

Multi-model Isoconversional kinetic and pyrolysis behaviour of waste sawdust towards its bioenergy potential

Sonal Vithoba Tarkar

Manipal Academy of Higher Education

Deepraj Sarkar

Manipal Academy of Higher Education

Jyothi Acharya

Manipal Academy of Higher Education

Ranjeet Kumar Mishra

`ranjeet.mishra@manipal.edu`

Manipal Academy of Higher Education

Srinivas Kini

Manipal Academy of Higher Education

Article

Keywords: Waste mixed wood sawdust (WMWS), Pyrolysis, Kinetic analysis, Thermogravimetric analysis (TGA), Bioenergy

Posted Date: September 25th, 2026

DOI: <https://doi.org/10.21203/rs.3.rs-10982176/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Additional Declarations: No competing interests reported.

**Multi-model Isoconversional kinetic and pyrolysis behaviour of waste sawdust towards
its bioenergy potential**

Sonal Vithoba Tarkar, Deepraj Sarkar, Jyothi Acharya, Ranjeet Kumar Mishra*, Srinivas Kini*

Manipal Institute of Technology, Manipal Academy of Higher Education, Manipal, India.

Corresponding author details: ranjeet.mishra@manipal.edu (Ranjeet Kumar Mishra)

Abstract

The study investigates the kinetic, thermodynamic, and thermal degradation behaviour of waste mixed wood sawdust (WMWS) to evaluate its potential as a sustainable bioenergy feedstock. Physicochemical characterisation revealed that WMWS possesses favourable properties, including a high volatile matter content (75.16 wt.%), a low ash content (3.12 wt.%), and a higher heating value (HHV) of 19.11 MJ/kg, indicating strong suitability for thermochemical conversion. Thermogravimetric analysis (TGA) showed a typical three-stage decomposition pattern, with the major degradation occurring between 150 and 550 °C due to the breakdown of hemicellulose and cellulose. The influence of heating rates (10-40 °C/min) showed a shift in peak degradation temperatures and reduced char residue at higher heating rates, indicating enhanced devolatilisation. Furthermore, the kinetic analysis was conducted using multiple model-free methods, including KAS, OFW, FM, ST, DAEM, LT, VZ, and AVZ. The average activation energy ranged from 168 to 187 kJ/mol, confirming the complex, multi-step nature of biomass pyrolysis. The variation in activation energy with conversion validated the presence of overlapping reactions involving hemicellulose, cellulose, and lignin. The pre-exponential factor showed significant variation, reflecting differences in reaction mechanisms and molecular interactions. Thermodynamic parameters indicate that the pyrolysis process is endothermic, with positive enthalpy values and a moderate Gibbs free energy. The findings demonstrate that WMWS is a promising feedstock for bioenergy production, offering efficient thermal decomposition, favourable kinetic behaviour, and good energy potential, thereby supporting its application in sustainable waste-to-energy systems.

Keywords: Waste mixed wood sawdust (WMWS), Pyrolysis, Kinetic analysis, Thermogravimetric analysis (TGA), Bioenergy.

1. Introduction

The search for innovative and sustainable feedstocks has become essential to achieve long-term clean energy goals. Rapid population growth and rising living standards worldwide have significantly increased global energy demand. Conventional energy sources, such as coal and petroleum, are finite and non-renewable, with limited reserves. In addition to concerns about their depletion, these fossil fuels are major contributors to environmental problems, including air pollution, acid rain, and greenhouse gas emissions [1]. Therefore, there is an urgent need to shift toward renewable, environmentally friendly, and sustainable energy alternatives. Transitioning to renewable energy sources can enhance energy security, ensure access for future energy generations, support socio-economic development, and mitigate climate change while minimising ecological damage. Currently, nearly 84% of global energy consumption is still dependent on fossil fuels [2]. However, biomass utilisation as an energy source has been increasing at an annual rate of approximately 2.5% [2]. Waste-derived biomass feedstocks are particularly attractive because such materials are carbon-neutral and contain very low levels of sulfur and nitrogen [2]. Biomass can be converted into energy through several pathways, including biological processes (such as fermentation), direct combustion, and thermochemical conversion techniques. Among these, pyrolysis is a highly efficient thermochemical process carried out in the absence of oxygen at moderate temperatures (450-800 °C) [3]. Pyrolysis produces three primary products: liquid fuel (bio-oil or pyrolysis oil), solid (biochar), and non-condensable gases. Liquid fuel can be refined to resemble conventional petroleum fuels for engine applications, whereas biochar has diverse applications, including wastewater treatment, soil improvement, production of mesoporous activated carbon, carbon sequestration, and use in energy storage devices such as fuel cells and supercapacitors [4,5].

Biomass feedstocks include agricultural crops and their residues, food processing wastes, wood and sawdust, and algae and other aquatic plants. Among these, wood sawdust is a significant by-product of the timber industry. Typically, processing 100 kg of wood generates approximately 12-25 kg of sawdust [2]. Common disposal methods for this waste include open-air burning, dumping at sawmills, and disposal in landfills and water bodies, all of which pose environmental concerns. Therefore, converting sawdust into bioenergy through pyrolysis offers a sustainable solution that addresses both energy production and waste management. Wood sawdust is primarily composed of cellulose, hemicellulose, and lignin, each of which decomposes over distinct temperature ranges. The yield and characteristics of pyrolysis products depend on operating conditions such as temperature, particle size, residence time, and

heating rate [6]. Pyrolysis oil production generally increases with temperature up to an optimal point, while residence time determines the duration of thermal interaction within the reactor. Particle size influences heat and mass transfer efficiency, and heating rate affects product distribution through variations in depolymerisation and secondary cracking reactions [6]. Consequently, a comprehensive understanding of biomass thermal degradation is crucial for optimising product yields and for the effective design and scale-up of a pyrolysis system.

Thermogravimetric analysis (TGA) is widely recognised as a fundamental experimental tool for investigating the thermal decomposition behaviour of biomass. TGA enables the determination of kinetic triplets and thermodynamic parameters as functions of temperature and time. The application of model-free (iso-conversional) methods represents a robust and widely accepted approach for analysing reaction mechanisms and degradation behaviour. It is also employed to evaluate solid yield distribution during torrefaction [7]. A thermogravimetric analyser continuously records mass variation, enabling the detection of rapid weight loss associated with thermal degradation. Two principal approaches are commonly used to interpret biomass degradation kinetics: isothermal (constant-temperature) and non-isothermal (variable-temperature) methods [7]. The non-isothermal approach (Model-free iso-conversional techniques), including methods such as the Friedman, Kissinger-Akahira-Sunose (KAS), Starink, and Flynn-Wall-Ozawa (FWO) methods, offers the advantage of conveniently capturing mass loss over a continuously changing temperature profile. These approaches also allow the estimation of the pre-exponential factor (A) and key thermodynamic parameters, including enthalpy change (ΔH), Gibbs free energy change (ΔG), and entropy change (ΔS). Therefore, non-isothermal analysis is often preferred for more reliable kinetic interpretation under controlled conditions. Several studies have been performed to determine the kinetic parameters of biomass using different model-free methods. Poletto et al. (2012) conducted a kinetic analysis of wood pyrolysis using the FWO method, which yielded activation energy (E_a) values ranging from 175 to 230 kJ/mol across conversion levels ($\alpha = 0.1$ - 0.8), reflecting multi-stage degradation. At low conversion ($\alpha < 0.4$), degradation is governed by diffusion mechanisms, while at higher conversion ($\alpha > 0.5$), it shifts to random nucleation (F1 mechanism). These results highlight the strong influence of biomass composition and cellulose crystallinity on degradation kinetics and thermal stability [8]. Ceylan and Topçu (2014) conducted a kinetic analysis of hazelnut husk using TGA and KAS, FWO, and the Coats-Redfern method. The activation energy varied from 95 to 162 kJ/mol across the conversion ($\alpha = 0.2$ - 0.8), indicating a shift in reaction mechanisms [9]. Kumar et al. (2020) conducted a kinetic analysis of banana (*Musa balbisiana*) trunk using iso-conversional models

