

Article

Thermal and Kinetic Study of Waste Polypropylene, Cardboard, Wood Biomass, and Their Blends: A Thermogravimetry Approach

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Abstract

In this study, a thermogravimetry approach was employed to investigate the thermal parameters of waste polypropylene (PP), mixed wood biomass (WB), cardboard (CB), and their blends during co-gasification under oxidative conditions at varying heating rates. The resulting data were used to quantify the mass loss profiles for each feedstock and to assess the effects of blending on process temperatures (onset and end), residual mass, and activation energies. Activation energies (E_a) were determined using three iso-conversional methods: Friedman, Kissinger–Akahira–Sunose (KAS), and Numerical Optimization. Among the feedstocks, PP exhibited the highest thermal stability. When blended with either CB or WB, both onset and end temperatures significantly ($p < 0.05$) increased with rising PP content. These trends were consistent at heating rates of 20 and 40 °C/min. In contrast, CB/WB blends showed no notable variation in onset temperature across blend ratios at either heating rate. However, PP/CB blends exhibited significantly lower residual masses (up to a six-fold decrease) with increasing PP content. Since both PP and WB individually yielded very low residual mass (<2 wt%), increasing PP content in PP/WB blends did not significantly affect the residual mass. Overall, higher heating rates shifted thermal decomposition into higher temperature regimes in both individual and blended feedstocks, but had no impact on residual mass. The E_a of WB was the highest (138–139 kJ/mol), followed by CB (113–116 kJ/mol) and PP (56–63 kJ/mol). The blending of PP/CB and CB/WB resulted in reduced E_a values compared to the pure feedstocks, indicating a positive synergistic effect during co-gasification. In essence, the co-gasification of mixed plastic waste presents a promising strategy for sustainable waste management and energy recovery.

Keywords: co-gasification; polypropylene; biomass; thermogravimetric analysis; process temperatures; activation energies



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1. Introduction

Sustainable management of residual municipal solid waste (MSW) is essential for achieving consistent environmental benefits. Residual MSW typically consists of a complex, heterogeneous mixture of materials that are often landfilled due to the limitations of mechanical recycling. However, its high content of combustible materials makes residual MSW a potential energy source [1]. Incineration is a widely used disposal method for

residual MSW, offering significant volume reduction and energy recovery. Nonetheless, challenges such as low net electrical efficiency, substantial solid by-product generation [2] and the release of toxic off-gases render incineration less environmentally sustainable [3].

Thermochemical treatments, capable of producing both syngas and valuable chemicals, present a more suitable alternative for large-scale sustainable recycling [4]. Pyrolysis, for instance, is a well-established process for generating chemicals, fuel oils, and energy [5]. Gasification, another alternative thermal treatment method, offers greater flexibility by accommodating a broader range of feedstocks [4]. In waste-to-energy applications, gasification is considered more environmentally friendly due to its lower greenhouse gas (GHG) emissions compared to other thermal methods. The resulting syngas has diverse applications in hydrogen production, methanol synthesis, chemical manufacturing, and power generation [6]. A review by Maya et al. [7] comparing the environmental performance of incineration and gasification found that incineration emitted at least twenty times more Hg and SO₂ than gasification, and NO_x levels were five times higher. The operating temperature of gasification (>1000 °C) in a limited oxygen environment suppresses the formation of dioxins and furans, whereas incineration's oxygen-rich conditions promote their formation [7]. In gasification, solid carbonaceous feedstocks are converted into a syngas mix of CO, H₂, and CH₄ under limited oxygen conditions, enabling the conversion of both pure and mixed waste into energy or chemical precursors [8].

Plastics, which constitute a significant portion of residual MSW, are ideal feedstocks for gasification due to their high energy density. The resulting syngas is rich in hydrogen and possesses high energy potential [9]. Single-feedstock gasification also allows for better control over product composition and reaction pathways, minimizing the formation of byproducts such as dioxins [10,11]. However, plastic gasification faces challenges including feedstock handling, agglomeration, and the generation of toxic pollutants [12,13]. High-tar formation, especially from aromatic polymers, can lead to clogging and reduced syngas quality. Additionally, mixed plastics exhibit varied thermal behaviors and elemental compositions, complicating process optimization. Additives and dyes may introduce heavy metals, further hindering gas cleanup and syngas quality [14].

Biomass is another abundant feedstock and can be carbon-neutral, as CO₂ emissions during gasification can be offset by absorption during biomass growth [15]. A wide range of lignocellulosic feedstocks from woody waste to paper can be gasified, contributing to waste reduction and circular economy goals [16]. Despite its high exergy efficiency [17], biomass generally has lower volatile matter and energy density, and higher tar and ash content, which is less favorable for gasification. Variability in mixed biomass also affects the moisture content and particle size, influencing syngas composition [18]. If not properly managed, contaminated biomass feedstocks may emit NO_x, SO_x, and dioxins [16].

The co-gasification process is governed by complex thermochemical interactions, with activation energy (*E_a*) serving as a critical indicator of reaction kinetics. Notably, the presence of alkali and alkaline earth metals (AAEMs) in biomass ash can catalyze the reaction [19], reducing *E_a* and enhancing conversion rates [20]. Methodological differences also influence *E_a* estimates; values derived from the Flynn–Wall–Ozawa (FWO) method tend to be higher than those from Kissinger–Akahira–Sunose (KAS) approach, with discrepancies of up to 9.4 kJ/mol at full conversion [21]. Process temperature is another decisive factor in co-gasification performance [22]. Optimal gasification typically occurs between 800 and 1200 °C, where elevated temperatures accelerate devolatilization and char breakdown, improving syngas yield and carbon conversion efficiency [23]. However, excessive temperatures may lead to slagging or ash fusion, complicating reactor operation and residue handling [24]. Residue formation, particularly coarse solid residue (CSR), is an inevitable by-product of co-gasification [25]. Recent research has explored the valorization of CSR,

demonstrating its potential as a catalyst for light olefin production due to its iron-rich composition and alkali content. These residues, once considered waste, now represent a secondary resource stream, especially when pre-treated to enhance catalytic activity [26]. Their composition and behavior under high-temperature conditions are crucial for reactor design, ash management, and downstream applications [27].

Thermogravimetry (TGA) is a thermochemical technique used to analyze degradation. It measures mass loss and heat flow using Differential Scanning Calorimetry (DSC) during thermal degradation [28]. TGA has broad applications, from detecting plastics in environmental samples [29], to studying the thermal degradation kinetics of plastics and biomass for gasification process development [30,31]. The combined use of TGA and DSC enables detailed kinetic studies, including devolatilization, pyrolysis and combustion. A key advantage is the ability to use small feedstock samples across wide temperature ranges under controlled conditions [32–34]. TGA also offers flexibility in rapidly evaluating factors influencing gasification, such as feedstock type, catalyst use and operational parameters.

The increasing complexity for heterogeneous waste streams and the global imperative for sustainable energy recovery have intensified interest in co-gasification as a viable thermochemical conversion pathway [35]. Despite its promise, the fundamental reaction kinetics, particularly activation energy variation across blended feedstock, remains insufficiently characterised, limiting predictive modelling and reactor optimization [36]. Moreover, the influence of process temperature on conversion efficiency and syngas composition demands deeper investigation, especially within the critical range of 800–1200 °C where devolatilization and char breakdown are most active [23]. Concurrently, the formation and behavior of coarse solid residues under high-temperature conditions present both operational challenges and untapped volatilization potential [25]. This research is motivated by the need to characterize these core parameters in co-gasification systems, thereby contributing to the development of more predictable, scalable, and more sustainable energy solutions.

