

Comparing the kinetic and thermodynamic behavior of mango kernel and its two main components through pyrolysis and combustion

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ABSTRACT

The agro-industrial and food industry generates tons of bio-waste such as mango waste (*Mangifera Indica*) that has a negative impact on the environment if not managed effectively. This study characterized the physico-chemical properties and thermal behavior of mango kernel and its components (seed and pericarp) to propose a suitable thermochemical conversion route for its valorization. The study revealed that mango kernel (MK), seed (MS), and pericarp (MP) possess high volatile matter and fixed carbon contents, making them well-suited for pyrolysis to generate biofuel and biochar. MK and MS showed better combustion performance than MP due to higher lower heating values (LHV) and lower ash content. Moreover, MK and MS exhibited greater potential for gasification and potassium recovery due to favorable thermal, chemical, and mineral compositions. Thermogravimetric analysis (TGA) using *iso-conversional* methods demonstrated significant thermal stability and non-spontaneous reactions across all samples, while Gibbs free energy changes (ΔG) indicated considerable energy extraction potential. Catalytic indices derived from metal content further confirmed the suitability of mango waste for thermochemical valorization. Although the components showed compatibility without negative synergistic effects, separating the seed and pericarp from the kernel could improve energy efficiency, product quality, and process flexibility. Kinetic analyses revealed activation energies (E_a) during pyrolysis ranging from 149–310 kJ/mol for MK, 190–407 kJ/mol for MS, and 157–366 kJ/mol for MP, with ΔG up to 194 kJ/mol. Combustion required lower activation energies, 122 kJ/mol for MK and ~133 kJ/mol for MS and MP, indicating easier ignition of MK. Reaction mechanism modeling confirmed complex kinetic transitions with the conversion. These findings offer a solid foundation for optimizing the thermochemical conversion of mango waste into energy products and enabling the synthesis of advanced materials.

1. Introduction

Biomass conversion plays a crucial role in sustainable energy and resource management by transforming organic waste into valuable products and renewable energy sources. Agricultural and agro-industrial waste biomass is viewed as a promising bio-resource for sustainable conversion at a local scale due to its low cost and high availability [1,2]. The global energy potential from biomass is estimated at 104 EJ per year on a sustainable basis, with woody biomass, energy crops, and straw contributing 40.1 %, 36 %, and 16.6 %, respectively. However, only

around 40 % of this potential is currently harnessed [3]. It is crucial to convert this waste into energy using a thermochemical process to power these often energy-deprived processing units. Therefore, research communities are increasingly shifting their focus from coal and oil to biomass, which offers carbon-neutral energy production while also addressing issues such as solid waste management and health hazards.

Biomass thermochemical conversion leads to valuable products and energy carriers, often within relatively short reaction times, with or without the use of inorganic catalysts [4]. Biomass composition and physicochemical properties influence its thermochemical conversion. More precisely, biomass macromolecular composition in cellulose,

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Nomenclature				
Symbol / Abbreviation	Description (Unit)			
AAEM	Alkaline and Alkaline Earth Metals	(–)	ΔS	Change in entropy ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
MK	Mango Kernel	(–)	K_B	Boltzmann constant (1.3819×10^{-23}) ($\text{J}\cdot\text{K}^{-1}$)
MP	Mango Pericarp	(–)	h	Planck constant (6.6269×10^{-34}) ($\text{J}\cdot\text{s}$)
MS	Mango Seed	(–)	R	Universal gas constant (8.314) ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$)
SME	Small and Medium-sized Enterprises	(–)	α	Degree of conversion (–)
DTG	Derivative Thermogravimetry curve	(%/°C)	β	Heating rate ($^{\circ}\text{C}\cdot\text{min}^{-1}$)
TG	Thermogravimetric curve (mass vs. temperature)	(–)	$d\alpha/dt$	Rate of conversion (s^{-1})
TGA	Thermogravimetric Analysis	(–)	$f(\alpha)$	Reaction model function (–)
ICTAC	International Confederation for Thermal Analysis and Calorimetry	(–)	$g(\alpha)$	Integral form of the reaction model function (–)
FC	Fixed Carbon	(wt.%)	$\lambda(\alpha)$	Generalized master plot function (–)
LHV	Lower Heating Value	($\text{MJ}\cdot\text{kg}^{-1}$)	R^2	Coefficient of determination (–)
MC	Moisture Content	(wt.%)	t	Time (s)
VM	Volatile Matter	(wt.%)	T	Absolute temperature (K)
EJ	Exajoule (10^{18} J)	(J)	T_m	Peak temperature (K)
wt. %	Weight percent	(%)	$T_{\max}$	Temperature at maximum weight loss rate ($^{\circ}\text{C}$)
A / A_0	Pre-exponential (Arrhenius) factor	(s^{-1})	X	Conversion degree (–)
E_a	Activation energy	($\text{kJ}\cdot\text{mol}^{-1}$)	y	Conversion rate (dependent variable in Gaussian fitting) (–)
ΔH	Change in enthalpy	($\text{kJ}\cdot\text{mol}^{-1}$)	y_0	Initial value of the Gaussian function (–)
ΔG	Change in Gibbs free energy	($\text{kJ}\cdot\text{mol}^{-1}$)	x	Temperature (independent variable) ($^{\circ}\text{C}$)
			H_i	Amplitude of Gaussian function for component i (–)
			x_{ci}	Center temperature for component i ($^{\circ}\text{C}$)
			w_i	Width of the Gaussian function for component i ($^{\circ}\text{C}$)

hemicellulose and lignin directly impacts its thermal conversion, as these polymers degrade in different temperature ranges in pyrolysis. Previous research identified the temperature ranges of 200 °C to 320 °C and 320 °C to 400 °C as characteristic of hemicellulose and cellulose devolatilization, respectively, as polysaccharide-based components. Lignin devolatilization, distinctive among biomass components due to its phenylpropane basis, spans a broader temperature range (180 °C to 800 °C) during both active and passive pyrolysis stages [5,6]. Minor amounts of extractives and proteins are also present in biomass macromolecular composition but have a lower influence on their thermal behavior. Indeed, Alkaline and Alkaline-Earth (AAEM) metals in biomass ash were reported to present a catalytic effect on thermochemical conversion, reducing degradation temperatures and reaction times to some extent [7]. On the contrary, other elements such as silicon and alumina may have an inhibitor effect [8]. This influence is particularly remarkable for agricultural and agro-industrial waste, due to their typically high ash content (>5 wt%) compared to wood (<2 wt%) [9]. Ratios of these elements, such as K/Al, K/Si and K/(Si + P) ratios, were suggested as indicators of the catalytic or inhibitory potential of a biomass resource [8]. The mass loss during pyrolysis occurs in multiple stages, typically indicating moisture evaporation, hemicellulose decomposition, and cellulose decomposition, and lignin and char carbonization [10]. As a result, a deep physicochemical characterization of biomass needs to be coupled to the elucidation of conversion mechanisms to determine the most suitable conversion routes and operating conditions for biomass thermochemical valorization.

Bio-refineries utilize various feedstocks, including municipal solid waste, food and feed grains, as well as forest and lignocellulosic biomass. Due to their composition and availability, mango waste can represent a promising feedstock for an integrated bio-refinery, enabling the co-production of energy and bioactive compounds. Indeed, more than 100 countries around the world grow mango trees to harvest their fruit. Mangoes occupy a more important place on the world market than other well-known tropical fruits, surpassing them in both quantity and monetary value [11]. The total volume of mangoes produced globally in 2021 was 58.3 million metric tons, which was projected to increase by 1.9 %, reaching 65 million metric tons by 2026. Asia is the largest region in terms of mango production, contributing to over 70 % of the total mango produced yearly. Africa contributes to 10 % of the total mangoes

produced yearly [12]. During processing, 35–60 % of the mango fruit weight is discarded as waste in the form of cull fruits, peels, and seeds [13]. In Burkina Faso, more than 19 million tons of agricultural and agro-industrial non-edible waste are annually produced, including cotton stalks, rice husks, cashew nutshells, mango kernels and peels [14]. Among them, mango production is significantly increasing each year. A significant part of this production is processed locally by small and medium-sized enterprises (SMEs) into dried mango and juices. As a result, a substantial amount of non-valorized waste is generated, which is currently open-air exposed causing pollution and mosquito proliferation. While mango kernel thermochemical behavior and characterization were already preliminary explored [15], the behavior of its components, namely seed and pericarp, remains to be elucidated. This may provide an orientation regarding the need for pretreatment by separation of the components, particularly if their physicochemical properties differ significantly. Determining the mechanisms involved in the thermochemical conversion of mango waste is essential to define the optimal conditions for their valorization. As a result, a thorough understanding of the thermal behavior coupled to physicochemical properties is crucial for developing optimized mango waste valorization through thermochemical conversion processes like combustion, torrefaction, gasification, and pyrolysis [16].