(FWO, KAS, Starink, Tang, and Vyazovkin), showing that the activation energy varies significantly with conversion due to multi-component degradation. The average activation energies range from 292.78 to 386.21 kJ/mol, depending on the model applied. Furthermore, the thermodynamic parameters, such as enthalpy (374-389 kJ/mol) and Gibbs free energy (148-225 kJ/mol), confirm the reaction's feasibility and complexity, highlighting the dependence of kinetics on biomass composition and the modelling approach [10]. Arumugam et al. (2024) reported a detailed kinetic analysis of co-pyrolysis using KAS, FWO, Starink, and Friedman methods, yielding average activation energies of 244.94, 231.86, 195.19, and 224.59 kJ/mol, respectively, with high R^2 values (0.96-0.98). The KAS model shows the highest accuracy ($E_a = 369.11$ kJ/mol at $\alpha = 0.7$). Despite strong model fitting, a limited mechanistic interpretation of biomass-plastic interactions is evident [11]. Agnihotri et al. (2024) provide a robust kinetic analysis using iso-conversional methods (KAS, FWO, and Starink), reporting activation energies of 161-163 kJ/mol with high R^2 (0.939-0.999), indicating reliable fitting. Also, thermodynamic results ($\Delta H = 155$ -157 kJ/mol, $\Delta G = 185$ kJ/mol) confirm endothermic behaviour. However, limited mechanistic insight into multi-step degradation reduces critical depth [2]. Despite extensive research on biomass pyrolysis and kinetic modelling, significant gaps remain in understanding the thermal degradation behaviour of heterogeneous waste-derived feedstocks, such as mixed-waste wood sawdust (WMWS). Most existing studies focus on single, limited model-free methods, often neglecting a comparative evaluation of multiple advanced isoconversional approaches across varying heating rates. Additionally, the integration of kinetic, thermodynamic, and mechanistic analyses to elucidate complex multi-step degradation pathways remains insufficient. It was also noted that limited attention has been given to correlating physicochemical properties with kinetic behaviour and energy potential for real waste biomass systems. Furthermore, the application of advanced models such as Vyazovkin and Advanced Vyazovkin, along with Criado master plots for mechanism identification, is still scarce. Therefore, a comprehensive, multi-model kinetic and thermodynamic investigation is essential to improve the reliability of pyrolysis predictions and to support the design and optimisation of efficient waste-to-energy conversion systems.

To address existing research gaps, the study aims to investigate the kinetics, thermodynamics, and thermal degradation behaviour of waste mixed-wood sawdust (WMWS). TGA was performed at heating rates of 10, 20, 30, and 40 °C/min under nitrogen to assess the thermal degradation of the samples. In addition, kinetic studies were done by applying various model-free methods, including KAS, OFW, Friedman, Starink, DAEM, Li-Tang, Vyazovkin, and Advanced Vyazovkin, in order to calculate important kinetic parameters such as activation

energy, pre-exponential factor, and reaction order, which are independent of mechanisms, for a better understanding of decomposition behaviour. Furthermore, Criado master plots were plotted to identify the mechanism of the degradation process. Also, physicochemical characterisation of WMWS was performed to explore their physical and chemical properties. The study provides comprehensive insights into thermal degradation, kinetic behaviour, and product characteristics, demonstrating the potential of these feedstocks for sustainable bioenergy production and clean fuel generation.

2. Materials and methods

2.1. Sample collection and preparations

Waste mixed wood sawdust (WMWS) was obtained from a local wood mill in Uttar Pradesh, India. The collected sample was initially sun-dried for 5-6 days under ambient conditions, then oven-dried at 105 °C overnight to achieve a consistent moisture level. The dried material was pulverised using a laboratory mixer grinder and sieved to obtain a uniform particle size of approximately 800 µm. Finally, the processed sample was stored in airtight plastic bags to prevent moisture uptake prior to further experimentation.

2.2. Physicochemical characterisation of feeds

Characterisation of the feedstock's physical and chemical properties is essential for evaluating its suitability for further applications. Proximate analysis, including volatile matter, fixed carbon, and ash content, was conducted in accordance with ASTM D5142 and D1762-84 standards. Elemental composition (carbon (C), hydrogen (H), nitrogen (N), and sulfur (S)) was determined using a FLASH 2000 elemental analyser (Thermo Fisher Scientific Inc., USA) following ASTM D5373, while oxygen (O) content was calculated by difference. The higher heating value (HHV) was measured using an oxygen bomb calorimeter (Model 1341 Plain Jacket Calorimeter). Furthermore, the biochemical composition, including cellulose, hemicellulose, and lignin, was analysed in accordance with the NREL Laboratory Analytical Procedures. Additionally, the feedstock's bulk density was determined using a measuring cylinder and a digital balance. The CHO index represents the carbon, hydrogen, and oxygen ratios in biomass, indicating its chemical composition and energy potential. It is useful for predicting product distribution, reactivity, and calorific value in biomass pyrolysis. Higher carbon and hydrogen favour bio-oil yield, while higher oxygen content leads to lower energy efficiency and more oxygenated compounds.

$$CHO\ Index = \frac{[2[O]-[H]]}{[C]} \quad (1)$$

The CHO index is calculated from the mole fractions of carbon (C), hydrogen (H), and oxygen (O) and typically ranges from -4 to +4. A negative value indicates a more reduced state with lower oxidation potential, whereas a positive value reflects a higher degree of oxidation. This index significantly influences the fuel's higher heating value (HHV) [11].

2.3. Thermal stability analysis feeds

The thermal stability of the feedstock and the derived char was evaluated using a TGA (TG 209F1 Libra, Netzsch). The samples were loaded into a platinum crucible and heated from 30 to 900 °C at 10, 20, 30 and 40 °C/min under an inert nitrogen atmosphere (50 mL/min). The resulting TG and DTG curves were processed and interpreted using Universal Analysis 2000 software (version 4.5A).

2.4. FTIR analysis of feeds

The functional groups in the sample were identified using FTIR-ATR (IRTracer-100, Shimadzu). A small quantity of the sample was placed directly on the ATR crystal for analysis. The spectra were collected over 400-4000 cm⁻¹, with 64 scans at a resolution of 4 cm⁻¹.

2.5. X-ray fluorescence (XRF) analysis

The inorganic ash residue derived from biomass was analysed via X-ray fluorescence (XRF; XGT-9000SL, HORIBA, Ltd.) for elemental characterisation. Based on the obtained composition, slagging and fouling indices were determined using standard correlations to assess its applicability as a pyrolysis feedstock.

$$\text{Base to Acid Ratio} \left(\frac{B}{A} \right) = \frac{\% [Fe_2O_3 + CaO + MgO + K_2O + Na_2O]}{\% [SiO_2 + TiO_2 + Al_2O_3]} \quad (2)$$

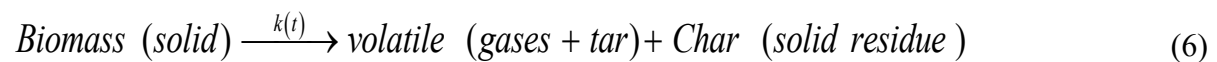
$$\text{Silica to Alumina Ratio} \left(\frac{S}{A} \right) = \frac{\% [SiO_2]}{\% [Al_2O_3]} \quad (3)$$

$$\text{Iron to Calcium Ratio} \left(\frac{I}{C} \right) = \frac{\% [Fe_2O_3]}{\% [CaO]} \quad (4)$$

$$\text{Total Alkalis (TA)} = \% Na_2O + \% K_2O \quad (5)$$

2.6. Kinetic study

Biomass composition varies with geographical origin and is inherently a complex biopolymeric material. Accurately predicting its reaction mechanisms during pyrolysis is challenging because multiple reactions occur simultaneously over very short timescales. Nevertheless, a simplified and generalised representation of biomass decomposition can be expressed as follows:



220 The ultimate form of the equation can be written by integrating the Arrhenius temperature
 221 relationship with the conversion function, as given below:

$$222 \quad g(\kappa) = \int_0^x \frac{dx}{f(x)} = \int_0^T \frac{A}{\delta} e^{-(E/RT)} dT \quad (7)$$

$$223 \quad g(\kappa) = \frac{AE}{\delta R} \int_0^x u^{-2} e^{-u} du = \frac{AE}{\delta R} p(x) \quad (8)$$

224 where $g(\kappa)$ implies integral conversion and $x = \frac{E}{RT}$. The value $p(x)$ is subject to
 225 approximation errors during analysis. In this study, the kinetic parameters of the sample were
 226 evaluated using model-free methods: KAS, FM, OFW, DAEM, ST, LT, VZ and AVZ. Detailed
 227 descriptions of the kinetic formulations are available in earlier work (Mishra & Mohanty,
 228 2020). The kinetic models applied in this study are summarized in **Table 1(a)**.