Accordingly, this study aims to contribute to the emerging field of co-gasification by examining how mixed feedstock blending influences key process parameters under varying heating rates. The initial phase focuses on the kinetic and thermal properties of waste polypropylene (PP), mixed woody biomass (WB), and cardboard (CB). These feedstocks were co-gasified at different blend ratios under oxidative conditions, with heating rates of 20 and 40 °C/min applied. Parameters assessed included onset and end temperatures, residual mass, and activation energies.

2. Materials and Methods

2.1. Materials

Three distinct waste feedstocks and their respective blends were used in this study. Waste PP and CB were sourced from a local resource recovery center in Lismore, Australia, while mixed woody biomass waste comprising local species was collected from the Southern Cross University campus in Lismore. Prior to milling, both WB and CB feedstocks were oven-dried for 24 h at 105 °C to remove moisture. Waste PP was also milled to reduce the sample. To ensure consistency during TG measurements, each blend was mixed manually just before measurement. No bulk or mechanical mixing was performed. This helped maintain the natural structure of the materials while ensuring that each sample was evenly distributed in the crucible.

The feedstock blending ratios used in subsequent experiments are presented in Table 1. These ratios were designed using the Design of Experiments functionality in Minitab 20.4 Statistical Software (Minitab, LLC., State College, PA, USA).

Table 1. Experimental materials and blend mix percentages.

CB (wt%)	WB (wt%)	Waste PP (wt%)
50	50	-
80	20	-
20	80	-
100	-	-
-	-	100
-	80	20
-	50	50
-	20	80
80	-	20
50	-	50
20	-	80
-	100	-

2.2. Test Methods

2.2.1. Thermogravimetric Analysis

All thermogravimetric (TG) analyses in this study were conducted using a laboratory-scale thermal analyzer (NETZSCH 449 F3 Jupiter Series, Dresden, Germany). The instrument comprises a balance system, hoisting device, gas control units, and a furnace compartment. Within the furnace are key components including the thermocouple, heating element, feedstock carrier, protective tubes, and radiation shields. The thermocouple serves as a temperature sensor, enabling precise thermal measurements during the heating process. The analyzer accommodates feedstock weights ranging from 1 mg to 50 mg within the carrier. An attached gas outlet valve facilitates the capture of evolved gas, which can be further analyzed using gas chromatography–mass spectrometry (GC-MS) or Fourier transform infrared spectroscopy (FTIR). Detailed specifications are presented in Table 2.

Table 2. TG Controls and parameters.

Apparatus/Controls	Description
Furnace	Silicon Carbide (0 °C to 1600 °C). Operational heating rates range from 0 °C/min to 50 °C/min.
Gas Controls	Purge Gas MFC—Air (N ₂ /O ₂ (80/20) at a flowrate of 50 L/min Protective Gas MFC—Air (N ₂ /O ₂ (80/20) at a flowrate of 20 L/min
Crucibles	Al ₂ O ₃ (temperature range of 0 °C to 1564 °C)
Temperature Resolution	0.001 °C

For all TG/DTG measurements, 25 ± 0.5 mg of representative feedstock was placed in a sample carrier and top-loaded into the furnace compartment. The feedstocks were heated from 30 °C to 850 °C, followed by cooling to 30 °C. This process was conducted at heating rates of 20 and 40 °C/min. The selection of 20 and 40 °C/min heating rates in this study reflects a balance between kinetic precision and operational relevance. A heating rate of 20 °C/min enables detailed resolution of thermal events such as onset and peak degradation temperatures, which is essential for accurate activation energy profiling using model-free methods. This rate aligns with laboratory-scale pyrolysis and staged gasification setups, where controlled thermal ramping is critical for characterizing feedstock behavior and optimizing reaction kinetics [37,38]. Conversely, the 40 °C/min heating rate simulates moderate thermal acceleration typical of industrial systems such as fluidized bed gasifiers, rotary kilns, and modular waste-to-energy reactors. It offers a realistic representation of

throughput-driven environments where rapid conversion is desired without compromising analytical clarity [35,39]. By avoiding excessively high heating rates, often associated with thermal lag and overlapping decomposition peaks, this study ensures that the kinetic and thermal data remain both scientifically robust and practically translatable. Together, these heating rates support applications ranging from reactor design and feedstock blending strategies to predictive modeling of energy recovery systems. They also provide a comparative framework for evaluating co-gasification performance under conditions that mirror both experimental and industrial thermal regimes. Air (N₂O₂ (80/20)) was used as a gasifying agent at a flow rate of 50 mL/min, introduced from below the pan and exiting at the top. In the top-loading TGA configuration, a stem support rod holds both the feedstock pan and the thermocouple above the balance. Instrument parameters and heating control were managed using STA 449 F3 Jupiter v8.0.3 software (NETZSCH, Dresden, Germany). The thermocouple enabled real-time temperature monitoring of the feedstock, which was recorded against corresponding mass losses to generate a thermogram. Thermogram analysis, including onset temperature, end temperature, and residual mass, was performed using a NETZSCH Proteus Analyzer v8.0.3 (NETZSCH, Germany). Activation energies were estimated from the TG thermograms using NETZSCH Kinetic Neo Software version 2.6.6 (Dresden, Germany) applying the Friedmann, KAS, and Numerical Optimization models. All experiments were conducted in triplicate to ensure reproducibility.

2.2.2. Activation Energy Determination

The activation energy (E_a) of the feedstocks was determined using the TG Data at heating rates of 20 and 40 °C/min. During the heating process, several phase transitions occur, including glass transition, crystallization, curing, melting, and decomposition [40]. TG Data enable the calculation of reaction order, activation energy, pre-exponential factor, and the rate constant [41]. It provides insight into mass changes during decomposition, which are dependent on both time and temperature. The derivative thermogravimetric (DTG) curve, representing the first-order derivative curve of the TG curve, reveals the shape and positions of peaks, which can be used to determine reaction rates. The Arrhenius equation describes the temperature dependence of the reaction rates. By plotting $\ln K$ versus $1/T$ (where K is the rate constant and T is the temperature in Kelvin), a linear relation can be obtained and a slope of the graph determined. This slope is $-E_a/R$, where R is the ideal gas constant and E_a is the activation energy [42]. Three comparative kinetic models were employed in this study to analyze activation energies across various conversion rates and temperatures: the Friedmann method, Kissinger–Akahira–Sunose method, and the Numerical Optimization model were used in this study to analyze the activation energies. Details of these models are presented in Table 3.

Table 3. Models for the kinetic analysis.

Method	Equation	Plot	Slope	Reference
Friedmann	$\ln RR = -\frac{E_a}{RT} + \ln A \cdot f(\alpha)$	$\ln R$ against $\frac{1}{T}$	$-\frac{E_a}{R}$	[43,44]
Kissinger–Akahira–Sunose (KAS)	$\ln \frac{\beta}{Ta^2} = \ln \left(\frac{AR}{E_a g(a)} \right) - \frac{E_a}{RT}$	$\ln \frac{\beta}{Ta^2}$ against $\frac{1}{T}$	$-\frac{E_a}{R}$	[45–47]
Numerical Optimization	$\ln RR = -\frac{E_a}{RT} + \ln A \cdot f(\alpha)$			[48]

Here, β = constant heating rate (°C/min); T = temperature (°C); a = conversion rate (min^{-1}); A = pre-exponential factor (s^{-1}); R = ideal Gas constant (8.314 J/(mol·K)); E_a = activation energy (kJ/mol); and $f(\alpha)$ = function of kinetic mechanism (in this case, the conversion degree)(dimensionless). The Numerical Optimization model-free method is specific to Kinetic Neo Software. It is based on the Friedmann method. The method searches for the optimal functions for E_a and $\log A$ to obtain the best fit for the conversion.