Thermogravimetric analysis (TGA) is a widely used technique for studying the decomposition and chemical kinetics of biomass. In this method, biomass is heated at a controlled rate in an inert atmosphere, and the mass loss is recorded as a function of time and temperature. The resulting data are analyzed using mathematical models. These models fall into two categories: model-fitting and model-free methods. Model-fitting methods depend on assumptions about the underlying model, whereas model-free methods do not, making them more reliable as they avoid the need for prior knowledge of reaction mechanisms [17]. However, evaluating reaction mechanisms using the master plot remains crucial for a deeper understanding of the decomposition model that describes the process. Iso-conversional methods, include the Flynn-Wall-Ozawa (FWO) method, the Kissinger-Akahira-Sunose (KAS) method, Friedman, and Starink methods [18,19]. In lignocellulosic biomass pyrolysis and combustion, the complex reaction process involves multiple overlapping partial reactions, making a single-step kinetic analysis insufficient [20]. Pyrolysis of lignocellulosic biomass can be divided into

three or more distinct parallel devolatilization events, each with its own unique kinetic parameters [6,21]. Thermal analysis techniques, encompassing both isothermal and non-isothermal approaches with single and multiple heating rates, have been employed to study chemical kinetics. The use of techniques with multiple heating rates instead of single heating rate methods is recommended by the kinetics committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) to obtain reliable kinetic analyses [22,23]. The thermodynamic parameters, including changes in enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS), also provide valuable insights into the feasibility of reactions, reactivity, and energy conversion direction [24]. Kinetic data are crucial for designing efficient thermochemical treatment plants, as they guide reactor design and process optimization.

Although the thermochemical conversion of mango waste has been previously investigated, comprehensive comparative analyses of its structural components such as the kernel, seed, and pericarp remain limited in the literature. The present study contributes to filling this gap by systematically evaluating and contrasting the physicochemical properties, thermal degradation behavior, and kinetic and thermodynamic parameters of these components. The results aim to support the development of fraction-specific valorization strategies and improve the efficiency of thermochemical processing of mango residues.

Recent studies have demonstrated the effective use of isoconversional and model-fitting methods to investigate the thermochemical behavior of biowaste components under pyrolysis and related processes. Research has increasingly focused on the kinetic and thermodynamic characterization of individual biomass fractions, revealing the influence of synergistic interactions between components as well as the catalytic effects of inherent mineral matter [25]. Investigations into seed and husk residues from fruit-processing waste have highlighted the potential of component-specific analysis to improve conversion efficiency. Advanced kinetic models, including generalized logistic and multi-step approaches, have also been employed to better resolve overlapping reaction mechanisms [26]. These developments underline the importance of fraction-resolved studies and advanced kinetic modeling in biomass valorization, providing a relevant context for the present comparative analysis of mango kernel, seed, and pericarp components.

In this context, the study aims of characterizing the physicochemical properties and thermal behavior in TGA of mango waste components, including mango kernel (MK), seed (MS) and pericarp (MP), through thermochemical conversion, namely pyrolysis and combustion. To do this, the catalytic potential, thermal stability, and calorific value of mango components will be addressed. In parallel, physicochemical properties, decomposition behavior, kinetics, and thermodynamics of mango kernel, seed, and pericarp were investigated with the aim of optimizing their valorization as energy vectors.

2. Materials and methods

2.1. Sample preparation

Mango kernel (MK) and its components, namely the seed (MS) and the pericarp (MP), from Burkina Faso were the samples selected for this study. Initially, MK were naturally sun-dried to reduce moisture content. Then, MS and MP were manually separated. All samples were ground using a FRITSCH 55743 Idar-Oberstein grinder and then sieved with a mesh size $\leq 200 \mu\text{m}$ prior to their characterization.

2.2. Sample characterization

MK, MS and MP were characterized in terms of proximate analysis, including moisture (MC, ISO 18134), volatile matter (VM, ISO 18123), fixed carbon (FC, by difference), and ash content (ISO 18122) [27]. Ultimate analysis (CHNS-O) was carried out with a Thermoquest NA 2000 elemental analyzer, with oxygen percentage determined by difference. LHV was measured using an IKA C 5000 bomb calorimeter.

Inorganic elements were analyzed using a HORIBA Jobin Yvon Ultima 2 ICP-OES, after an alkaline fusion mineralization. To ensure repeatability, all procedures were performed in triplicate, with results calculated as mean values.

2.3. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed using a SETARAM LabSys evo 1600 analyzer under a slow pyrolysis regime, with heating rates of 2, 10, and 20 °C/min under 50 ml/min of nitrogen (pyrolysis) or air (combustion). The temperature program ranged from 30 to 1000 °C with a 1-hour additional residence time at 1000 °C for complete decomposition. A sample mass around 30 mg with particle size $\leq 200 \mu\text{m}$ was used to prevent heat and mass transfer limitations [27,28].

2.4. Deconvoluting the pyrolysis behavior

The kinetic scheme for this study considers four independent devolatilization reactions, each corresponding to a specific biomass component (extractives, hemicellulose, cellulose, and lignin). This approach decomposes the devolatilization process into separate reactions for each constituent, improving the understanding of decomposition mechanisms and allowing the estimation of biomass macromolecular composition. The Gaussian function (Eq. (1)) was used to fit the DTG curves due to its ability to accurately represent the complex pyrolysis behavior of lignocellulosic biomass [29].

$$y = y_0 + \sum_{i=1}^N H_i \exp\left(-0.5 \times \frac{x - x_{ci}}{w_i^2}\right) \quad (1)$$

where x the independent variable is the temperature, y_0 the initial value of the Gaussian function is the conversion rate at x_0 ; H_i the amplitude; x_{ci} the center value; w_i is the width, i is the biomass component.

The coefficient of determination R^2 (Eq. (2)) was used to assess the consistency between simulated and experimental data:

$$R^2 = 1 - \frac{\sum \left[\left(\frac{d\alpha}{dt} \right)_{\text{exp}} - \left(\frac{d\alpha}{dt} \right)_{\text{sim}} \right]^2}{\sum \left[\left(\frac{d\alpha}{dt} \right)_{\text{exp}} - \left(\frac{d\alpha}{dt} \right)_{\text{average}} \right]^2} \quad (2)$$

where $\left(\frac{d\alpha}{dt} \right)_{\text{exp}}$, $\left(\frac{d\alpha}{dt} \right)_{\text{sim}}$ and $\left(\frac{d\alpha}{dt} \right)_{\text{average}}$ represent the experimentally measured conversion rates, the simulated conversion rates, and the average measured conversion rates, respectively.

2.5. Kinetic and thermodynamics analysis

Four of these iso-conversional methods (Friedman (FR) [30], Flynn-Wall-Ozawa (FWO) [31], Kissinger-Akahira-Sunose (KAS) [32,33] and Starink (STK) [34,35,36]) were used to calculate the kinetic parameters, namely activation energy E_a and frequency factors A . The thermodynamic parameters such as enthalpy change (ΔH), Gibbs free energy (ΔG) and entropy (ΔS) were also calculated from kinetic parameters. The Friedman method uses:

$$\ln\left(\frac{d\alpha}{dt}\right) = \ln\left[\beta\left(\frac{d\alpha}{dT}\right)\right] = \ln(A_0 f(\alpha)) - \frac{E_a}{R} \left(\frac{1}{T}\right) \quad (3)$$

FWO method uses Doyle's approximation of $P(x)$ [31,37]:

$$\ln(\beta) = \ln\left(\frac{A_0 E_a}{g(\alpha) R}\right) - 2.315 - \frac{0.4567 E_a}{R} \left(\frac{1}{T}\right) \quad (4)$$

The KAS method uses the following approximation $P(x) = \int_x^\infty \frac{\exp(-x)}{x^2} dx$, where $20 \leq x \leq 50$ [38].

$$\ln \left[\frac{\beta}{T^2} \right] = \ln \left[\frac{A_0 R}{E_a} \right] + 0.6075 - \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (5)$$

The Starink method uses more improved approximation of the $P(x)$ [34] as follows:

$$\ln \left(\frac{\beta}{T^{1.92}} \right) = \text{Constant} - 1.0008 \frac{E_a}{R} \left(\frac{1}{T} \right) \quad (6)$$

To calculate the activation energy, a graph was drawn between $\ln \left[\beta \left(\frac{d\alpha}{dT} \right) \right]$, $\ln(\beta)$, $\ln \left[\frac{\beta}{T^2} \right]$, $\ln \left(\frac{\beta}{T^{1.92}} \right)$ Respectively for Friedman, FWO, KAS and STK and $\frac{1}{T}$ for each value of α , and the slope of the straight line obtained was used for the computation of the activation energy. Activation energy values from these models were used to calculate the pre-exponential factor (A), enthalpy change (ΔH), Gibbs free energy change (ΔG), and entropy change (ΔS) using Eqs. (7)–(10) [39,40]. The use of Kissinger-derived expressions to estimate the pre-exponential factor A_0 typically assumes that the activation energy E_a remains constant over the conversion range, which may not always hold true. To address this limitation, in the present study, A_0 was estimated independently at each conversion level α , using the corresponding $E_a(\alpha)$ values obtained from iso-conversional methods. This approach avoids the assumption of a constant E_a , and limits potential inaccuracies from a global application of Kissinger equation.

$$A_0 = \beta E_a \exp \left(\frac{-E_a}{RT_m} \right) / RT_m^2 \quad (7)$$

$$\Delta H = E_a - RT \quad (8)$$

$$\Delta G = E_a + RT_m \ln \left(\frac{K_B T_m}{h A_0} \right) \quad (9)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \quad (10)$$

where K_B represents the Boltzmann constant ($1.3819 \times 10^{-23} \text{ JK}^{-1}$), h = Planck constant ($6.6269 \times 10^{-34} \text{ Js}$) and T_m the peak temperature.