229 Table 1 (a). Lists of the kinetic models used to calculate the kinetic parameters.

KAS	$\ln\left(\frac{\delta}{T^2}\right) = \ln\left[\frac{AE}{Rg(x)}\right] - \frac{E}{RT}$ (9)
OFW	$\ln(\delta) = \ln\left[\frac{AE}{Rg(x)}\right] - 2.315 - 0.457 \frac{E}{RT}$ (10)
FM	$\ln\left(\frac{dx}{dt}\right) = -\frac{E}{RT} + \ln(Af(x)^n)$ (11)
ST	$\ln\left(\frac{\delta}{T^{1.8}}\right) = C_s - 1.0037 \frac{E}{RT}$ (12)
DAEM	$\ln\left(\frac{\delta}{T^2}\right) = \ln\left(\frac{AR}{E}\right) + 0.6075 - \frac{E}{RT}$ (13)
LT	$\int_0^\alpha \ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = G(\alpha) - \frac{E_\alpha}{R} \int_0^\alpha \left(\frac{1}{T}\right)_{\alpha,i} d\alpha$ (14)
VZ	$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{I(E_\alpha, T_{\alpha,i}) \delta_j}{I(E_\alpha, T_{\alpha,j}) \delta_i}$ (15) <i>The temperature integral is given as.</i>

	$I(E_{\alpha}, T_{\alpha}) = \int_{T_{\alpha-\Delta\alpha}}^{T_{\alpha}} \exp\left(\frac{-E_{\alpha}}{RT}\right) dT \quad (16)$
AVZ	$J(E_{\alpha}, T(t)) = \int_{T_{\alpha-\Delta\alpha}}^{T_{\alpha}} \exp\left(\frac{-E}{RT(t)}\right) dt \quad (17)$
	$\Psi(E_{\alpha}) = \sum_i^n \sum_{j \neq 1}^n \frac{I(E_{\alpha}, T_i(t_{\alpha}))}{I(E_{\alpha}, T_j(t_{\alpha}))} = \min \quad (18)$

n= reaction order, T= absolute temperature (K), β= heating rate (°C/min), R= universal gas constant (J/mol. K), A= pre-exponential factor (1/min), E_α= activation energy (kJ/mol).

2.7. Criado method (CM)

Biomass breakdown involves highly complex mechanisms, as numerous reactions occur simultaneously within a very short time span. In this study, the decomposition behaviours of the biomass were analysed using the Criado method. This approach is applied to identify and control the reaction pathway of the solid matrix due to its higher reliability and consistency, and can be expressed as follows:

$$Z(x) = \frac{\left(\frac{dx}{dt}\right)}{\delta} \pi(x) T \quad (19)$$

Where $x = \frac{E}{RT}$ and $\pi(x)$ is the temperature integral is approximated in a simplified analytical form. The Senum-Yang approximation was applied in this study, which introduces minimal error (on the order of 10⁻⁵ % for x>20). The master curve, expressed as a function of the degree of conversion and corresponding to the modified models listed in **Table 1(b)**, was obtained using Eq. (16).

$$Z(x) = f(x) \times g(x) \quad (20)$$

Further arranging Eq. (16) and (17) equations becomes,

$$Z(x) = \frac{dx}{dT} \times \frac{E_a}{R} \times e^{\frac{E_a}{RT}} \times P(x) \quad (21)$$

Equation (21) is used to construct experimental curves. By comparing these curves with the theoretical ones, the reaction pathways governing the thermal decomposition process can be identified.

Table 1(b). Algebraic expressions for $f(\alpha)$ and $g(\alpha)$ for the most frequently used mechanisms of solid-state processes [12][13].

Reaction mechanisms Order of reaction	Symbols	$f(\alpha)$	$g(\alpha)$
First order	F_1	$(1-\alpha)$	$-\ln(1-\alpha)$
Second order	F_2	$(1-\alpha)^2$	$(1-\alpha)^{-1}-1$
Third order	F_3	$(1-\alpha)^3$	$[(1-\alpha)^{-2}-1]/2$
Diffusion			
One-way transport	D_1	$0.5x$	α^2
Two-way transport	D_2	$[-\ln(1-\alpha)]^{-1}$	$\alpha+(1-\alpha)\ln(1-\alpha)$
Three-way transport	D_3	$1.5(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$	$[1-(1-\alpha)^{1/3}]^2$
Ginstling-Brounshtein equation	D_4	$1.5[(1-\alpha)^{1/3}-1]^{-1}$	$(1-2\alpha/3)-(1-\alpha)^{2/3}$
Limiting the surface reaction between both phases			
One dimension	R_1	1	α
Two-dimension	R_2	$2(1-\alpha)^{1/2}$	$1-(1-\alpha)^{1/2}$
Three-dimension	R_3	$3(1-\alpha)^{2/3}$	$1-(1-\alpha)^{1/3}$
Random nucleation and nuclei growth			
Two dimensional	A_2	$2(1-\alpha)[- \ln(1-\alpha)]^{1/2}$	$[- \ln(1-\alpha)]^{1/2}$
Three dimensional	A_3	$3(1-\alpha)[- \ln(1-\alpha)]^{2/3}$	$[- \ln(1-\alpha)]^{1/3}$
Exponential nucleation			
Power law, $n=1/2$	P_2	$2\alpha^{1/2}$	$\alpha^{1/2}$
Power law, $n=1/2$	P_3	$3\alpha^{2/3}$	$\alpha^{1/3}$
Power law, $n=1/4$	P_4	$4\alpha^{3/4}$	$\alpha^{1/4}$

2.8. Thermodynamic analysis

Thermodynamic properties in pyrolysis, such as enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS), are essential for understanding reaction feasibility, heat requirements, and system spontaneity. They help determine energy efficiency, reaction pathways, and stability of intermediate and final products. These parameters guide reactor design, optimisation of operating conditions, and prediction of product distribution. The thermodynamic analysis enables better control and improves the efficiency and sustainability of biomass pyrolysis processes. The thermodynamic parameters, including Gibbs free energy (ΔG), enthalpy (ΔH), entropy change (ΔS), and the pre-exponential (frequency) factor (A), were determined using the following relationships:

$$A = \frac{\delta \times E \times e^{\left(\frac{E}{RT_m}\right)}}{RT_m^2} \quad (22)$$

$$\Delta H = E - RT_m \quad (23)$$

$$\Delta G = E + R \times T_m \times \ln\left(\frac{K_B T_m}{h A}\right) \quad (24)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_m} \quad (25)$$

Where A is the frequency factor (1/s), T_m is the peak decay temperature in (K), K_B is the Boltzmann constant, and h is the Planck constant (6.626×10^{-34}).