2.2.3. Statistical Analysis

Two-way ANOVA statistical analyses were performed using IBM SPSS Statistics Software 29.0.2.0 (IBM, Armonk, NY, USA). The objective was to evaluate the effects of the blending ratio and heating rate on three dependent variables: onset temperature, end temperature, and residual mass. Additionally, interaction effects between blending ratio and heating rate were assessed for each of these variables to determine their combined influence on thermal behavior.

3. Results

3.1. Thermal Parameters for Individual Feedstocks

The thermal behavior of PP, CB, and WB at heating rates of 20 °C/min and 40 °C/min was characterized using a thermogravimetric analyzer under oxidative conditions. Onset temperature is defined as the point on the TGA curve where a deflection from the baseline is first observed prior to a thermal event [49], while end temperature represents the maximum temperature at which mass loss ceases, beyond which no further decomposition is recorded. The first derivative (DTG) of the TGA curve is used to identify the peak temperature associated with each mass loss event and to delineate the decomposition stages of the material. DTG analysis also enables the evaluation of volatile components present at every mass loss peak based on the temperatures [50]. The TG/DTG thermograms for PP, CB, and WB at both heating rates of 20 and 40 °C/min are presented in Figure 1a–d.

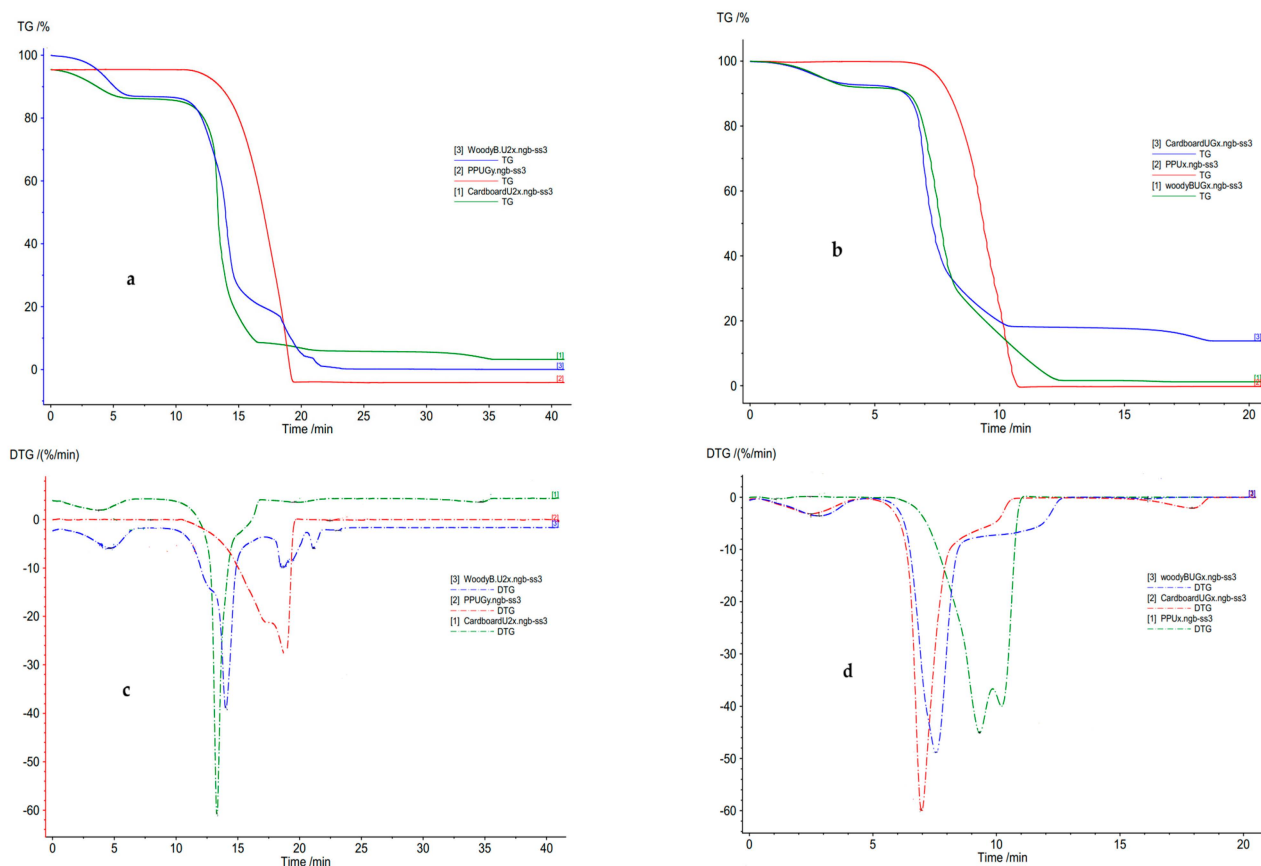


Figure 1. TG/DTG thermograms for individual components (a) TG for 100% PP, CB, and WB at 20 °C/min; (b) TG for 100% PP, CB, and WB at 40 °C/min; (c) DTG for 100% PP, CB, and WB at 20 °C/min; (d) DTG for 10% PP, CB, and WB at 40 °C/min.

For PP, increasing the heating rate from 20 to 40 °C/min resulted in a shift in the thermogram toward higher temperature ranges. At both heating rates, PP exhibited a

single-step degradation as indicated by a dominant peak observed in the DTG curves (a). At 20 °C/min, the mean onset and end temperature were 350.2 °C and 432.2 °C, respectively (Figures 2a and 3a). At 40 °C/min, these values increased to 372.1 °C and 495.4 °C, respectively (Figures 2b and 3b). Under both heating rates, PP underwent near-complete degradation with residual mass recorded at less than 2% (Figure 4a,b).

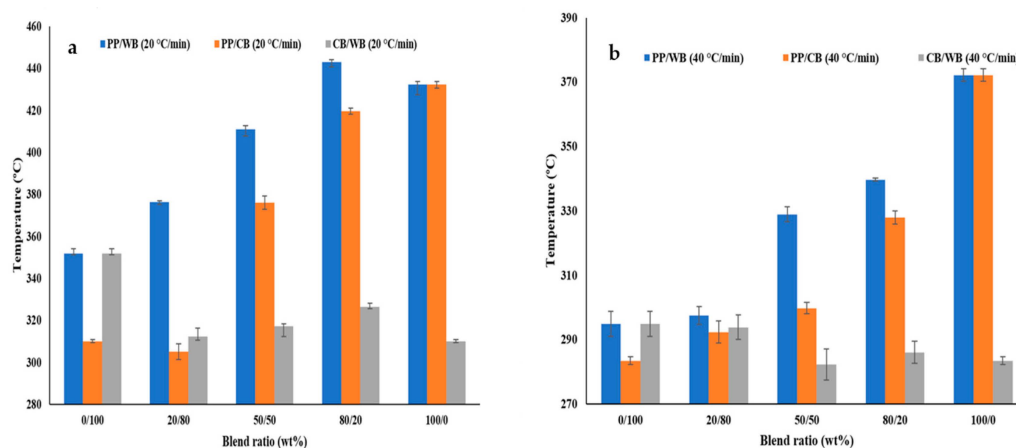


Figure 2. Onset temperatures for PP/WB, PP/CB, and CB/WB at various blend ratios at heating rates of (a) 20 °C/min and (b) 40 °C/min.