Using reference point at $\alpha = 0.5$ and E_a , the generalized master plots equation is expressed:

$$\lambda(\alpha) = \frac{f(\alpha)}{f(\alpha = 0.5)} = \frac{d\alpha/dt}{d\alpha/dt_{\alpha=0.5}} \times \frac{\exp(E_a/RT)}{\exp(E_a/RT_{\alpha=0.5})} \quad (11)$$

Besides the calculation of the apparent activation energy, the appropriate determination of the decomposition model describing the process needs to be selected [19,41].

3. Results and discussion

3.1. Physicochemical properties

Ultimate analysis results (Table 1) showed the highest carbon content for MS (48.32 wt%), followed by MK (47.37 wt%) and MP (45.61 wt %), indicating a higher energy yield for MS during combustion [42]. MS also had the highest hydrogen content (6.77 wt%), enhancing its calorific value, while MP had the lowest (6.07 wt%). Nitrogen content was highest in MS (1.18 wt%), whereas MK and MP had lower values. Oxygen content was highest for MP (45.79 wt%), correlating with lower energy yield, compared to MK (42.24 wt%) and MS (41.39 wt%). H/C ratios were similar and low across all samples (0.14), which was reported as an indication of durability in the environment and thermal stability ($H/C < 0.4$) [43]. The O/C ratio was highest in MP (1.00), indicating lower energy density due to the lower energy content of C-O bond compared to C-H bond [44].

According to proximate analysis (Table 1), MS had the lowest moisture content (2.15 wt%), beneficial for combustion efficiency. MP

Table 1
Physicochemical properties of mango components.

		Samples		
		Kernel (MK)	Seed (MS)	Pericarp (MP)
Ultimate analysis (%wt. dry basis)	C	47.37 ± 0.08	48.32 ± 0.16	45.61 ± 0.06
	H	6.60 ± 0.01	6.77 ± 0.03	6.07 ± 0.01
	N	0.99 ± 0.01	1.18 ± 0.01	0.48 ± 0.01
	S	< d.l.	< d.l.	< d.l.
	O*	42.24 ± 0.09	41.39 ± 0.19	45.79 ± 0.08
	O/C	0.89	0.86	1.00
	H/C	0.14	0.14	0.13
	MC	3.07 ± 0.07	2.15 ± 0.05	3.29 ± 0.07
	VM	79.02 ± 0.25	79.72 ± 0.23	80.75 ± 0.21
	FC*	18.18 ± 0.36	17.93 ± 0.33	17.20 ± 0.32
Proximate analysis (% wt. dry basis)	Ash	2.80 ± 0.11	2.35 ± 0.10	2.04 ± 0.11
	LHV	19.38 ± 0.04	20.21 ± 0.38	18.10 ± 0.05
	Hemicellulose	10.99	10.67	12.78
	Cellulose	54.85	57.20	60.74
	Lignin	34.14	29.96	23.18

*: calculated by difference; < d.l.: under the detection limit.

exhibited the highest VM content (80.75 wt%), suggesting easy ignition and rapid combustion, with MS and MK closely following. MK exhibits the highest fixed carbon content (18.18 wt%), indicating more residual char after decomposition. The lowest ash content was found for MP (2.04 wt%), which is preferable for combustion and pyro-gasification efficiency.

The highest LHV was found for MS (20.21 MJ/kg, Table 1) followed by MK (19.38 MJ/kg) and MP (18.10 MJ/kg). Mango components (kernel, seed and pericarp) exhibited all an energy density similar to that of wood and eucalyptus (18.80–20.10 MJ/kg) [45,46].

In terms of macromolecular composition (Table 1), MP exhibits the highest hemicellulose (12.78 wt%) and cellulose (60.74 wt%) contents. This may indicate a higher proportion of structural components that decompose into volatile compounds during pyrolysis [47]. MK contained the highest lignin content (34.14 %), contributing to its higher fixed carbon content and more significant post-combustion residue [48].

The mineral composition of biomass significantly influences pyro-gasification reactions, affecting the efficiency and yield of syngas production. The highest K/Si and K/Al ratio were found for MS (48.09 and 375.54, respectively, Table 2), suggesting a predominant catalytic effect of K compared to the inhibitor effect of Si. When considering other potential catalytic elements among metals, such as Ca, Na, Mg, Fe, Ba and Mn, higher values are found for MS. If other inhibitor elements are taken into account, such as Al, P, S, Zn and Pb, values are still higher for

Table 2
Main inorganic elements classification according to their catalytic or inhibitor effect.

Inorganic elements	MK mg/kg (biomass dry basis)	MS	MP
Alkali metals: K	28051.81	28050.68	15119.18
Alkaline-earth metals: (Ba + Mg + Ca)	2455.54	2465.57	3113.44
Transition metals: (Mn + Fe)	171.36	185.81	335.49
Post transition metals: (Al + Zn + Pb)	145.05	144.53	249.98
Non-metals: (Si + P + S)	4549.90	4138.69	3489.21
K/Si	26.87	48.09	8.21
K/Al	366.71	375.54	76.49
K/(Si + P)	10.53	11.76	6.36

MS, indicating a predominant effect of catalytic metals compared to inhibitor ones. MP, although high in VM content, has a lower catalytic potential due to higher Si content, as silica was reported to reduce char reactivity and prolong reaction times by more than 2.5 times [49].

3.2. Thermal degradation behavior (TGA)

The thermal decomposition behavior was analyzed in TGA for MK, MS, and MP under N_2 and air. Three heating rates were used for kinetic calculations (2 °C/min, 10 °C/min, and 20 °C/min, Supplementary Materials, S1). As TGA experiments are in chemical regime, only 2 °C/min results were considered to explore the influence of the feedstock (MK, MS, and MP) on its thermal decomposition in pyrolysis (Fig. 1) and combustion (Fig. 2).

3.2.1. Pyrolysis

The three samples exhibited similar mass loss patterns in pyrolysis (Fig. 1). Firstly, moisture evaporation occurred (3 wt%, ambient temperature to around 160 °C). Then, active pyrolysis took place (160 to 345 °C), resulting in the highest mass loss (64 wt%), due to devolatilization of hemicellulose and cellulose, with a minor contribution of lignin. Passive pyrolysis occurred at a slower heating rate (11 wt%, 345 to 650 °C), due to lignin decomposition and biochar formation. MK and MS showed similar thermal degradation behavior with a lower residual mass compared to MP, making them suitable for processes requiring less char formation, such as rapid thermal conversion processes like pyrolysis or gasification. MS shows a higher decomposition rate (79 %), indicating less thermal stability but higher reactivity. MK exhibited a balance between thermal stability and reactivity. MP presented the highest thermal stability with a more gradual decomposition process. The final residual mass after 1000 °C is relatively low for all samples (21 %). However, this 21 % includes residual carbon and ash, indicating efficient thermal degradation during pyrolysis.

3.2.2. Combustion

Combustion results were also similar for the three mango waste samples (Fig. 2). First of all, moisture and light volatile species were removed (8 wt% of the mass loss, 32 °C to 200 °C). A second stage (88 wt %, 200 °C to around 500 °C) is associated with the decomposition of hemicellulose, cellulose, and the initial decomposition of lignin. Then, above 500 °C, pyrolysis and oxidation of the remaining lignin occurs, together with the combustion of carbonization residues. The final

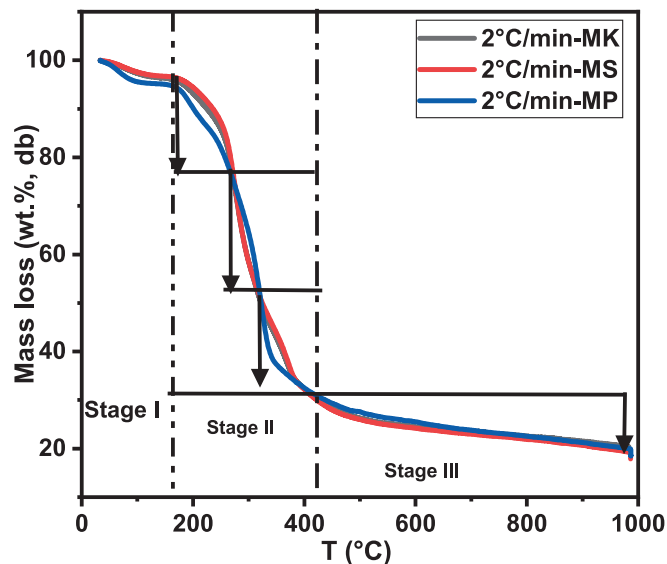


Fig. 1. Pyrolysis mass loss as a function of temperature in TGA at 2 °C/min for mango kernel, seed and pericarp.