3. Results and discussion

3.1. Physicochemical characterisation of biomass

The physico-chemical characterisation of Waste Mixed Wood Sawdust (WMWS) was evaluated through proximate, ultimate, and compositional analyses and compared with previously reported lignocellulosic biomass, such as rubber wood sawdust [14], wood sawdust [15], oil palm trunk [14] and wood sawdust [16] in **Table 2**. The results provide significant insights into its suitability for thermochemical conversion, particularly pyrolysis. The moisture content of WMWS was determined to be 6.32 wt.%, which is sufficiently low to minimise energy loss during thermal processing. Biomass with lower moisture content is advantageous as it reduces the energy required

for drying and enhances overall process efficiency [17]. In comparison with previously reported biomasses such as rubberwood sawdust (4.95 wt.%) and oil palm trunk (9.65 wt.%), WMWS exhibits acceptable moisture levels for direct utilisation. Furthermore, the volatile matter (VM) content of WMWS was found to be 75.16 wt.%, indicating a high proportion of thermally labile components. The higher VM is directly associated with an enhanced bio-oil yield during pyrolysis due to increased release of condensable volatiles. This value is comparable to that of other lignocellulosic feedstocks (rubber wood sawdust, oil palm trunk, and wood sawdust), confirming the strong potential of WMWS for liquid fuel production. The ash content of WMWS was relatively lower (3.12 wt.%), which is beneficial for thermochemical applications. The lower ash content of WMWS reduces the likelihood of operational issues such as slagging, fouling, and catalyst deactivation [18]. Compared to other reported biomasses, WMWS exhibits moderate inorganic content, suggesting improved reactor performance and reduced maintenance requirements. The fixed carbon (FC) content was determined to be 15.40 wt.%, indicating its potential for char formation. Fixed carbon indicates the char-forming potential during pyrolysis and contributes to solid residue yield, energy density, and carbon stability. Higher fixed carbon enhances biochar production, improves calorific value, and supports carbon sequestration applications [16]. The VM/FC ratio of 4.88 suggests a predominance of volatile constituents while maintaining adequate carbon content for solid residue formation. The VM/FC ratio significantly influences pyrolysis behaviour, with higher ratios promoting volatile release and bio-oil yield, while lower ratios enhancing char formation and carbon retention [19].

The elemental composition of WMWS revealed carbon, hydrogen, oxygen, and nitrogen contents of 48.65 wt.%, 6.89 wt.%, 43.57 wt.%, and 0.89 wt.%, respectively. The relatively high carbon content contributes to improved calorific value and energy density, making WMWS a promising feedstock for bioenergy applications [13]. The atomic ratio analysis shows that WMWS exhibits balanced fuel characteristics compared to other biomasses (**Fig. 1(a)**). Its H/C ratio (1.69) is comparable to that of oil palm trunk and higher than that of rubber wood, indicating better hydrogen availability and enhanced reactivity for bio-oil formation. The O/C ratio (0.67) is lower than that of wood sawdust (0.98), suggesting improved fuel quality and higher calorific value due to reduced oxygen content. Additionally, the VM/FC ratio (4.88) is slightly lower, indicating a balanced distribution between volatile release and char formation. WMWS demonstrates an optimal combination of reactivity, energy potential, and product yield efficiency compared to the

listed biomasses [20]. The Van Krevelen diagram illustrates the relationship between H/C and O/C ratios, indicating fuel quality and energy potential of the studied biomasses (**Fig. 1(b)**). WMWS exhibits moderate H/C (1.69) and O/C (0.67) ratios, positioning it between high-oxygen wood sawdust and lower-oxygen rubberwood. Compared to wood sawdust, WMWS has a lower oxygen content, improving its calorific value and fuel stability. Although oil palm trunk shows slightly higher H/C, its higher O/C reduces efficiency. The trend indicates that lower O/C and higher H/C enhance heating value; thus, WMWS demonstrates a balanced composition, making it a promising feedstock for efficient pyrolysis and energy production [20]. Biomass with higher H/C ratios generally yields higher liquid fuel yields with improved combustion properties. The O/C ratio of WMWS was 0.67, lower than the reported biomass O/C ratio, indicating better fuel quality. Lower O/C ratios are desirable because they correspond to reduced levels of oxygenated compounds in liquid fuel, thereby improving its stability and calorific value [20]. The nitrogen content is minimal (0.89%), which is advantageous from an environmental perspective as it limits the formation of nitrogen oxides (NO_x) during combustion. The absence of sulphur further enhances its suitability as a clean energy feedstock [21]. The HHV of WMWS was determined to be 19.11 MJ/kg, which is higher than that of reported lignocellulosic biomass, including rubberwood sawdust (17.70 MJ/kg) and oil palm trunk (16.31 MJ/kg). This indicates a high energy potential and highlights WMWS as a viable candidate for renewable energy generation [22].

The CHO index indicates the relative oxidation state of biomass based on its carbon, hydrogen, and oxygen composition. As shown in **Table 2**, WMWS exhibits a CHO index of -0.34, which is comparable to the value reported for wood sawdust (-0.34) and slightly more negative than those of rubber wood sawdust (-0.21) and oil palm trunk (-0.17). A negative CHO index indicates a relatively reduced chemical state, suggesting favourable characteristics for thermochemical conversion [23]. The negative value observed for WMWS is consistent with its relatively high carbon content (48.65 wt.%) and moderate hydrogen content (6.89 wt.%), with an oxygen content of 43.57 wt.%. In comparison, the second reported wood-sawdust feedstock exhibited a positive CHO index of 0.37, indicating a relatively more oxidised composition [23]. The CHO-index values suggest that WMWS has a relatively reduced elemental composition, comparable to other wood-based feedstocks, supporting its suitability for thermochemical conversion. Bulk density plays a significant role in biomass handling and logistics [23]. WMWS exhibited a bulk density of 345.26 kg/m³, which is higher than that of rubberwood sawdust and oil

88 palm trunk. The higher bulk density enhances storage efficiency, reduces transportation costs, and
89 improves feeding consistency in reactors, thereby contributing to overall process optimisation [23].

90 The lignocellulosic composition of WMWS significantly influences its thermal
91 degradation behaviour. The hemicellulose, cellulose, and lignin contents were found to be 24.12
92 wt.%, 46.25 wt.%, and 10.05 wt.%, respectively. Hemicellulose decomposes at relatively lower
93 temperatures (200-350 °C), contributing to the initial release of volatiles. The moderate
94 hemicellulose content in WMWS ensures a steady onset of thermal degradation. Cellulose is the
95 dominant component and decomposes at 300-450 °C, playing a crucial role in bio-oil formation.
96 The higher cellulose content of WMWS suggests strong potential to produce high yields of
97 condensable volatiles during pyrolysis. Finally, lignin decomposes over a broader temperature
98 range (200-900 °C) and primarily contributes to char formation [24]. The relatively low lignin
99 content in WMWS suggests higher liquid yields and reduced char production. Its moderate
100 moisture content, high volatile matter, and lower ash content collectively enhance its suitability
101 for thermochemical conversion processes. Moreover, the higher carbon and hydrogen content,
102 along with moderate oxygen levels, support efficient energy conversion and improved fuel quality.

105 Table 2. Physicochemical studies of WMWS were compared with the published literature.

Analysis	WMWS	Rubber wood sawdust [14]	Wood sawdust [15]	Oil palm trunk [14]	Wood sawdust [16]
Proximate analysis (wt.%)					
Moisture	6.32±0.20	4.95±0.02	3.07	9.65 ± 0.03	6.70
Volatile matter	75.16±1.12	77.65±0.36	80.87	74.1 ± 0.3	73.40
Ash content	3.12±0.20	2.10±0.18	3.38	2.3 ± 0.03	5.20
Fixed carbon	15.40±0.20	15.30±0.47	12.68	13.96 ±0.31	14.70
VM/FC	4.88	5.07	6.37	5.31	4.99
Elemental analysis (wt.%)					
C	48.65±0.20	45.43±0.04	46.09	41.63 ±0.17	40.30
H	6.89±0.20	6.01±0.05	7.02	5.99 ± 0.23	5.37
O	43.57±1.20	41.72±0.28	46.39	43.02 ±0.12	53.05
N	0.89±0.18	0.09	0.50	0.15	1.28
S	-	0.07	-	0.10	-
O/C	0.67	0.24	0.75	0.77	0.98
H/C	1.69	1.58	1.83	1.73	1.59
CHO Index	-0.34	-0.21	-0.34	-0.17	0.37
Higher Heating Value (MJ/kg)	19.11±1.20	17.70 ± 0.09	18.67	16.31±0.05	18.24
Bulk density (Kg/m ³)	345.26±4.56	290.40±0.45	-	189±0.27	-