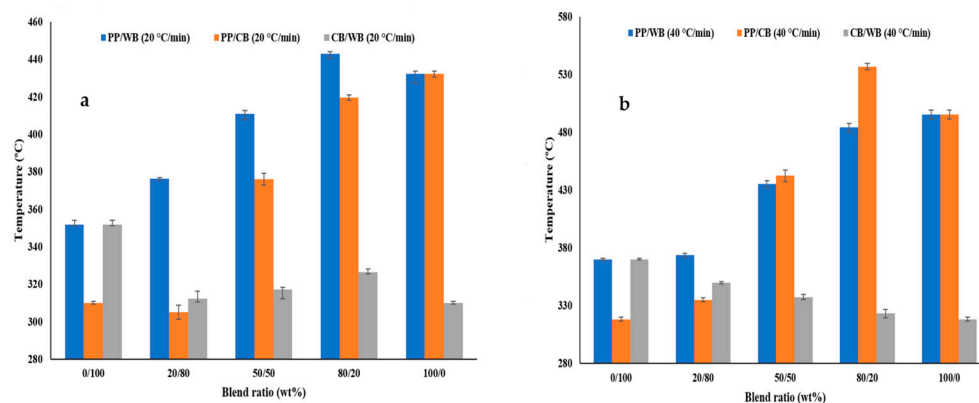


Figure 3. End temperatures for PP/WB, PP/CB, and CB/WB at various blend ratios at heating rates of (a) 20 °C/min and (b) 40 °C/min.

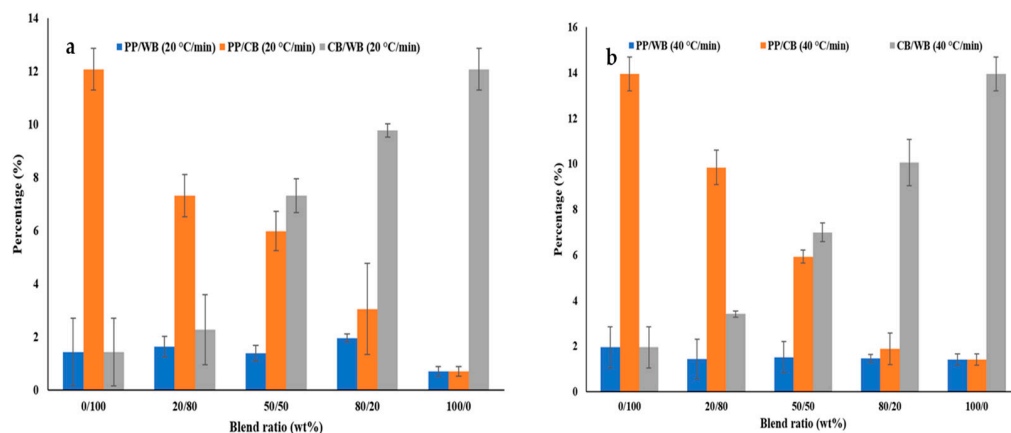


Figure 4. Residual mass for PP/WB, PP/CB, and CB/WB at (a) 20 °C/min and (b) 40 °C/min.

For WB and CB, three distinct degradation regimes were observed in the DTG curves at both heating rates (b and c). The first mass loss event occurs below 100 °C, followed

by a second regime between 315 and 320 °C, and a third regime between 400 and 440 °C. The final mass loss corresponds to the oxidation of remaining char after volatile matter removal [51]. As with PP, increasing the heating rate shifted the thermogram of CB and WB into higher temperature ranges. For WB, the mean onset and end temperatures at 20 °C/min were 283.4 °C and 351.8 °C, respectively (Figures 2a and 3a), while at 40 °C/min, they increased to 294.9 °C and 370.0 °C (Figures 2b and 3b). For CB, the mean onset and end temperatures at 20 °C/min were 292.2 °C and 310.9 °C, respectively (Figures 2a and 3a), and at 40 °C/min, they were 283.5 °C and 318.1 °C, respectively (Figures 2b and 3b). Residual mass for WB remained low across both heating rates, ranging between 1.4 – and 2%. In contrast, CB exhibited significantly higher residual mass (~12%) at both heating rates (Figure 4a,b).

3.2. Thermal Parameters of Blended Feedstocks

For PP/CB blends, a consistent increase in onset temperatures was observed with rising PP content at both heating rates (Figure 2a,b). Specifically, onset temperatures increased from 292.20 °C to 350.20 °C at 20 °C/min, and from 283.50 °C to 372.13 °C at 40 °C/min, corresponding to blends ranging from 20% PP to pure PP. Statistical analysis confirmed that increasing PP mass significantly elevated onset temperatures across both heating rates and blend ratios ($p < 0.05$). Similarly, end temperatures for PP/CB blends increased with higher PP content, a trend evident at both heating rates (Figure 3a,b). The increase was also statistically significant ($p < 0.05$) for both heating rate and blend ratio effects. Residual mass decreased with increasing PP content, from 7% at 20% PP to below 2% for pure PP (Figure 4a). The effect of blend ratio on residual mass was statistically significant with $p < 0.05$, while the effect of heating rate alone was statistically insignificant ($p > 0.05$). However, the interaction between heating rate and blend ratio was significant with $p > 0.05$, indicating a combined influence on residual mass.

For PP/WB blends, similar trends were observed. Increasing the PP content led to higher onset temperatures overall. Onset temperatures rose from 283.40 °C to 350.23 °C at 20 °C/min, and from 294.87 °C to 372.13 °C at 40 °C/min (Figure 2a,b). Comparatively, onset temperatures were higher at 40 °C/min across all blend ratios. End temperatures for PP/WB also increased with rising PP content, mirroring the pattern seen in PP/CB blends (Figure 3a,b). These increases were statistically significant ($p < 0.05$) across both heating rates and blend ratios. Given that both PP and WB exhibited low residual individually, increasing PP content in PP/WB blends did not significantly affect the residual mass. Across all PP/WB blends, the residual mass ranged between 1 and 3% with no consistent increasing or decreasing trend (Figure 4a,b).

For the CB/WB blends, onset temperature at both heating rates showed no notable variation with changing blend ratios. Across all compositions, onset temperatures ranged from 280 to 297 °C (Figure 2a,b). At 20 °C/min, the onset temperature increased from 283.4 °C for pure WB to 292 °C for pure CB. Conversely, at 40 °C/min, pure WB recorded an onset temperature of 294.8 °C, while pure CB showed a lower value of 283.5 °C. Increasing CB content generally resulted in reduced end temperatures at both heating rates (Figure 3a,b). A positive correlation was observed between increasing CB and a higher residual mass value, which ranged from 1% to 12–14% for pure CB across both heating rates (Figure 4a,b). Overall, the effect of blending CB with WB was statistically significant ($p < 0.05$) with respect to residual mass. However, the interaction effect between blend ratio and heating rate was statistically insignificant ($p > 0.05$).

3.3. Kinetic Analysis for Individual Feedstocks and Blends

In the second phase of this study, the activation energies (E_a) of individual feedstocks and their blends under oxidative conditions were investigated. Activation energy represents the minimum energy required for reactants to transition into products, with higher E_a values indicating greater energy barriers to reaction [52]. E_a values were evaluated using NETZSCH Kinetic Neo Software 2.6.6 (NETZSCH, Germany). The model-free kinetic methods applied included the Friedmann, Kissinger–Akahira–Sunose (KAS) method, and the Numerical Optimization (Num. Op.) model. Table 4 summarizes the E_a of individual PP, CB, and WB across a conversion range of $\alpha = 10$ –90%. The corresponding plots of E_a versus conversion (%) are presented in Figures 5–7.

Table 4. Activation energies of individual feedstocks using model-free isoconversional methods.