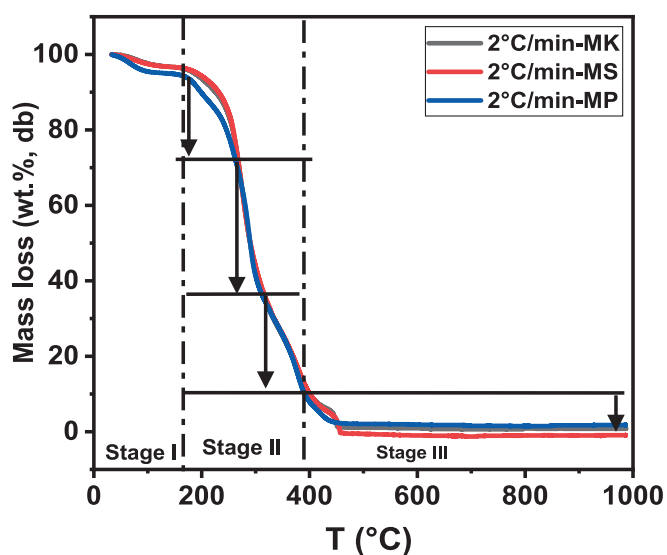


Fig. 2. Combustion mass loss as a function of temperature in TGA at 2 °C/min for mango kernel, seed and pericarp.

residue mass (around 0.5 wt%) was lower than the ash content (2.04–2.80 wt%, Table 1), probably due to the loss of some metals volatilized at 1000 °C. The introduction of oxygen leads to a more complete oxidation of the pyrolysis products as it facilitated bond breaking and the degradation of biomass components [50].

3.2.3. Biomass macromolecular composition

DTG curves of the three samples were analyzed through deconvolution using the Gaussian method to assess sample macromolecule composition (Fig. 3). The results indicated that considering the three decomposition zones corresponding to the moisture removal zone, the active pyrolysis zone and the passive pyrolysis zone satisfies the experimental data with a coefficient of determination (R^2) greater than 0.998 for all heating rates. Hemicellulose degradation happened between 200 °C and 250 °C for all samples. Cellulose decomposition occurred within the ranges of 250 °C to 350 °C for MK, 250 °C to 340 °C for MS, and 250 °C to 400 °C for MP. Lignin degradation began above 350 °C, with char degradation temperatures reaching around 700 °C for MK, MS, and MP. These findings are consistent with existing literature. Hemicellulose devolatilization peaks occur between 213.9 °C and 242.7 °C, while cellulose shows maximum mass loss between 284 °C and 317 °C, both within the active pyrolysis region [15]. Previous research also identifies the temperature ranges of 200 °C to 320 °C and 320 °C to 400 °C as characteristic of hemicellulose and cellulose devolatilization, respectively. Lignin devolatilization, distinctive among biomass components, spans a broad temperature range (180 °C to 800 °C) during both active and passive pyrolysis stages [5,6].

3.3. Kinetic and thermodynamic parameters

In this section, average values of kinetic and thermodynamic parameters are shown. Detailed calculated values depending on conversion are included in the Supplementary Material (S2).

3.3.1. Pyrolysis

For mango kernels (MK), the KAS method showed activation energy (E_a) values between 148.53 and 292.83 kJ/mol, with enthalpy (ΔH) ranging from 144.52 to 288.10 kJ/mol (Table 3). Gibbs free energy (ΔG) increased with conversion (α), reaching 194.45 kJ/mol, while entropy (ΔS) generally increased with conversion. The coefficient of determination (R^2) is high, ranging from 0.9715 to 0.9991, indicating a good fit. The Friedman method gives activation energy (E_a) between 150.62 and

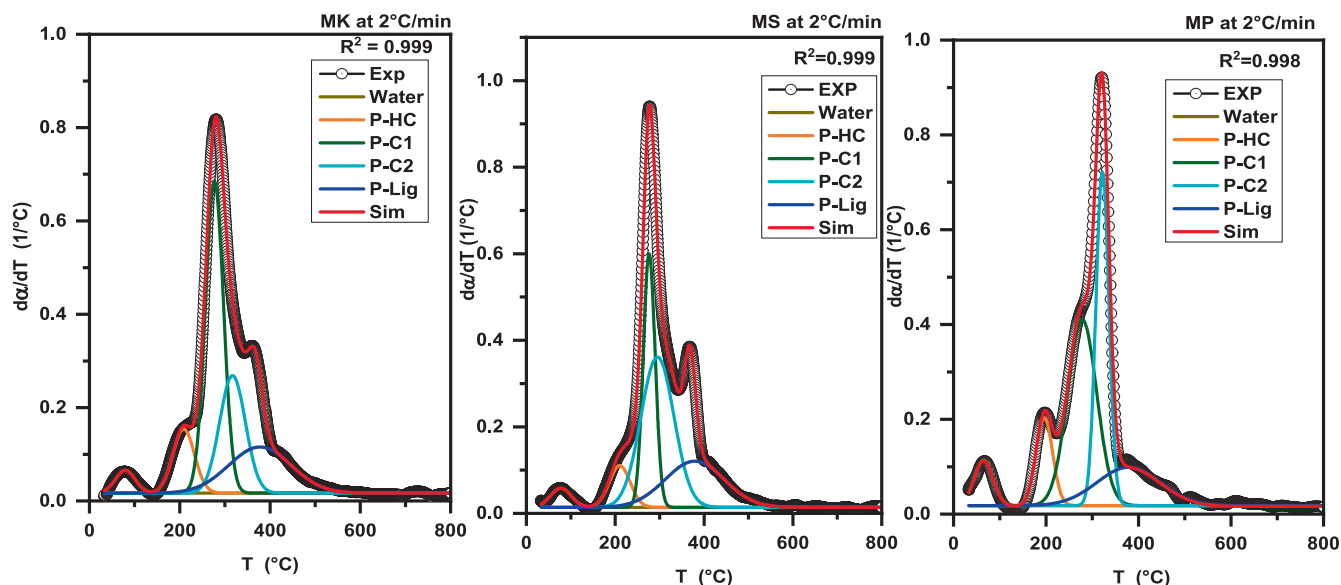


Fig. 3. Pyrolysis conversion rate ($d\alpha/dT$) in TGA at 2 °C/min as a function of temperature for mango kernel (left), seed (center) and pericarp (right), experimental results (full line) and simulation results (dashed line).

Table 3

Pyrolysis kinetic parameters of thermal degradation of MK, MS and MP.

Average values	Mango Kernel (MK)			Mango Seed (MS)			Mango Pericarp (MP)		
	Ea kJ/mol	A s ⁻¹	R ²	Ea kJ/mol	A s ⁻¹	R ²	Ea kJ/mol	A s ⁻¹	R ²
KAS	240.07 ± 2.00	1.80E + 25	0.9772	194.03 ± 2.51	1.49E + 33	0.9724	194.03 ± 1.96	7.69E + 27	0.8858
Friedman	247.06 ± 2.05	6.73E + 26	0.9765	186.16 ± 2.72	1.84E + 34	0.9670	177.39 ± 1.93	1.25E + 22	0.8707
FWO	237.73 ± 1.98	5.92E + 24	0.9789	194.05 ± 2.45	1.98E + 32	0.9725	193.98 ± 1.92	1.83E + 27	0.8842
STK	240.27 ± 2.00	1.86E + 25	0.9773	194.28 ± 2.51	1.52E + 33	0.9724	194.28 ± 1.96	7.90E + 27	0.8857

309.86 kJ/mol, with (ΔH) ranging from 146.60 to 305.13 kJ/mol. Gibbs free energy ΔG also increased with conversion, reaching 193.85 kJ/mol, while ΔS varied significantly with conversion. The (R^2) values remain high, between 0.8784 and 0.9999. Using the FWO method, (E_a) increased from 149.09 to 287.63 kJ/mol, and (ΔH) from 145.08 to 282.89 kJ/mol. ΔG underwent an increase with conversion, reaching 194.49 kJ/mol, and ΔS also varied with increasing α -conversion. The (R^2) values, between 0.8912 and 0.9992, confirming a strong fit. The STK method produces similar results, with (E_a) between 148.74 and 292.99 kJ/mol and (ΔH) between 144.73 and 288.25 kJ/mol. The ΔG value reached 194.44 kJ/mol as conversion increased, and R^2 values ranged from 0.8829 to 0.9991.