Hemicellulose (wt.%)	24.12±1.20	17.40±0.26	-	20.84 ±0.12	-
Cellulose (wt.%)	46.25±1.20	56.60 ± 0.8	-	46.24 ±0.04	-
Lignin (wt.%)	10.05±1.20	17.56±0.52	-	4.95 ± 0.08	-

106

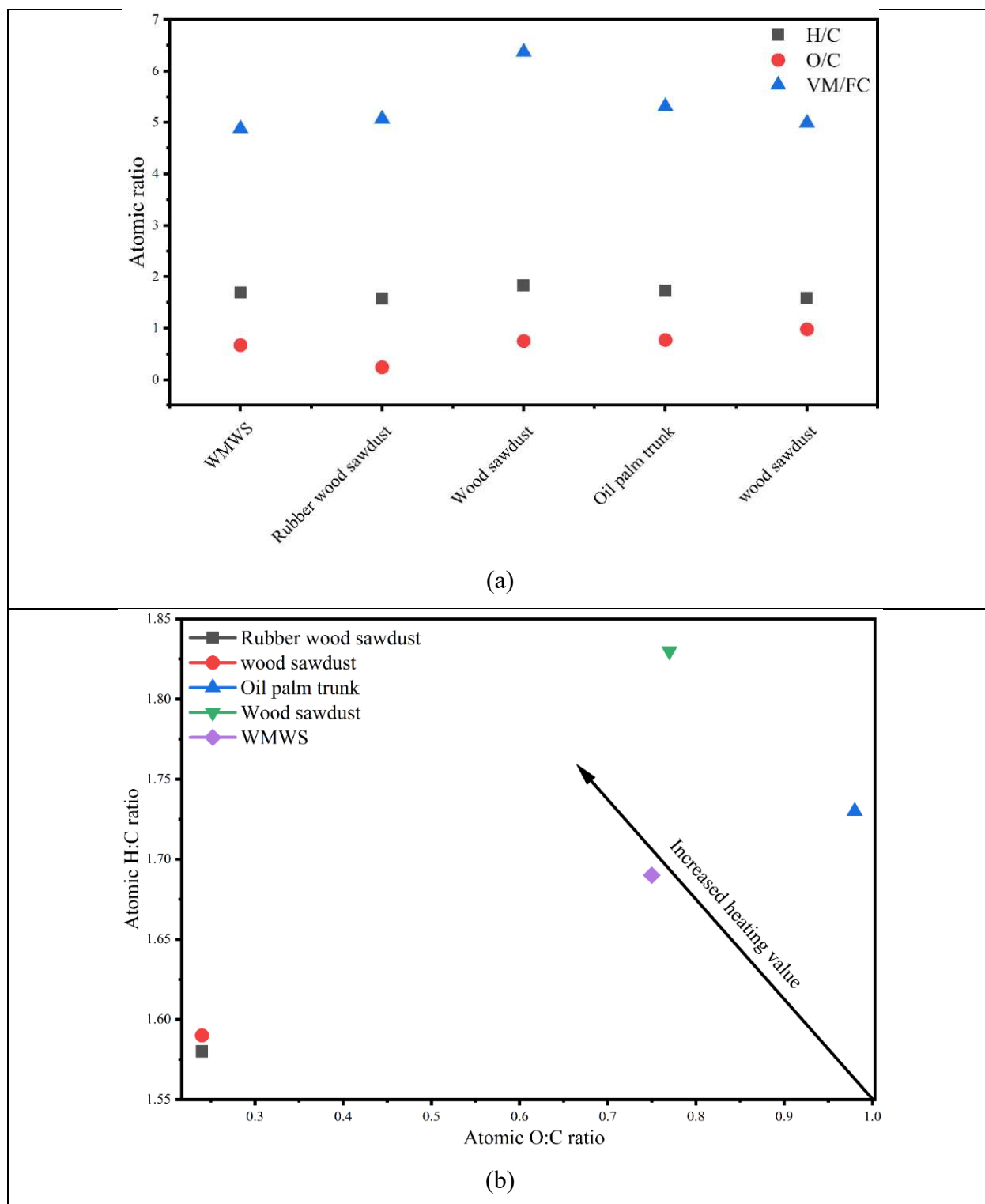


Fig. 1. (a) Comparison of fuel-related physicochemical ratios of WMWS and reference feedstocks, and (b) Van-Krevelen diagram of WMWS, along with other feedstocks.

3.2. XRF analysis

The ash derived from WMWS exhibits a distinct distribution of mineral oxides, which significantly influences its thermochemical behaviour, energy recovery performance, and possible operational challenges during combustion and pyrolysis. The composition of mineral and metallic constituents is detailed in **Table 3**. The major oxides identified include SiO₂ (33.16 wt.%), CaO (27.12 wt.%), Al₂O₃ (10 wt.%), and Fe₂O₃ (11.56 wt.%), along with minor constituents such as K₂O, MgO, Na₂O, and SO₃. It was found that silicon dioxide (SiO₂) is the dominant acidic oxide in WMWS, although its content is significantly lower than rice straw (73.26 wt.%) and peanut shells (56.38 wt.%). The higher silica content is typically associated with slagging resistance but can reduce reactivity. The moderate SiO₂ content in WMWS suggests a balanced behaviour, providing sufficient thermal stability without significantly hindering conversion efficiency [25]. Calcium oxide (CaO) is present in higher concentration (27.12 wt.%) than other biomass, such as rice straw (4.46 wt.%) and corncob (5.59 wt.%). The relatively high CaO content may potentially influence secondary cracking and char reactivity during thermochemical conversion. It also contributes to CO₂ capture and improves overall combustion efficiency [26]. Moreover, results also confirmed that aluminium oxide (Al₂O₃) and iron oxide (Fe₂O₃) are present in notable amounts (10 wt.% and 11.56 wt.%, respectively). These oxides contribute to structural stability and catalytic activity. Fe₂O₃ can enhance redox reactions during thermochemical processes, thereby influencing gas composition and improving conversion efficiency [27]. Alkali metals, such as K₂O (5.10 wt.%) and Na₂O (0.69 wt.%), are present in moderate amounts. The alkali metals can catalyse devolatilization and char gasification reactions; excessive amounts may lead to operational issues such as slagging, fouling, and agglomeration [28]. WMWS exhibits significantly lower alkali content, indicating reduced risk of ash-related problems than corncob (K₂O: 27.55 wt.%). Magnesium oxide (MgO) and phosphorus pentoxide (P₂O₅) are present in smaller amounts and contribute to the catalytic effects and the nutrient value of ash [29]. The presence of SO₃ (5.10 wt.%) indicates the presence of sulphur compounds, which may influence emission characteristics, although the overall sulphur impact remains moderate.

Based on the XRF results and using equations (2-5), the base-to-acid ratio, silica-to-alumina ratio, iron-to-calcium ratio, and total alkali content were determined. The calculated ash indices play a crucial role in governing biomass behaviour during pyrolysis by influencing catalytic activity, product distribution, and ash-related issues. The base-to-acid ratio (B/A = 0.995)

indicates a balanced distribution of basic and acidic oxides, suggesting moderate intrinsic catalytic activity [29]. Basic oxides such as CaO, K₂O, and Na₂O promote secondary cracking of volatiles, leading to increased formation of permanent gases and char while reducing the yield of condensable bio-oil. The high silica-to-alumina ratio (S/A=3.316) reflects a silica-rich ash composition [28]. Silica is relatively inert compared to alumina; therefore, a higher S/A ratio reduces the catalytic upgrading of pyrolysis vapours and may contribute to slagging at elevated temperatures due to its low ash fusion stability. The iron-to-calcium ratio (I/C=0.426) indicates calcium dominance over iron. Calcium improves char stability and can capture CO₂, whereas iron facilitates deoxygenation and gas formation [28]. Hence, lower I/C favours char production with moderate gas evolution. Finally, the high total alkali content (TA=5.79 wt.%) significantly enhances reactivity by accelerating biomass decomposition and volatile cracking.