		Conversion Rate (%)									Mean (kJ/mol)
Models		10	20	30	40	50	60	70	80	90	
Friedmann	PP ($r^2 = 0.9966$)	120.10	68.90	54.25	57.80	77.22	81.81	54.61	32.82	17.99	63.70
	CB ($r^2 = 0.9947$)	59.33	73.21	130.89	121.62	110.79	157.78	181.69	102.98	107.80	116.20
	WB ($r^2 = 0.9998$)	231.51	262.71	304.84	200.09	95.54	59.61	54.13	36.25	9.12	139.31
KAS	PP ($r^2 = 0.8753$)	84.22	60.49	59.86	48.32	64.31	66.62	50.21	40.26	34.74	56.36
	CB ($r^2 = 1.0000$)	73.21	99.13	117.98	146.49	160.81	165.59	162.51	141.13	45.50	113.48
	WB ($r^2 = 0.9980$)	125.74	190.6	235.678	227.37	169.38	120.31	85.36	54.83	36.56	138.43
Num. Op.	PP ($r^2 = 0.9998$)	119.66	68.49	53.76	57.93	77.72	81.47	54.92	32.88	17.99	63.89
	CB ($r^2 = 0.9964$)	58.71	140.10	120.50	122.30	111.54	158.61	120.48	108.66	107.48	116.27
	WB ($r^2 = 0.9999$)	231.31	262.76	304.94	200.09	95.54	59.62	54.02	36.02	9.06	139.26

Under oxidative conditions, the activation energy of PP was evaluated using the Friedmann, KAS, and Num. Op models. The mean E_a values calculated were 63.7 kJ/mol (Friedmann), 56.4 kJ/mol (KAS), and 63.9 kJ/mol (Num. Op.) with corresponding R^2 values of 0.99661, 0.87527, and 0.99978, respectively. The Friedmann and Num. Op. models showed good agreement, whereas the KAS model yielded a slightly lower E_a .

For WB, all three models produced closely aligned results with the mean E_a values of 139.309 kJ/mol (Friedmann), 138.429 kJ/mol (KAS), and 139.261 kJ/mol (Num. Op.) and a high R^2 of 0.99984, 0.99803, and 0.99997, respectively. Similarly, for CB, the models were in good agreement with mean E_a values ranging from 113.483 kJ/mol to 116.270 kJ/mol and R^2 values of 0.99470 to 1.0000.

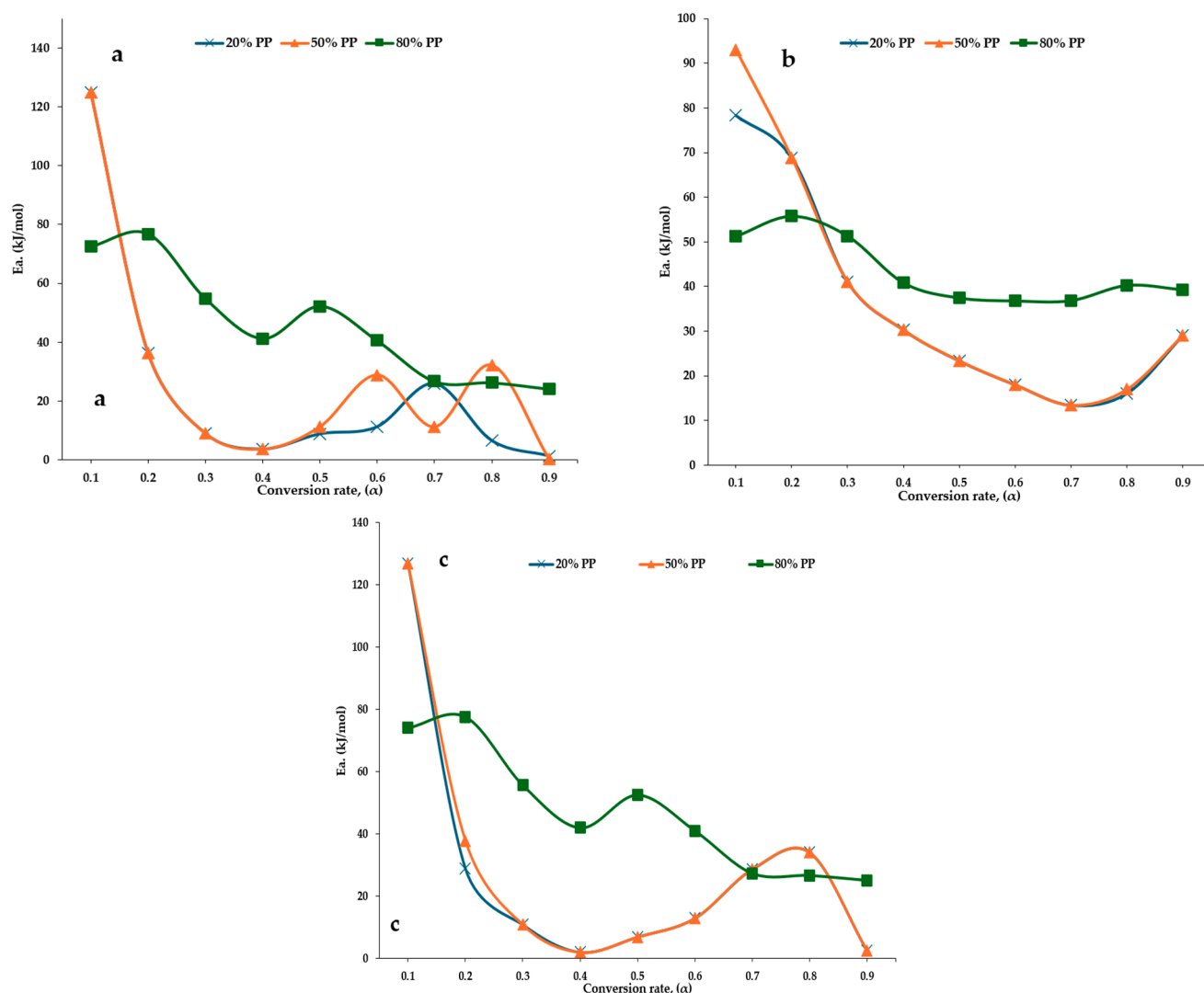


Figure 5. E_a for PP/CB blends using model-free methods: (a) Friedmann model, (b) Kissinger–Akahira–Sunose, and (c) Numerical Optimization.

3.4. Activation Energies of the Blended Feedstocks

The influence of feedstock blending on activation energy (E_a) was further investigated using the same three model-free kinetic methods: Friedmann, KAS, and Num. Op. Table 5 presents the mean E_a across a conversion range of $\alpha = 0.1$ – 0.9 for various blend ratios of PP/CB, PP/WB, and CB/WB under thermal oxidative conditions. Figures 5–7 illustrate the variation in E_a across conversion rates for each blend, as determined by the three kinetic models.

Table 5. Mean activation energies of blended feedstocks using model-free isoconversional methods.

Blend	Blend Ratio (w/w%)	Model	R ² Value	Mean E_a (kJ/mol)
PP/CB	20/80	Friedmann	0.9932	22.54
		KAS	1.0000	35.41
		Num. Op.	0.9952	26.21
	50/50	Friedmann	0.9932	27.83
		KAS	1.0000	37.14
		Num. Op.	0.9952	27.22
	80/20	Friedmann	0.9735	46.17
		KAS	1.0000	43.32
		Num. Op.	0.9983	46.96

Table 5. Cont.