For mango seeds (MS), the KAS method indicated higher E_a values, ranging from 191.86 to 395.32 kJ/mol, and ΔH values ranging from 187.73 to 390.37 kJ/mol (Table 3). Gibbs free energy ΔG reached 175.83 kJ/mol with increasing conversion. High R^2 values between 0.8653 and 0.9998 were obtained. The Friedman method gave E_a values between 193.49 and 407.37 kJ/mol and ΔH between 189.36 and 402.42 kJ/mol. Gibbs free energy ΔG values of up to 175.04 kJ/mol were also obtained. The entropy ΔS showed significant variation with conversion. The determination coefficient R^2 remained high, ranging from 0.8669 to 0.9996. The FWO method showed activation energies E_a between 190.49 and 385.45 kJ/mol, and ΔH between 186.36 and 380.51 kJ/mol. Gibbs free energy ΔG showed an increase with conversion, reaching 175.86 kJ/mol, and R^2 values ranging from 0.8653 to 0.9999. The STK method gave similar results, with E_a increasing from 192.05 to 395.41 kJ/mol and ΔH from 187.92 to 390.46 kJ/mol, while ΔG reached 175.82 kJ/mol. The R^2 values ranged from 0.8710 to 0.9998.

For mango pericarp (MP), using the KAS method, the activation

energy (E_a) ranged from 157.19 to 365.98 kJ/mol. The enthalpy change (ΔH) varied from 153.33 to 360.59 kJ/mol. Gibbs free energy (ΔG) increased with conversion, reaching 171.20 kJ/mol (Table 3). Coefficients of determination (R^2) were consistently high, close to 0.9999. With the Friedman method, E_a values ranged from 162.86 to 261.30 kJ/mol, while ΔH increased from 159.01 to 255.91 kJ/mol. Gibbs free energy ΔG reached its maximum at 173.02 kJ/mol. The R^2 values remained high, close 0.9999. The FWO method yielded E_a values between 157.00 and 366.12 kJ/mol, and ΔH ranged from 153.15 to 360.74 kJ/mol. ΔG increased with conversion, reaching 171.32 kJ/mol, while entropy change (ΔS) varied with the degree of conversion (α) and the R^2 values stayed close to 0.9999. The STK method produced similar results with E_a values ranged from 157.38 to 366.12 kJ/mol, while ΔH ranged from 153.52 to 360.74 kJ/mol. The Gibbs energy ΔG increased with conversion, reaching 171.20 kJ/mol.

Enthalpy change (ΔH) follows a similar trend to E_a , indicating that the energy barrier for decomposition increases with conversion (Table 4). Gibbs free energy change (ΔG) increases with conversion, suggesting the decomposition process becomes less favorable thermodynamically. Entropy change (ΔS) values vary significantly, reflecting changes in disorder during the decomposition process. In general, ΔS values increase with the conversion rate, which indicates a higher degree of randomness or disorder in the system as decomposition progresses. This increase in entropy suggests that the thermal decomposition leads to a greater distribution of energy states and molecular motion within the system. The variability in ΔS values across different methods and parts of the mango highlights the complexity of the decomposition process and the different pathways it can follow. The high R^2 values indicate a good fit for the kinetic models, though some anomalies are present at higher conversions (0.8 to 0.9) resulting in

Table 4

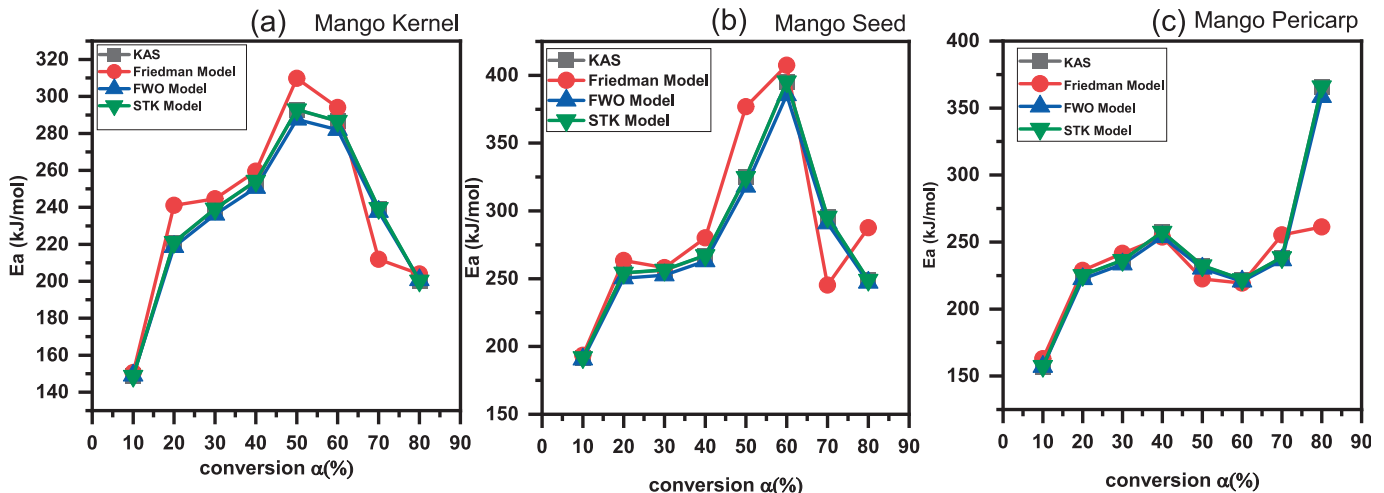
Pyrolysis thermodynamic parameters of thermal degradation of MK, MS and MP.

Average values	Mango Kernel (MK)			Mango Seed (MS)			Mango Pericarp (MP)		
	ΔH kJ/mol	ΔG kJ/mol	ΔS J/(K mol)	ΔH kJ/mol	ΔG kJ/mol	ΔS J/(K mol)	ΔH kJ/mol	ΔG kJ/mol	ΔS J/(K mol)
KAS	235.21	155.09	138.12	189.08	151.22	214.46	189.11	149.46	151.64
Friedman	242.20	154.97	150.11	181.21	151.08	231.96	172.47	149.65	134.84
FWO	232.87	155.14	134.00	189.11	151.29	206.58	189.06	149.51	146.87
STK	235.42	155.09	138.47	189.33	151.22	214.76	189.35	149.45	151.98

negative activation energy for seed (MS) and pericarp (MP) (Table S1). This could be attributed to secondary reactions or changes in the decomposition mechanism and mainly to the low order of lignin decomposition reactions [51,52]. Negative values of apparent activation energy indicates that the decomposition reaction slows as temperature increases, adding complexity to the thermal behavior of the material [53]. From a reaction engineering perspective, negative activation energy suggested that the reaction can proceed without additional energy input [54]. Reactions exhibiting negative activation energies are referred as barrier less reactions in which the reaction proceeding relies on the capture of molecules [55,56]. For palm leaves (PF), olive leaves (OL), and wheat straw (WS), the average activation energies (E_a) were 91.9, 69.1, and 65.2 kJ/mol, respectively, using the OFW method, and 87.5, 101.8, and 63.4 kJ/mol, respectively, with the KAS method [57]. For coconut husk, the average activation energy was determined using various model-free approaches, with values of 99.15 kJ/mol for both the KAS and DEAM methods, and 103 kJ/mol for the FWO method [58]. These results indicate that the mango kernel components analyzed in this study exhibited greater thermal stability. A comparison with rice husk reveals similarities with mango kernels. For rice husk biomass, the average activation energy values were 179.88, 179.59, and 176.81 kJ/mol, as determined by the FWO, KAS, and Starink models. Additionally, the Gibbs free energy for rice husk biomass averaged 187.01, 187.02, and 187.09 kJ/mol, while the enthalpy values were 174.44, 174.14, and 171.36 kJ/mol for the FWO, KAS, and STK models, respectively [59]. This thermal stability in mango waste pyrolysis, driven by significant changes in the H/C and O/C ratios in these samples above 400 °C, could enhance the formation of thermally stable biochar. This, in turn, suggests potential avenues for valorization, particularly in the production of activated carbon due to its higher carbon content [60]. In particular, high thermal stability is a crucial requirement for biochar intended for certain coal replacement applications, especially since biochar generally exhibits lower thermal stability than coal [61]. A study on quince waste (QW and PFQW) reveals a higher thermal reactivity, with significantly

lower activation energies (30–91 kJ/mol) [62] compared to mango fractions (MK, MS, MP), which exhibit much higher values (177–247 kJ/mol). This difference reflects an easier pyrolysis process for quince, especially after pectin extraction, enabling faster and more cost-effective conversion. However, mango residues, although less reactive, offer a unique valorization potential due to their enhanced thermal stability. This resistance to decomposition promotes more controlled pyrolysis, leading to a higher yield of quality biochar, as well as better control over complex thermochemical processes such as combustion or gasification. These characteristics make mango by-products valuable candidates for sustainable energy applications and high-value bio-based materials.