Table 3. XRF analysis of WMWS ash content obtained from ash content analysis.

Mineral (wt.%)	Waste mixed wood sawdust (WMWS)	Rice straw [30]	Peanut shells [30]	Corn cob [30]
SiO ₂	33.16	73.26	56.38	31.82
Al ₂ O ₃	10.00	0.25	8.73	2.75
CaO	27.12	4.46	8.26	5.59
Fe ₂ O ₃	11.56	0.49	3.87	0.83
K ₂ O	5.10	13.46	10.40	27.55
MgO	1.01	2.14	4.92	4.81
Mn ₃ O ₄	1.62	-	-	-
Na ₂ O	0.69	0.93	0.67	6.18
P ₂ O ₅	0.78	1.94	2.46	2.90
SO ₃	5.10	2.41	3.42	4.85
ZnO	0.86	-	-	-
TiO ₂	2.56	0.05	0.51	-
Cl	0.23	0.57	0.24	12.56
Base to Acid Ratio (B/A)		0.995		
Silica to Alumina Ratio (S/A)		3.316		
Iron to Calcium Ratio (I/C)		0.426		

Total Alkalis (TA) (%)	5.790
------------------------	-------

3.3. FTIR analysis of biomass

The FTIR spectrum in the range of 400-4000 cm^{-1} provides important insights into the functional groups and chemical structure of the biomass sample. The FTIR spectrum of WMWS, plotted as transmittance versus wavenumber, is presented in **Fig. 2**. The broad absorption band observed around 3338 cm^{-1} is attributed to O-H stretching vibrations, indicating the presence of hydroxyl groups associated with alcohols, phenols, and moisture content [13]. The peak at 2928 cm^{-1} corresponds to C-H stretching of aliphatic hydrocarbons, suggesting the presence of cellulose and hemicellulose components. In the fingerprint region, the strong peak at 1022 cm^{-1} is assigned to C-O stretching vibrations characteristic of polysaccharides such as cellulose [15]. The band near 1150 cm^{-1} supports C-O-C glycosidic linkages, confirming the structural backbone of lignocellulosic material [31]. Moreover, the peaks at 1262 cm^{-1} and 1363 cm^{-1} are associated with C-H bending and C-O stretching in lignin and hemicellulose. The absorptions at 1456 cm^{-1} and 1512 cm^{-1} indicate aromatic skeletal vibrations, suggesting the presence of lignin-derived phenolic structures. Similarly, peaks at 1642 cm^{-1} and 1692 cm^{-1} can be attributed to C=O stretching of conjugated carbonyl groups or adsorbed water bending vibrations [14]. The region between 1999-2296 cm^{-1} shows weak bands that may correspond to overtones or combination bands, often observed in complex biomass matrices [15]. The peak at 2129 cm^{-1} may indicate the presence of triple bond stretching ($\text{C}\equiv\text{C}$), though such signals are typically weak and could arise from minor components or instrumental artefacts [14]. Finally, the low-wavenumber peak at 589 cm^{-1} corresponds to out-of-plane bending vibrations, possibly associated with aromatic structures or mineral components [31]. The spectrum confirms the lignocellulosic nature of the biomass, dominated by cellulose, hemicellulose, and lignin, with various oxygenated functional groups that contribute to its reactivity and suitability for thermochemical conversion.

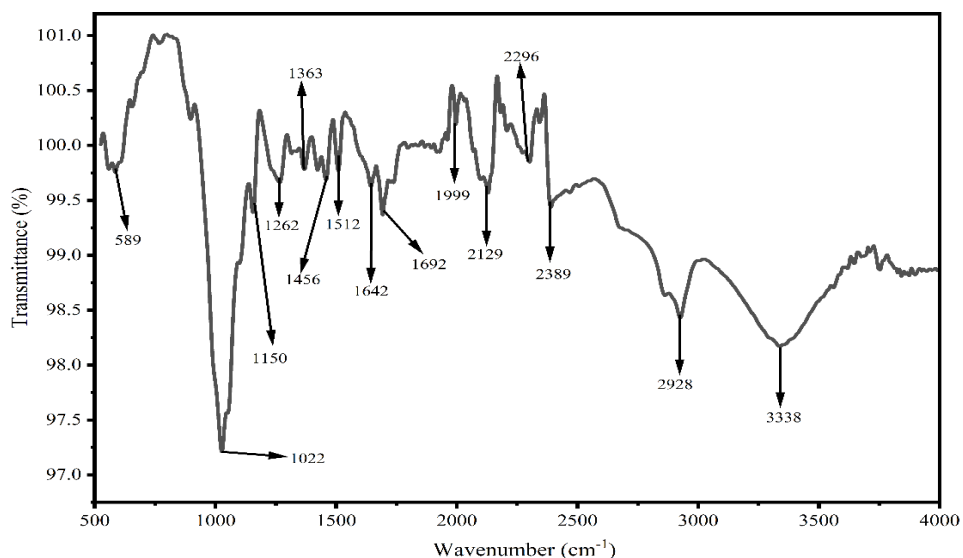


Fig. 2. Functional group analysis of WMWS biomass using FTIR.

3.4. Thermal profile and effect of heating rates

The thermal profile of WMWS was analysed using a TGA at a heating rate of 10 °C/min. The obtained thermograph is shown in **Fig. 3(a) and 3(b)**. The result confirmed that, at a heating rate of 10 °C/min, the biomass thermal degradation profile exhibits a clear, well-resolved three-stage decomposition pattern, indicating a controlled, efficient conversion process. In the first stage (ambient to 150 °C), a slight weight loss of about 3.60% is observed. This stage is mainly associated with the evaporation of free and bound moisture, as well as the release of light volatile compounds [10]. Kumar et al. (2020) and Bhardwaj et al. (2023) reported similar results for banana trunk biomass, printing paper (AP), filter paper (FP), newspaper (NP), writing paper (WP), and reed pith (RP) [10] [32]. Furthermore, the second stage (150-550 °C) represents the principal degradation zone, where rapid mass loss occurs, with the mass decreasing sharply from approximately 95% to nearly 15%. This stage corresponds to the thermal decomposition of hemicellulose (200-300 °C) and cellulose (300-400 °C), along with partial breakdown of lignin [33]. The main degradation occurs over approximately 250-450 °C, with the maximum degradation rate occurring at approximately 375 °C, indicating intense devolatilisation and evolution of combustible gases such as CO, CO₂, and hydrocarbons [34]. The relatively sharp slope of the curve suggests a well-defined reaction mechanism under slower heating conditions. In the third stage (>550 °C), the rate of weight loss becomes gradual, ultimately leaving a residual mass of approximately 15% at 900 °C. The gradual mass loss above 550 °C may be associated