Blend	Blend Ratio (w/w%)	Model	R ² Value	Mean Ea (kJ/mol)
PP/WB	20/80	Friedmann	0.9932	25.39
		KAS	1.0000	37.14
		Num. Op.	0.9952	27.21
	50/50	Friedmann	0.9988	82.89
		KAS	1.0000	66.00
		Num. Op.	0.9992	83.72
	80/20	Friedmann	0.9610	55.10
		KAS	1.0000	63.28
		Num. Op.	0.9860	50.83
CB/WB	20/80	Friedmann	0.9979	32.40
		KAS	0.9999	48.76
		Num. Op.	0.9987	32.97
	50/50	Friedmann	0.9982	79.42
		KAS	0.9999	82.90
		Num. Op.	0.9986	80.56
	80/20	Friedmann	0.9981	101.89
		KAS	0.9995	102.02
		Num. Op.	0.9983	102.25

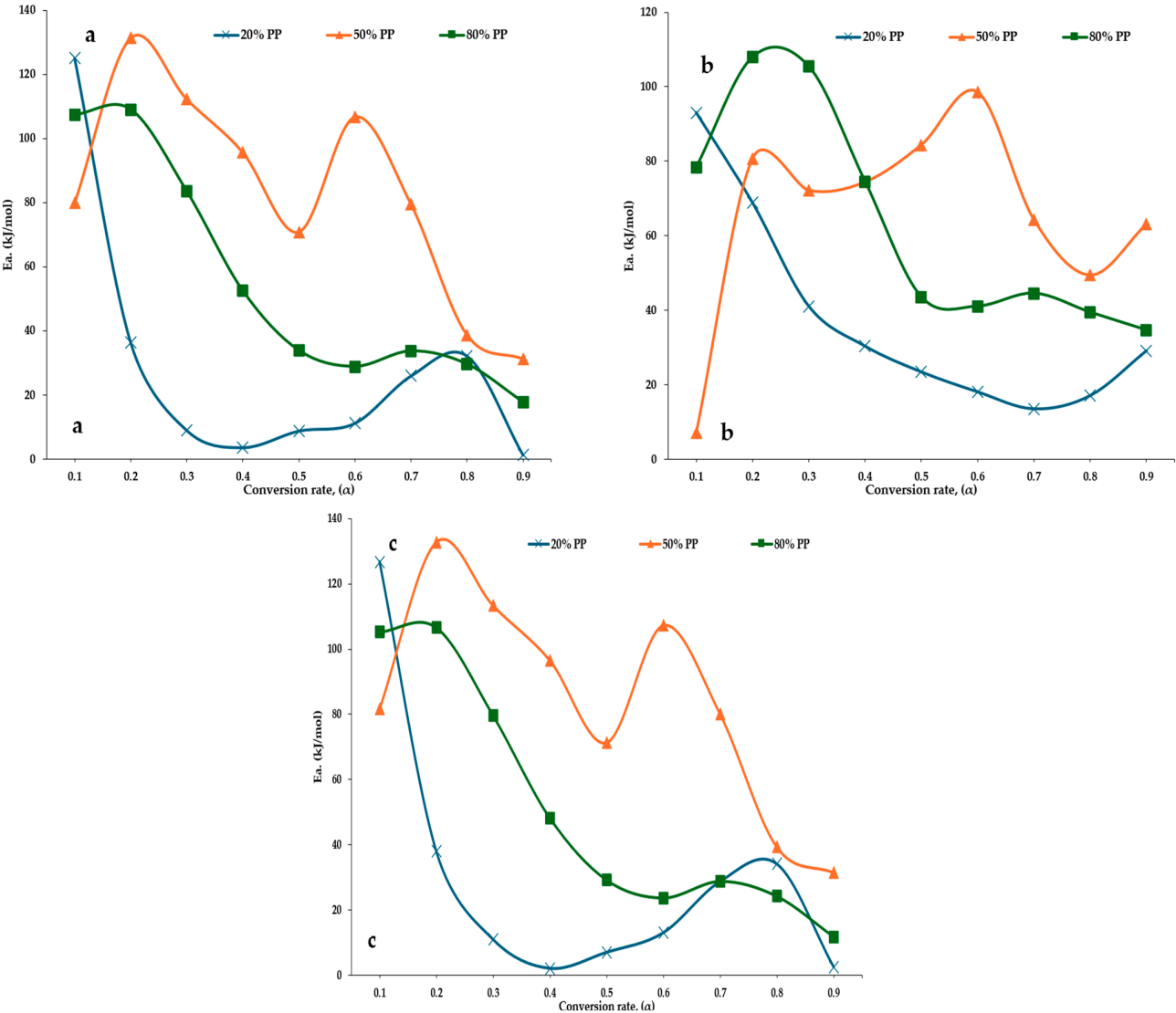


Figure 6. Ea for PP/WB blends using three model-free methods: (a) Friedmann, (b) KAS model, (c) Numerical Optimization.

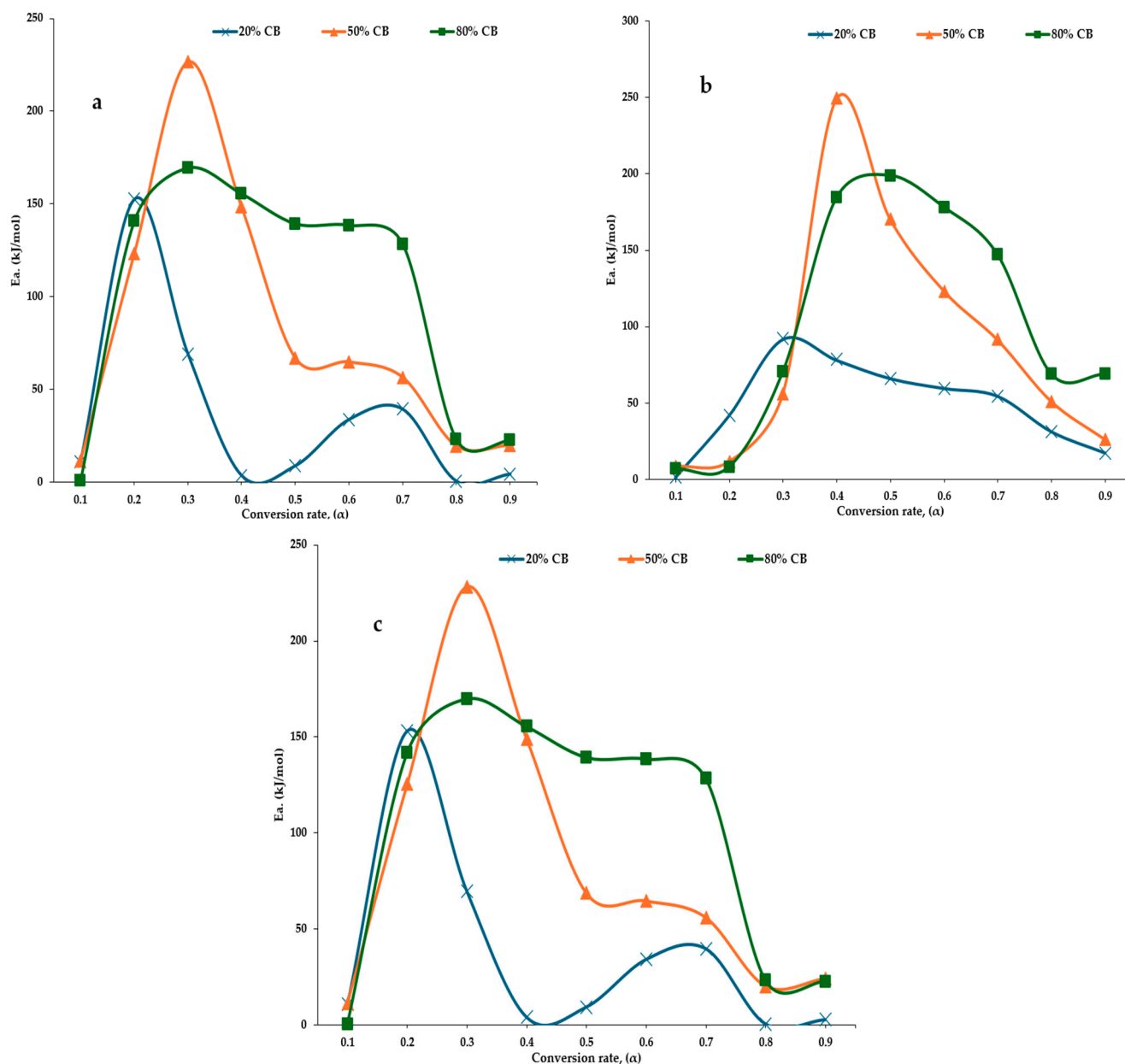


Figure 7. E_a for CB/WB blends using three model-free methods: (a) Friedmann, (b) KAS model, (c) Numerical Optimization.