Activation energy (E_a) was calculated as a function of the conversion rate (α) for the thermal decomposition of mango residues by KAS, Friedman, FWO, and STK methods (Fig. 4). The initial increase in (E_a) for all parts (MK, MS, and MP) suggested that the decomposition process required more energy as the reaction progressed, so higher conversion was required to decompose the most stable components [63,64]. Peaks around 50–60 % conversion corresponded to the highest energy barrier during the decomposition process. This could be due to the decomposition of the most stable components, namely active cellulose and lignin [5]. The significant drop in (E_a) at higher conversions (80–90 %) for MP suggested a change in the decomposition mechanism or the completion of the primary decomposition process [65]. Hemicellulose, composed of various polysaccharides such as xylose, mannose, glucose, and galactose, adopts a random amorphous structure with abundant branching, facilitating easy detachment of branches from the main structure. Previous studies have reported the existence of two types of hemicellulose, cellulose, and lignin in certain biomass resources. Specifically, hemicellulose based on Xylan is less thermally stable compared to Mannan-based hemicellulose [66,67]. During biomass degradation, two forms of cellulose can be distinguished: amorphous cellulose, characterized by a less ordered crystalline structure and therefore lower thermal stability than active cellulose, which exhibits a highly ordered microcrystalline structure [68]. Active cellulose can be formed through partial


Fig. 4. Activation energies (E_a) as a function of conversion α (%) for all methods used for MK, MS and MP pyrolysis.

depolymerization of cellulose, producing levoglucosan, which will then decompose into char and volatile species. The initial stage of lignin decomposition primarily involves the breakdown of aromatic compounds, while the latter stage is more associated with char formation and its degradation. Comparing the kinetic models for the thermal decomposition of the samples reveals that KAS, FWO, and STK models provided smoother and more consistent trends in activation energy, indicating reliable kinetic parameters. In contrast, Friedman model exhibits greater sensitivity to conversion rates, characterized by pronounced peaks and troughs that reflect the complexity and variability of decomposition processes. This sensitivity is likely due to the differential nature of the Friedman method, which may introduce errors from differentiation and its heightened sensitivity to experimental noise [69].

3.3.2. Pyrolysis reaction mechanism

Biomass pyrolysis is a multi-stage, complex reaction phenomenon characterized by a series of sequential side reactions [70]. Estimating a single reaction model for the entire process is challenging due to the complexity of the reactions involved. Pyrolysis was modelled through seventeen theoretical models and the results were compared to experimental curves for MK, MS, and MP (Fig. 5).

By comparing the experimental and theoretical curves, precise models of the reaction mechanism were identified. In the initial stages (0–15 % conversion), the thermal behavior of MK and MS was closely aligned with reaction order models P_n and D_1 . The P_n model suggests that the degradation process follows a specific reaction order, indicating that the rate of degradation is proportional to the concentration of the reactant raised to a power n . The D_1 model corresponds to one-dimensional diffusion, implying that the initial degradation might be controlled by the diffusion of molecules within the sample structure. This alignment with P_n and D_1 models suggests that the early stages of degradation for MK and MS involve both reaction kinetics and diffusion processes. As conversion increases from 15 % to 50 %, the reaction model for MK and MS transitions through a succession of different mechanisms. This indicates a more complex degradation process where multiple mechanisms might be at play, possibly involving a combination of reaction orders, diffusion processes, and other kinetic factors [41]. The shift away from P_n and D_1 models suggests that as the conversion progresses, the degradation dynamics become more intricate, likely due to changes in the material structure and composition. Throughout the initial to mid-stage conversion (0–50 %), MP behavior remained close to reaction order models P_n and D_1 . This indicated a relatively simpler degradation mechanism compared to MK and MS, dominated by reaction order kinetics and one-dimensional diffusion [19]. In the higher conversion range (50–90 %), the behavior of all three samples (MK, MS, and MP) aligns with reaction order models F_1 , F_2 and diffusion models D_5 , D_3 and A_3 . The F_1 model represents first-order kinetics, indicating that the degradation rate was directly proportional to the concentration of the reactant. F_2 suggests a second-order reaction, implying a more

complex dependency on reactant concentration. The diffusion D_5 , and D_3 models suggest higher-dimensional diffusion processes, indicating that as the conversion progresses, the degradation becomes increasingly controlled by the diffusion of molecules within a three-dimensional structure [41]. The A_3 model represents nucleation and growth, suggesting that the final stages of degradation might involve the formation and growth of new phases or structures within the material. This alignment with various models indicated that in the later stages, the degradation processes for MK, MS, and MP through pyrolysis became highly complex, involving a mix of kinetic and diffusion-controlled mechanisms [71].

3.3.3. Combustion

For combustion, the same methods used in pyrolysis were employed to determine kinetic (Table 5) and thermodynamic (Table 6) parameters.

MK exhibit lower activation energy (122.26 kJ/mol, Table 5) compared to MS (132.99 kJ/mol) and MP (132.88 kJ/mol, Table 5), suggesting that it has a relatively easier combustion initiation [72]. This could be advantageous for applications requiring rapid energy release with minimal energy input to start the reaction. The activation energy decreased with increasing conversion for all samples and methods used, except for $\alpha = 0.1$ to 0.2 for KAS, FWO and STK methods and Friedman method for MP combustion. The correlation coefficients (R^2) were from 0.7260 to 0.9999, which validated the activation energies calculated. The reduction of the activation energy values can be associated with the catalytic effect of AAEMs in all samples, particularly potassium [73]. Additionally, high temperatures lead to the release of potassium, indicating that, from the start of the reaction up to 1000 °C, reactive organic minerals in biomass, such as oxalates or phosphates of Ca and K, underwent thermal reactions to form more stable compounds, which also influenced biomass reactivity [74]. Previous studies suggested that the catalytic activity of Ca is limited to its ability to migrate and react with organic species in the carbon matrix. As a result, calcium transformation enhances its catalytic effect on the char matrix during combustion [75]. The frequency factor followed the same trend as the activation energy in the combustion process (Table 5), which indicated the presence of a surface reaction, but also suggested a simple complex reaction [15,76].

Calculated values for ΔH for the three samples were all positive (99.57 to 131.30 kJ/mol, Table 6), indicating the heat required for combustion to take place [77]. Similar results were found for Bamboo combustion, with average ΔH values for devolatilization and coal combustion of 112.92 kJ/mol and 105.06 kJ/mol (for the FWO method), 109.93 kJ/mol and 99.36 kJ/mol (for the KAS method), and 110.21 kJ/mol and 99.73 kJ/mol (for the STR method) respectively [78]. The ΔH values in the main pyrolysis stage are significantly higher than those in the main combustion stage, indicating that a greater amount of energy is required for the dissociation of chemical bonds in the pyrolysis process [79]. MS and MP had higher average enthalpies of activation (108.70 to

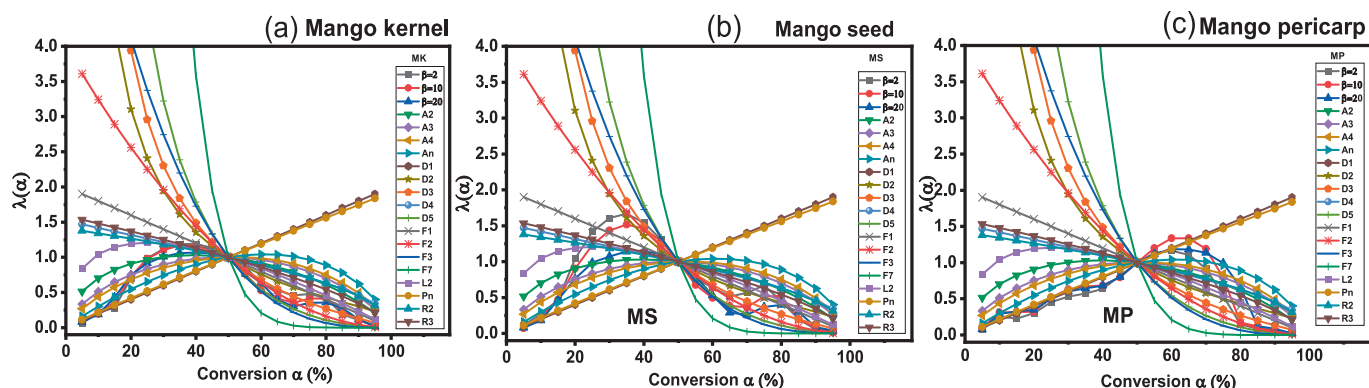


Fig. 5. Generalized master-plots of the reaction models and experimental pyrolysis data.

Table 5

Combustion Kinetic parameters of thermal degradation of MK, MS and MP.

