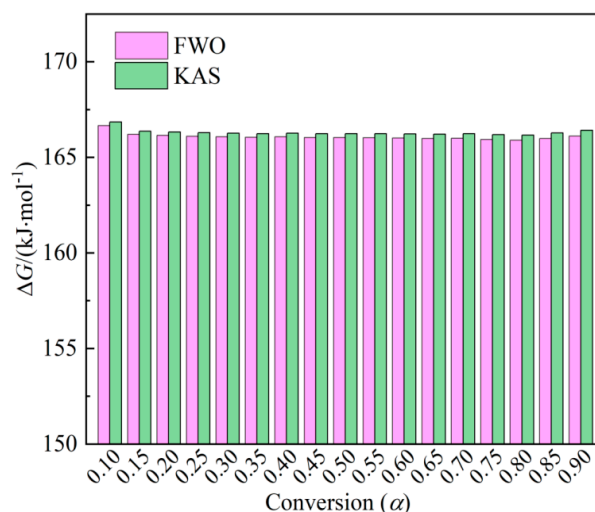


Figure 5. Variations of Gibbs free energy (ΔG) upon conversion (α).

Entropy (ΔS) is an indicator reflecting the degree of system disorder, with reaction systems exhibiting low ΔS values more readily reaching thermodynamic equilibrium. Figure 6 reveals that the entropy changes calculated by the FWO and KAS methods range from -136.27 to -108.75 J/(mol×K) and -142.91 to -119.37 J/(mol×K), respectively. ΔS for peanut shell falls within the negative range of -136.27 to -108.75 J/(mol×K) and -142.91 to -119.37 J/(mol×K) across the conversion range of 0.10–0.90, indicating proximity to thermodynamic equilibrium [40]. This range corresponds to volatile combustion and fixed carbon combustion, where a thermally stable product is produced and the degree of disorder in the products is lower than that in the reactants.

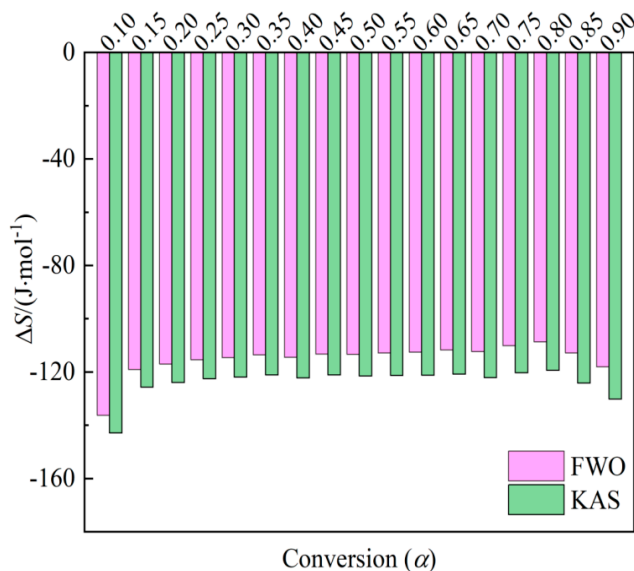


Figure 6. Variations of entropy (ΔS) upon conversion (α).

4. Conclusions

This study uses thermogravimetric analysis (TGA) to investigate combustion characteristics and kinetics at three different heating rates under atmospheric air for peanut shell. Meanwhile, the thermodynamic parameters are obtained based on the activation energy (E_a) and pre-exponential factor (A) at the heating rate of 10 K/min. The main achievements can be summarized as follows:

(1) The combustion of peanut shell is mainly divided into three stages: water evaporation, volatile and fixed carbon combustion, and burnout stage. As the heating rate increases, the combustion characteristics temperature of peanut shell transitions to a high-temperature zone. Meanwhile, the combustion performance parameters analysis of volatile matter release (D_v), ignition index (D_i), burnout index (D_b), combustion intensity (H_i), combustion stability index (D_{si}), and comprehensive combustibility (S) indicate that the heating rate has obvious influence on the combustion performance parameters, a higher heating rate could intensify and improve the combustion performance.

(2) Activation energy (E_a) determined through the FWO and KAS model-free methods falls within the range of 93.30 to 109.65 kJ/mol and 89.72 to 103.88 kJ/mol, respectively, with average values of 105.60 kJ/mol and 100.93 kJ/mol. All correlations exhibit statistical adequacy, with coefficient of determination values (R^2) ranging from 0.9901 to 1.0. Notably, all values of pre-exponential factor (A) are below 10^9 s⁻¹, suggesting that the combustion process of peanut shell primarily includes surface reactions associated with a closed complex.

(3) The thermodynamic analysis reveals that the difference between ΔH and E_a values is within ± 6 kJ/mol, suggesting a favorable formation of the activated complex due to the low potential energy barrier. Additionally, the ΔG values fluctuate within ± 1 kJ/mol for each conversion rate, indicating a stable energy output throughout the combustion process. Furthermore, all ΔS values are negative, indicating a tendency towards thermodynamic equilibrium. The results indicate that the combustion of peanut shell was an endothermic and non-spontaneous process, and more homogeneous or well-ordered products are generated with the progress of combustion.

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