In PP/CB blends, an increase in mean E_a was observed with rising PP content. The Friedmann and Num. Op. models showed strong alignment, with mean E_a ranging from 22.5 kJ/mol (20% PP) to 46.2 kJ/mol (80% PP) for the Friedmann model. The KAS model yielded slightly higher E_a values at 20% and 50% PP (~35–37 kJ/mol), but was consistent with the other models at 80 wt% PP, recording 43.3 kJ/mol (Table 5). Across all models, peak E_a in PP/CB was recorded at the initial stage of decomposition ($\alpha = 0.1$), particularly for 20% and 50% PP compositions (Figure 5). A general downward trend in E_a was observed as conversion progressed. The blend with the highest overall mean E_a was the 80/20 (PP/CB) composition with E_a values of 46.166, 43.318, and 46.961 kJ/mol for Friedmann, KAS, and Num. Op. models, respectively.

For PP/WB blends, mean E_a ranged from 25.4 kJ/mol (20% PP) to 55.1 kJ/mol (80% PP) using the Friedmann Model. Notably, the highest mean E_a values across all three models were recorded at 50% PP, with 82.9 kJ/mol (Friedmann), 66.0 kJ/mol (KAS), and 83.7 kJ/mol (Num. Op.) (refer to Table 5). Peak E_a values were observed early in the

decomposition process ($\alpha = 0.1$ – 0.2), following a general decline with increasing conversion for both Friedman and Num. Op models (Figure 6). For the 50% PP blend, a distinct pattern emerged with peak E_a at $\alpha = 0.2$ and a second peak at $\alpha = 0.6$ across all models. Overall, the 50/50 blend exhibited the highest mean E_a values of 82.895, 66.004, and 83.724 kJ/mol for the Friedmann, KAS, and Num. Op. models, respectively.

In the CB/WB blends, a consistent increase in mean E_a was observed with rising CB content across all models (Table 5). E_a values ranged from 32.96 kJ/mol (20% CB) to 102.25 kJ/mol (80% CB) for the Num. Op. model, 48.76 kJ/mol to 102.02 kJ/mol for the KAS model, and 32.40 kJ/mol to 101.89 kJ/mol for the Friedmann model (Table 5). The E_a profiles across the decomposition range were similar for all models (Figure 7), typically, starting low and peaking between $\alpha = 0.2$ to 0.4 . The highest peak E_a values (~226–250 kJ/mol) were recorded for the 50% CB blend at $\alpha = 0.3$ – 0.4 . However, the highest overall mean E_a was observed in the 80/20 blend, with values of 101.894, 102.015, and 102.250 kJ/mol for the Friedmann, KAS, and Num. Op. models, respectively. Across all blends and models, statistical correlation was good, with R^2 factor all >0.96 for a conversion range of $\alpha = 0.1$ – 0.9 .

4. Discussion

4.1. Thermal Parameters

During the oxidative decomposition of PP, CB, WB, and their blended ratios (PP/WB, PP/CB, and CB/WB), onset and end temperatures as well as residual masses were investigated. TGA provided valuable insight into the thermal behavior of these feedstocks. For PP, increasing the heating rate resulted in elevated onset and end temperatures. This effect is attributed to shorter retention times at higher temperature rates, which limit molecular motion prior to decomposition [53]. The degradation of PP is further influenced by radical random scission, a mechanism commonly associated with the thermal breakdown of olefins [54]. Consequently, PP decomposition is influenced by both time and temperature factors.

For WB and CB, the DTG curves revealed three distinct mass loss events. The first regime, occurring below 100 °C, corresponds to moisture release, the volatilization of light compounds and other dehydration reactions within the feedstock [55]. The second regime, around 315–320 °C, represents the primary mass loss event, attributed to the oxidation and removal of the volatile matter. The third regime, observed between 400 and 440 °C, involved the oxidation of residual char following volatile matter removal [51]. Given that WB and CB are primarily composed of hemicellulose, cellulose, and lignin, their similar mass loss profiles are expected. These components decompose within overlapping temperature ranges: hemicellulose (150–250 °C), cellulose (250–400 °C), and lignin (280–450 °C) [56–58]. These overlapping decomposition intervals form the core mass loss regime for both WB and CB. An increase in heating rate led to higher onset and end temperature. At lower heating rates, heat release occurs more gradually, allowing for more effective water removal from the feedstock. In contrast, higher heating rates initiate decomposition more rapidly, limiting the time available for complete moisture diffusion. As a result, the drying phase is significantly influenced by the internal diffusion of water within the biomass structure [59].

When PP was blended with either CB or WB, both onset and end temperatures increased with rising PP content. Conversely, residual masses decreased with increasing PP mass, consistent with trends observed in other blends. A study by Chen et al. [60] confirms the low-to-negligible residual mass of waste PP following thermal degradation at 1000 °C. This minimal residue is characteristic of PP and other polyolefins, and this can be attributed to several factors: (1) the use of neutralizing agents during manufacturing to stabilize the low chloride ash levels, (2) the inherently low inorganic content compared to

natural feedstocks, and (3) the inclusion of additives such as antioxidants, antistatic agents, slip agents, and UV stabilizers to enhance PP's resistance to thermal degradation [61,62].

In PP/WB blends, the observed increase in temperature at higher heating rates is likely due to heat transfer limitations caused by temperature gradients between the particle surface and its core, which restricts the release of volatiles [63]. The rise in temperature with increasing PP mass is attributed to the enhanced thermal stability of the blend, driven by PP's high-temperature resistance [64]. Interestingly, even a small proportion of wood in PP can significantly increase its thermal stability. This aligns with findings by Poletto et al. [65], who studied PP/wood fiber composites (70/30 wt%) heated to 700 °C without additives. The PP/WB blend recorded a maximum temperature of 451 °C, compared to 439 °C for pure PP [65]. Similarly, Stančin et al. [66] investigated PP/sawdust blends (a mixture of fir, oakwood, and beech wood) and observed elevated end temperatures at higher heating rates, at 25% PP blend compared to pure PP. Specifically, pure PP recorded end temperatures of 445 °C, 455 °C, 470 °C, and 475 °C at heating rates of 5 °C/min, 10 °C/min, 20 °C/min, and 30 °C/min, respectively, while the 25% sawdust blend recorded higher values of approximately 470 °C, 480 °C, 490 °C, and 500 °C under the same conditions [66]. These findings, along with results from the present study, suggest that even minimal wood biomass inclusion can enhance the thermal stability of PP. Notably, heating rate had a limited effect on final residual mass, accounting for less than a 3% change. The broader decomposition temperature ranges and shifts to higher temperatures observed in this study have also been reported in other investigations involving PP-rich feedstock blends [66–68].