Average values	Mango Kernel (MK)			Mango Seed (MS)			Mango Pericarp (MP)		
	Ea kJ/mol	A s ⁻¹	R ²	Ea kJ/mol	A s ⁻¹	R ²	Ea kJ/mol	A s ⁻¹	R ²
KAS	122.26 ± 1.02	2.26E + 18	0.9853	132.99 ± 1.11	1.85E + 20	0.9903	132.88 ± 1.10	3.54E + 18	0.9816
Friedman	104.35 ± 0.87	9.52E + 19	0.9491	113.50 ± 0.94	1.40E + 20	0.9632	116.15 ± 0.97	3.00E + 18	0.9361
FWO	125.95 ± 1.05	1.67E + 18	0.9914	136.10 ± 1.13	1.09E + 20	0.9927	135.86 ± 1.13	2.52E + 18	0.9883
STK	122.57 ± 1.02	2.37E + 18	0.9857	133.29 ± 1.11	1.93E + 20	0.9905	133.17 ± 1.11	3.70E + 18	0.9820

Table 6

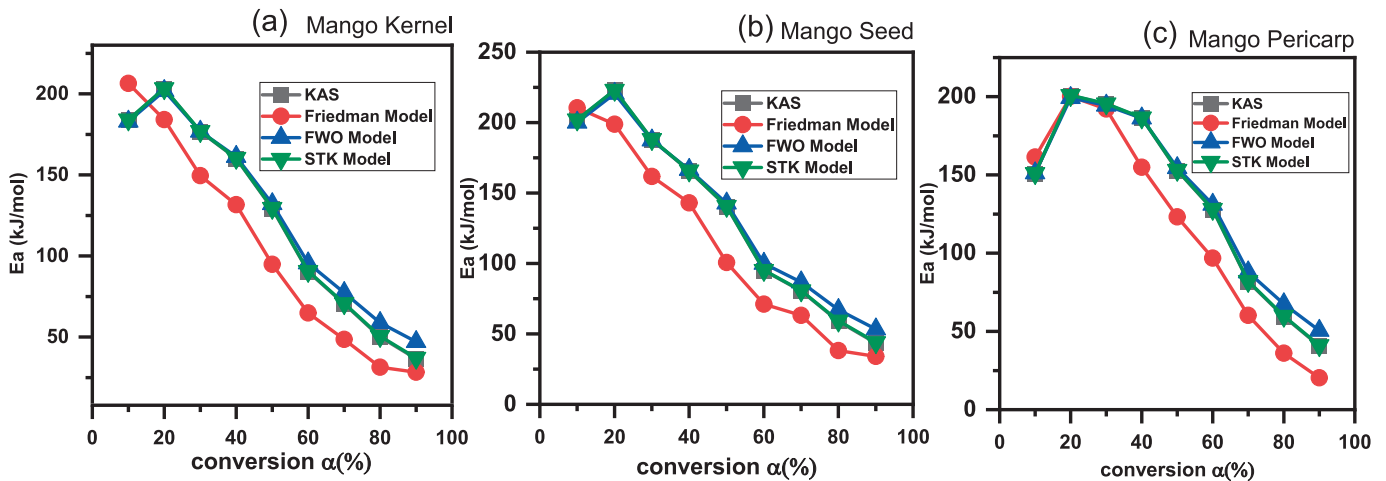
Combustion thermodynamic parameters of thermal degradation of MK, MS and MP.

Average values	Mango Kernel (MK)			Mango Seed (MS)			Mango Pericarp (MP)		
	ΔH kJ/mol	ΔG kJ/mol	ΔS J/(K mol)	ΔH kJ/mol	ΔG kJ/mol	ΔS J/(K mol)	ΔH kJ/mol	ΔG kJ/mol	ΔS J/(K mol)
KAS	117.47	156.71	−57.52	128.19	156.67	−38.26	128.15	154.12	−35.17
Friedman	99.57	157.88	−90.09	108.70	157.73	−73.83	111.42	155.34	−65.08
FWO	121.17	156.37	−51.12	131.30	156.40	−33.01	131.13	153.86	−30.05
STK	117.78	156.69	−56.96	128.49	156.65	−37.73	128.44	154.10	−34.64

131.30 kJ/mol) compared to MK (99.57 to 121.17 kJ/mol). Gibbs free energy change (ΔG) increased with conversion (132.73 to 191.47) regarding the method (Table S4), suggesting the decomposition process became less favorable thermodynamically but as a positive indicator for producing energy from the biomass conversion process [73,77]. Calculated ΔS values are partly negative (mainly for $\alpha = 0.5$ to 0.9), suggesting a higher degree of randomness in biomass compared to the products formed. High entropy values imply greater reactivity and a shorter time to reach the activated complex, leading to a reduced overall reaction time. Conversely, lower ΔS values suggest reduced reactivity, as the material is closer to its thermodynamic equilibrium state [80,81].

The variation in activation energy with conversion was assessed for all samples and models (Fig. 6). A consistent trend was found for all samples, with activation energy E_a rapidly decreasing beyond $\alpha = 0.2$ as conversion increases. The KAS model MK showed a significant decrease in E_a with increasing conversion. Initially, E_a was relatively high and then decreases sharply, which indicated that early degradation stages required the breaking of stronger bonds [82]. For MS, the KAS model also started at a high E_a but showed a more gradual decrease compared to MK, suggesting that MS had more complex components requiring more energy to degrade initially. The KAS model for MP followed a similar trend to MK, with a strong initial decrease in E_a , indicating that the initial degradation of MP is also energy-intensive, but becomes easier as conversion proceeds. The Friedman model for MK shows a high

initial E_a , which decreases steadily with conversion, suggesting a more uniform degradation process than that described by the KAS model. For MS, the Friedman model showed the highest initial E_a among the models. However, the activation energy decreased progressively with conversion, underlining its resistance to degradation and the complex nature of its structure. The Friedman model for MP showed a similar trend to MK, with a moderate decrease in E_a . The FWO model for MK shows a similar trend to the Friedman model, with a moderate initial E_a and a steadily decreasing E_a . This indicated a relatively uniform degradation process. For MS, the FWO model started at a high E_a and gradually decreased, like the Friedman model. The FWO model for MP followed a similar pattern to MK and MS, with moderate initial E_a and steadily decreasing. This also indicated a relatively consistent degradation process for different conversions α . The STK model for MK showed a slightly different trend, with a lower initial E_a than the Friedman and FWO models but decreasing more rapidly. This suggested that the STK model assumes a more rapid reduction in energy requirements as conversion progresses. For MS, the STK model also showed a high initial E_a , which decreases more rapidly than the Friedman and FWO models, indicating a more rapid transition between high-energy and low-energy stages of degradation. The STK model for MP followed a similar trend to that of MK, with a lower initial E_a and a rapid decrease, suggesting a more rapid reduction in energy barriers during its decomposition.

**Fig. 6.** Activation energies (E_a) as a function of conversion α (%) for all methods used for MK, MS and MP combustion.

The choice of kinetic model has a significant impact on the predicted activation energy. This comparison has shown, for example, that the KAS model may be more appropriate for processes where a strong reduction in initial energy is expected, while the Friedman and FWO models offer a more uniform perspective. This sensitivity is likely due to the differential nature of the Friedman method, which may introduce errors from differentiation and its heightened sensitivity to experimental noise [69].

3.3.4. Combustion reaction mechanism

Combustion was also modelled through seventeen theoretical models and the results were compared to experimental curves for MK, MS, and MP (Fig. 7). The results showed that the combustion reaction mechanism behaved differently depending on the conversion range (α). MK at low conversion (0–40 %) was best-fitted with D_1 , D_2 , and some Avrami models (A_2 , A_3). At the initial stage, biomass undergoes drying and devolatilization, releasing volatile compounds such as CO , CH_4 , and H_2 . Oxygen triggers heterogeneous oxidation reactions, leading to the formation of both gas and char. The reactions are primarily diffusion-controlled (D_1 , D_2), as oxygen penetration into the solid matrix governed the process. Additionally, nucleation-based models may contribute by facilitating the formation of new reaction sites. In diffusion-limited reactions, the rate of product formation depends on the thickness of the barrier layer, as molecules must permeate solid lattices while facing mobility restrictions [83]. As mango waste biomasses, being carbonaceous solids, were heated, their porous networks expanded, increasing surface area. During devolatilization, gaseous products must diffuse through these porous structures before reaching the particle surface, where they mix with air and undergo combustion. Rather than combustion in an oxygen-rich environment, this diffusion process likely becomes the rate-limiting step. At medium conversion range (40–60 %), the reaction order models (F_1 , F_2 , F_3) and nucleation models (A_2 , A_3 , A_4) seem to fit well with the experimental master plot data and at higher conversions (60–100 %), models such as R_2 , R_3 , and some diffusion models (D_3 , D_4) align better with the experimental data (Fig. 7a). Models referred to as reaction order indicate that the chemical reaction is controlled by chemical kinetics, and models F_1 , F_2 and F_3 correspond to first, second and third order respectively [84]. Similar behavior was observed with MS with a distinctive feature being the variability of the reaction mechanism in the high-conversion region (Fig. 7b). For MP at initial combustion phase (0–40 % Conversion) the experimental data aligns well with diffusion-controlled models D_1 and nucleation models (A_3 , A_4 and A_n). The curves converged in the vicinity of $\alpha = 50$ %, where the reaction order models (F_1 – F_3) best described the process. At high conversion levels (60–100 %), phase-boundary models (R_2 , R_3) dominated (Fig. 7c). Phase-boundary controlled models become significant as the reaction slows due to the reduction in available

reactive sites [84].