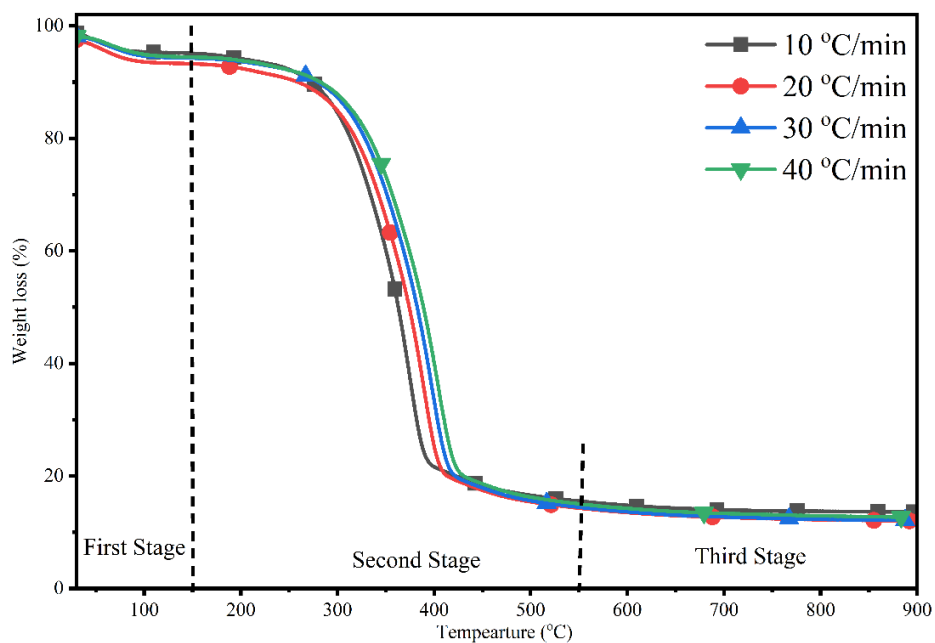
with the slow decomposition/rearrangement of lignin-derived structures and secondary devolatilization of the carbonaceous residue. The lower heating rate provides sufficient residence time for heat transfer and reaction completion, resulting in more stable char formation and more efficient burnout than higher heating rates [33]. The DTG curve of the biomass exhibits a well-defined, sharp degradation profile, indicating controlled thermal decomposition at a heating rate of 10 °C/min. A small initial peak below 120 °C corresponds to moisture evaporation and release of light volatiles. The main decomposition occurs in the 150-550 °C range, where a prominent, narrow DTG peak is observed. The maximum degradation rate is reached at approximately 375 °C, which is lower than that observed at higher heating rates. This shift towards a lower peak temperature indicates that slower heating allows sufficient time for heat transfer and enhances the breakdown of hemicellulose and cellulose [10]. The sharpness of the peak suggests a well-defined and efficient devolatilization process. Beyond 550 °C, the DTG curve flattens significantly, indicating a lower mass-loss rate. This region corresponds to the gradual decomposition/rearrangement of lignin-derived structures, as well as secondary reactions involving the carbonaceous residue [23].

The influence of different heating rates (10, 20, 30, and 40 °C/min) on the thermal decomposition behaviour of WMWS was investigated and presented in **Fig. 3(a) and (b)**. The influence of heating rate on the thermal degradation behaviour of WMWS is evident from the TG and DTG profiles, which show significant shifts in decomposition characteristics, reaction kinetics, and residue formation. As the heating rate rises from 10 to 40 °C/min, the TGA curves shift systematically toward higher temperatures (**Fig. 3(a)**). This behaviour indicates that at higher heating rates, the material experiences thermal lag due to insufficient time for heat transfer, resulting in delayed decomposition [10]. It was noted that increasing the heating rate from 10 to 40 °C/min shifted the thermal decomposition temperature to 375, 389, 398, and 404 °C, respectively. As the heating rate increases, the pyrolysis residence time decreases, thereby reducing heat and mass transfer times. Higher heating rates increase thermal lag and reduce the time available for heat transfer and reaction at a given temperature, shifting the DTG peak toward higher temperatures. Despite these changes, the overall weight-loss behaviour remains nearly the same across different heating rates, suggesting that the fundamental heat transfer mechanisms and reaction pathways are largely comparable, leading to analogous degradation patterns [35]. In the second stage, it was also noted that increasing the heating rate from 10 to 40 °C/min increased the

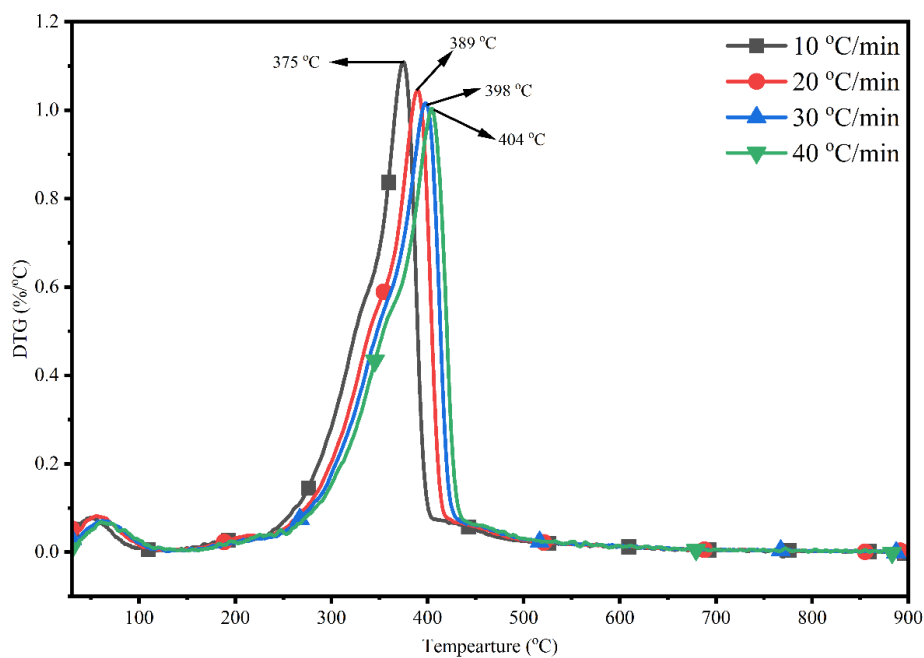
decomposition of WMWS (78.57, 78.94, 79.84, and 79.89%, respectively). The slight increase in WMWS decomposition with higher heating rates is due to enhanced reaction kinetics and rapid temperature rise, which promote faster bond cleavage and volatilisation. Additionally, reduced residence time limits secondary char-forming reactions, resulting in marginally higher mass loss during the main decomposition stage [10]. It was observed that at the end of the experiment, the residue (char or fixed carbon) decreased (13.52, 12.03, 12.11, and 12.09%) as the heating rate increased from 10 to 40 °C/min. Increasing the heating rate slightly increased the apparent mass loss within the main degradation region, which promotes greater conversion of fixed carbon into volatile products. Moreover, the higher heating rates reduce char stability and limit secondary char-forming reactions, resulting in lower residual mass at the end of the process.

The DTG profiles (**Fig. 3(b)**) confirm that the peak degradation temperature increases from approximately 375 °C at 10 °C/min to about 389 °C at 20 °C/min, and from 398 °C at 30 °C/min to 404 °C at 40 °C/min. This progressive shift in peak temperature reflects the increased energy requirement for bond cleavage due to reduced residence time. Additionally, the DTG peaks become sharper and slightly higher at higher heating rates, indicating an accelerated reaction rate and overlapping decomposition processes. Similar trends have been documented in earlier studies by Mishra and Mohanty (2018) and Kumar et al. (2019) [36,37]. Mishra and Mohanty (2018) examined the non-isothermal pyrolysis behaviour of sawdust biomass at heating rates of 5, 10, 15, 20, and 25 °C/min. Their results showed a consistent shift of peak degradation temperatures toward higher values with increasing heating rate. Specifically, peak temperatures for pine sawdust increased from 353 to 386 °C, for sal sawdust from 341 to 374 °C, and for areca nut husk from 325 to 355 °C [36]. Similarly, Kumar et al. (2019) analysed the pyrolysis kinetics of sugarcane (*Saccharum officinarum* L.) leaves using TGA under an inert atmosphere at heating rates of 5-40 °C/min. They observed that the temperature ranges corresponding to different stages of biomass decomposition progressively shifted to higher temperatures as the heating rate increased. Despite these shifts, the authors concluded that the fundamental thermal degradation mechanism remained unchanged across all heating rates, indicating that heating rate primarily influences the kinetics rather than the reaction pathway [37]. The thermal analysis of WMWS demonstrates that the heating rate significantly influences its thermal behaviour by altering the onset, peak, and completion temperatures of degradation. Lower heating rates favour more complete and controlled decomposition with better heat transfer and reaction uniformity, while higher heating rates enhance

259 reaction intensity but delay degradation and may reduce overall conversion efficiency. These
 260 findings are crucial for optimising thermochemical processes such as pyrolysis and combustion,
 261 where heating rate must be carefully controlled to balance reaction kinetics, energy efficiency, and
 262 product yield.