In the CB/WB blends, the most pronounced effect was on the residual mass, which increased with higher CB content. This is likely due to the elevated inorganic content of CB. Leyssens et al. [69] reported a dry-basis ash content of 7.7 wt% in cardboard, compared to 0.2 wt% in milled wood. When blended at 50/50 wt% and 74/26 wt% CB/WB ratios, residual mass increased to 3.9 wt% and 6.2 wt%, respectively. The high residual mass in CB may be attributed to (1) chemical residues from the manufacturing process, (2) mineral matter formed during pulp production, (3) metallic contaminants from piping and machinery, and (4) added inorganic materials such as fillers, coatings, and pigments. The final residue content is influenced by these factors, as well as operational parameters such as temperature and feedstock size [70].

4.2. Activation Energy

In this phase of the study, Ea values were calculated for the thermal oxidative treatment of PP, WB, CB, and their blends using three model-free kinetic models: the Friedmann, KAS, and Num. Op. models. For PP, the Friedmann and Num. Op. models yielded closely aligned mean Ea values of 63.7 kJ/mol and 63.9 kJ/mol, respectively, while the KAS model produced a slightly lower one at 56.4 kJ/mol. Comparative literature reveals a wide range of Ea values for PP, depending on the kinetic model and experimental conditions. Mohammad et al. [71] using the Freeman–Carroll approach, recorded an Ea of 306.8 kJ mol^{−1}. Paik and Karl [72] applied multiple kinetic models to PP degradation: the Coats–Redfern technique yielded Ea values of 98, 100, and 108 kJ/mol at heating rates of 5, 10, and 15 °C min^{−1}, respectively; the second Kissinger technique produced Ea values of 76, 120, and 180 kJ/mol; and the first Kissinger method recorded Ea values as high as 229 kJ/mol. These variations underscore the model dependence of Ea estimation [73]. Additionally, recycled PP, used in this study, tends to exhibit lower Ea than virgin PP. Repeated reprocessing breaks down long polymer chains, resulting in lower molecular weight species that are more susceptible to thermal degradation, thereby lowering Ea [74]. Thus, recycled PP may be advantageous in processes where a lower Ea is desirable. Across all three kinetic models, PP consistently exhibited the lowest activation energy values, ranging from approximately 56 to 64 kJ/mol.

This trend reflects PP's relatively simple polymeric structure and low thermal resistance, which facilitate rapid chain scission during oxidative decomposition.

Among the individual feedstocks, WB recorded the highest E_a (~138–139 kJ/mol). The literature reports a broad range of E_a values for wood species under varying conditions. Tsapko et al. [67] reported significantly lower E_a values for pine, hornbeam, and ashwood under pyrolysis: 13.47 kJ/mol, 23.28 kJ/mol, and 19.95 kJ/mol, respectively. Shen et al. [75], using both the global kinetic model and the Distributed Activation Energy Model (DAEM), found E_a values ranging from 180 to 220 kJ/mol under inert conditions and 170 to 235 kJ/mol under oxidative conditions, across conversion rates of 10–85%. These studies were conducted at heating rates of 5 °C/min to 40 °C/min, with the correlation coefficient exceeding 0.9. This elevated thermal threshold is attributed to WB's lignin-rich composition and structural complexity, which slow down devolatilization and char breakdown [76]. Ajourloo et al. (2025) emphasizes that biomass with high lignin content requires more energy for conversion, especially under oxidative co-gasification conditions [77].

Most studies on CB have focused on pyrolysis rather than oxidative conditions. Delgado et al. [55] estimated E_a for torrefied CB under oxidative conditions using the Starink and Coats–Redfern models, reporting values between 80 and 242.3 kJ/mol. CB showed intermediate E_a values, with mean estimates between 113 and 116 kJ/mol across models. These values suggest a more complex thermal degradation pathway than that in PP, likely due to CB's semi-crystalline cellulose content and hydrogen bonding networks, which require greater energy input to initiate and sustain decomposition [78]. Among the iso-conversional methods used in the thermal analysis, the Kissinger–Akahira–Sunose (KAS) technique consistently produced lower activation energy estimates compared to both the Friedman and Num. Op. models, primarily due to its integral formulation and smoothing effects [79]. As an integral method, KAS averages temperature data over a conversion range, which dampens the influence of local fluctuations and experimental noise, factors that often inflate activation energy in differential approaches like Friedman's [79]. The Friedman method calculates activation energy from the slope of $\ln(d\alpha/dt)$ versus $1/T$ at each conversion point, making it highly sensitive to noise and steep conversion gradients, especially in overlapping or multi-step reactions [80]. Numerical Optimization, while more robust and iterative, fits simulated curves to experimental data across multiple heating rates and conversion levels, often capturing mechanistic complexity more accurately but at the cost of higher apparent activation energies due to its precision in resolving reaction steps [81]. In contrast, KAS assumes a relatively constant reaction mechanism and does not deconvolute overlapping processes, leading to smoother and generally lower activation energy profiles [79].

Overall, the trend reveals a clear hierarchy in thermal reactivity: PP < CB < WB. These differences underscore the importance of feedstock selection in co-gasification systems, as E_a directly influences process efficiency, temperature requirements, and residue formation.

Blending studies further illuminate the influence of feedstock composition on E_a . Kabir et al. [82] investigated the thermo-oxidative stability of polyolefins blended with lignocellulosic biomass, finding increased E_a values (112–145 kJ/mol) compared to pure recycled PP (100 kJ/mol), correlating with higher phenolic content and longer oxidation induction times. Stančin et al. [66] attributed increased E_a in PP/wood blends to mutual feedstock interactions that hinder volatile release, delaying decomposition and increasing kinetic energy. Esmizadeh et al. [83] reported E_a values of 150 and 125 kJ/mol for PP blends containing 40% and 60% wood, respectively, compared to 75 kJ/mol for pure recycled PP. Consistent with these findings, the present study observed a higher mean E_a for 50 wt% PP/WB blends than for pure recycled PP. The increase was attributed to the high volatile content from wood degradation, which reduces oxygen diffusion and delays

decomposition, thereby elevating E_a . Feedstock mixtures exhibit distinct decomposition mechanisms, and their heterogeneity significantly influences E_a [66]. Interestingly, while PP/WB blends showed increased E_a , the blending of PP/CB and CB/WB resulted in reduced E_a compared to the pure feedstocks. This suggests that blending alters reaction pathways during gasification, with shifts in E_a indicating the emergence of new dominant mechanisms. Given the wide range of E_a values reported in the literature, largely dependent on experimental conditions and kinetic models, process optimization will require careful selection of blend ratios to achieve the desired outcomes.

5. Conclusions

This study used thermogravimetric analysis to assess the thermal and kinetic behavior of waste polypropylene (PP), woody biomass (WB), and cardboard (CB), both individually and in blends. PP showed high thermal stability and minimal residue (<2%), with small additions of WB enhancing its end temperature. CB retained more residue than WB due to its inorganic content. Higher heating rates shifted decomposition to higher temperatures, influencing reactor design. Waste PP had lower E_a than virgin PP, and blending, especially CB/WB, which further reduced E_a , indicating synergistic reactivity. The recommended ratios include PP/CB (20/80 or 50/50) for reduced energy demand, PP/WB (50/50 or 80/20) for thermal resistance and low residue, and CB/WB (80/20) for high char yield. These synergistic blends enhance combustion efficiency by combining complementary thermal behaviors, such as PP's volatile release and CB's oxygenated groups or CB/WB's lignocellulosic structure, resulting in optimized thermal stability, enhanced char yield, and optimal energy demand in waste-to-energy systems, aligned with circular economy goals.

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