3.4. General comparison for the sustainable utilization of the analyzed bio-waste

Given the physical and chemical properties of the analyzed bio-waste, the valorization through various thermal techniques appeared promising, requiring minimal pre-treatment. This analysis supports the potential for utilizing mango biomass for energy generation and other applications such as potassium synthesis, highlighting its role in sustainable waste management and resource valorization.

MK, MS and MP required drying as a pre-treatment, given the very high moisture content of the fruit before natural sun-drying (86.85 g/100 g) [85] highlighting the importance of moisture content in the thermochemical conversion of mango wastes. Reducing moisture improves energy density and overall efficiency. Torrefaction and separation of mango kernel components are unnecessary, which is advantageous as these processes are energy-intensive and would lead to increased energy consumption and costs during the recovery process. MK, MS and MP are well-suited for pyrolysis due to their high volatile matter content (79.02 %, 79.72 % and 80.75 %, respectively) and reasonable fixed carbon levels (18.18 %, 17.93 % and 17.20 %, respectively), making them efficient for biofuel and biochar production. The mango components are also well-adapted for combustion, particularly MK and MS due to their higher LHV (19.38 MJ/kg and 20.21 MJ/kg, respectively) and lower ash content (2.80 % and 2.35 %, respectively). While MP has slightly lower energy output, it remains viable for combustion. MK and MS are highly suitable for gasification, though MP is less so. High potassium content in MK, MS and MP (28051.81 ppm, 28050.68 ppm and 15119.18 ppm, respectively) enhances gasification through catalytic effects, but the high silica content (1816.01 ppm) in MP can cause slagging, reducing its gasification potential. The MP calcium content (2162.58 ppm) helps counteract the effects of silica, but it still performs less favorably compared to MK and MS. All three samples are good candidates for potassium synthesis, with the MK and MS being the most efficient. Overall, MK and MS show greater potential for thermochemical processes, especially for gasification and potassium recovery, due to their favorable thermal, chemical, and mineral properties.

4. Conclusions and perspectives

The physico-chemical analysis of mango kernel (MK), mango seed (MS), and mango pericarp (MP) showed high organic matter content across all samples. Among the three biomass types studied, MS stands out with the highest carbon and hydrogen contents, lowest moisture content, and highest LHV, making it the most suitable for energy

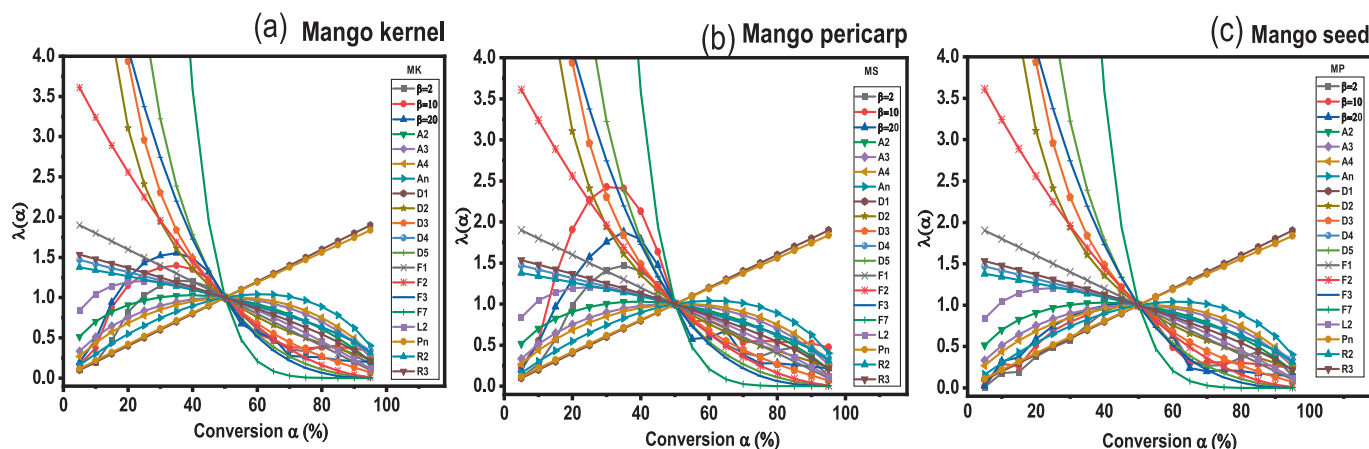


Fig. 7. Generalized master-plots of the reaction models and experimental combustion data.

production. MK also shows promise with high fixed carbon and lignin content but produces more residue. MP, while easy to ignite due to its high volatile matter and cellulose content, has the lowest energy yield and the highest moisture content. The mineral analysis reveals that MS has the most favorable elemental composition for catalytic activity in pyro-gasification, followed by MK and MP. The high K content in MS, coupled with favorable ratios like K/Si and K/Al, suggests that it will enhance the gasification process, leading to higher syngas yield and efficiency. Beyond the proximate and ultimate analyses, the kinetic and thermodynamic characterization of MK, MS, and MP provided crucial insights into their decomposition behaviors during pyrolysis and combustion. In pyrolysis, the activation energy (E_a) ranged from 148.53 to 309.86 kJ/mol for MK, 190.49 to 407.37 kJ/mol for MS, and 157.00 to 366.12 kJ/mol for MP, depending on the model used. These values confirm that MS is the most thermally resistant biomass, followed by MP and MK. The Gibbs free energy (ΔG) increased with conversion, reaching up to 194.49 kJ/mol, while the entropy (ΔS) generally increased as well, reflecting a rise in molecular disorder with progression of the reaction. Combustion analysis showed that MK had the lowest average activation energy (122.26 kJ/mol), confirming its higher reactivity and easier ignition compared to MS (132.99 kJ/mol) and MP (132.88 kJ/mol). Enthalpy values (ΔH) ranged from 99.57 to 131.30 kJ/mol, and the ΔG values suggested a favorable energy recovery potential despite the endothermic nature of the reactions. Reaction mechanism modeling confirmed the complex, multi-stage nature of thermal degradation of mango waste. In early conversion stages ($\alpha < 0.2$), MK and MS aligned with Pn and D1 models, indicating a mix of reaction-order kinetics and diffusion control. At higher conversions, more complex models such as F1, D3, D5, and A3 were dominant, highlighting a shift toward diffusion- and nucleation-controlled mechanisms. These findings deepen the understanding of mango biomass thermochemical behavior and provide critical parameters for reactor modeling and optimization. The strong thermal stability and diverse reactivity profiles of MS, MK, and MP make them promising feedstocks for targeted bioenergy applications, including bio-oil, biochar, and syngas production. While separating mango kernel components enhances process control and product quality, the absence of significant negative synergistic effects also supports the feasibility of co-processing the biomass fractions to simplify logistics and reduce preprocessing costs. To advance this research, future work should focus on pilot-scale pyrolysis and gasification to validate kinetic and thermodynamic models under real conditions. Real-time gas analysis will help clarify reaction pathways. Catalytic upgrading using MS-derived ash and activated carbon production from MK and MP biochar should be explored. Reactor-scale modeling can improve process optimization, while techno-economic and life cycle analyses are crucial to assess the sustainability of mango waste valorization. Integrating thermochemical conversion with advanced material synthesis provides valuable opportunities for holistic biomass utilization, promoting both economic and environmental benefits.

CRediT authorship contribution statement

Hamado OUEDRAOGO: Conceptualization, Methodology, Investigation, Software, Data Curation, Formal analysis, Writing - Original Draft, Writing - Review & Editing. **María González Martínez:** Supervision, Conceptualization, Methodology, Resources, Investigation, Writing - Review & Editing, Formal analysis and Validation. **Sayon dit Sadio SIDIBE:** Supervision, Conceptualization, Methodology, Resources, Investigation, Writing - Review & Editing, Formal analysis and Validation. **Yohan RICHARDSON:** Supervision, Conceptualization, Methodology, Resources, Investigation, Writing - Review & Editing, Formal analysis and Validation. **Ange NZIHOU:** Supervision, Conceptualization, Methodology, Resources, Investigation, Writing - Review & Editing, Formal analysis and Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.enconman.2025.120347>.

Data availability

Data will be made available on request.

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