(a)



(b)

Fig. 3. Thermal analysis of WMWS: (a) TGA and (b) DTG at dynamic heating rates.

3.5. Burnout Temperature

The burnout temperature profile demonstrates that changes in heating rate significantly govern the thermal response of the waste-derived feedstock, offering deeper insight into its combustion behaviour and thermal decomposition stability. Burnout temperature is the stage at which oxidation of volatile components and fixed carbon is nearly complete, resulting in the formation of residual ash with minimal remaining combustible matter [10]. This parameter serves as an important indicator of combustion efficiency, as lower burnout temperatures generally reflect improved fuel reactivity and more effective energy release [23]. Conversely, higher burnout temperatures may suggest greater resistance to degradation or incomplete combustion under the given conditions. The burnout point is strongly influenced by several factors, including the intrinsic composition of the biomass, particle size, residence time, heating rate, and the presence of catalysts or mineral additives, which can either accelerate or inhibit oxidation reactions [20] [23]. Therefore, analysing burnout temperature not only optimises thermal conversion processes but also supports the design of efficient energy recovery systems and the development of improved operational strategies for waste-to-energy applications. Burnout temperature is commonly regarded as an important parameter for assessing and comparing the pyrolysis behaviour of different biomass materials. Lignocellulosic materials such as pine, sal, and areca nut sawdust exhibit a gradual change in the combustion behaviour of biomass and waste-derived fuels [38] [33]. **Fig. 4** shows the variation in burnout temperature for WMWS at different heating rates and compared with other reported biomass, such as pine, sal, and areca nut sawdust [36], neem seeds [38], mango seeds [23] and banana trunk [10]. The burnout temperature profiles exhibit distinct feedstock-dependent behaviours as the heating rate increases, highlighting differences in thermal reactivity and combustion. Pine increases from 550 °C at 10 °C/min to 558 °C at 25 °C/min, sal from 560 °C to 567 °C, and areca nut from 570 °C to 576 °C. This modest rise (5-10 °C) suggests that higher heating rates reduce oxidation time, thereby delaying complete combustion [10]. The similarity in trends indicates comparable structural composition dominated by cellulose, hemicellulose, and lignin. Neem seeds display an opposite trend, with burnout temperature decreasing from 598 °C at 10 °C/min to 565 °C at 50 °C/min (33 °C reduction). This behaviour can be attributed to higher volatile and oil content, which enhances combustion reactivity and facilitates faster burnout even at elevated heating rates. In contrast, the banana trunk exhibits

significantly lower burnout temperatures, ranging from 325 °C to 365 °C, with a gradual increase as the heating rate rises. This indicates high reactivity and low thermal resistance, likely due to its fibrous structure, high moisture-derived porosity, and lower lignin content. Mango seeds exhibit relatively stable burnout temperatures (655-667 °C), suggesting greater resistance to thermal degradation, possibly due to their dense structure and higher fixed carbon content [23]. WMWS exhibits the highest burnout temperatures, increasing from 650 °C at 10 °C/min to 680 °C at 40 °C/min. This trend reflects the presence of inorganic constituents and complex compounds that hinder oxygen diffusion and require higher temperatures for complete oxidation. Critically, the results demonstrate two governing mechanisms: heat-transfer limitations in lignocellulosic and mineral-rich feedstocks, leading to increased burnout temperatures, and enhanced kinetic reactivity in volatile-rich materials, causing reduced burnout temperatures [33]. These findings emphasise the importance of optimising heating rates based on feedstock characteristics to achieve efficient combustion and improved energy recovery.

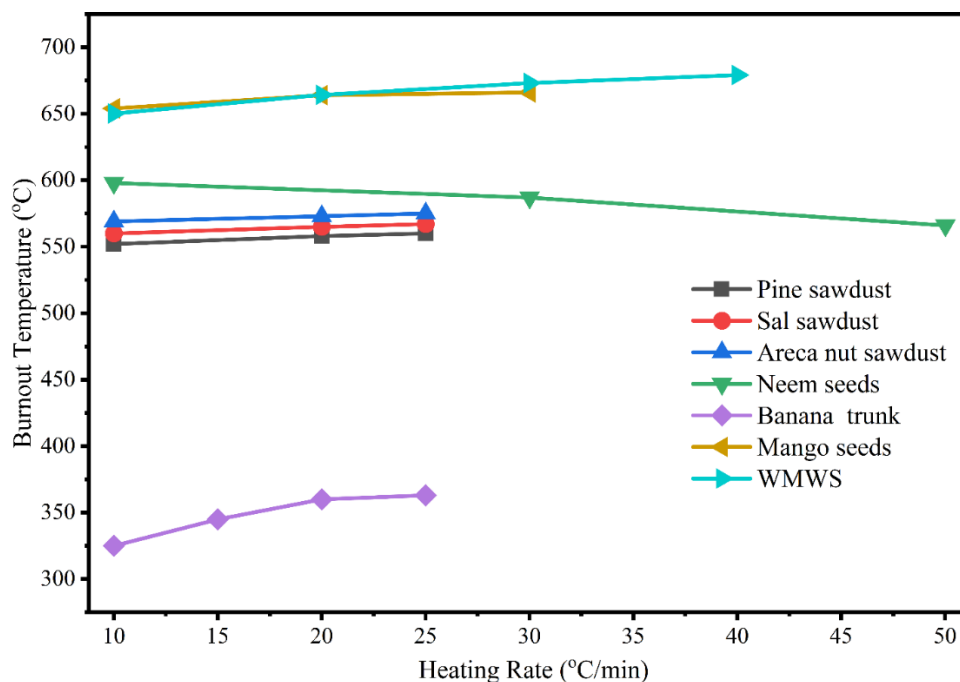


Fig. 4. Burnout temperatures of WMWS and compared with those of reported feedstocks.

3.6. Kinetics analysis

The model-free techniques, including KAS, OFW, FM, DAEM, ST, LT, VZ, and AVZ, were employed to evaluate the kinetic parameters of WMWS, namely the activation energy (E) and the pre-exponential (frequency) factor (A). These models provide comprehensive insights into

the thermal degradation mechanism by estimating activation energy (E_a), pre-exponential factor (A), and correlation coefficient (R^2) across a wide conversion range (0.10-0.80). However, during model fitting, it was observed that at higher conversion levels (0.80), the fitting accuracy decreased, as indicated by lower correlation coefficients (R^2) [10]. This deviation can be attributed to the increased complexity of the reaction mechanism at advanced stages of conversion, where secondary reactions such as char formation, diffusion limitations, and heat/mass transfer effects become dominant [10]. Consequently, the assumption of a single-step reaction becomes less valid, resulting in poorer model fit at higher conversions. The kinetic parameters of the WMWS were calculated and listed in **Table 4 (a and b)**. The results confirmed that a consistent trend across all models is the variation in activation energy with conversion, reflecting the multi-step nature of biomass pyrolysis [9]. The average apparent activation energy estimated using the KAS, OFW, FM, DAEM, ST, LT, VZ and AVZ models for WMWS was found to be 171.18, 181.61, 168.28, 176.41, 171.60, 172.98, 171.18 and 187.43 kJ/mol, respectively. Similarly, the average frequency factor obtained using KAS, OFW, FM, DAEM, ST, and LT models for WMWS was found to be $1.79\text{E}+11$, $4.45\text{E}+17$, $7.02\text{E}+14$, $2.82\text{E}+14$, $3.22\text{E}+11$ and $2.212\text{E}+09 \text{ min}^{-1}$, respectively. Furthermore, the coefficient of determination (R^2) for all models exceeded 0.90, indicating a strong agreement between the experimental data and the model predictions (**Table 4a**), thereby confirming the reliability and suitability of the applied kinetic models [39].

The apparent activation energy determined using KAS, OFW, FM, DAEM, ST, LT, VZ and AVZ models for WMWS was found to be 159.54-165.44, 168.71-176.56, 165.45-170.76, 164.13-171.00, 159.91-165.89, 165.20-165.60, 159.54-165.44, and 182.07-190.97 kJ/mol, respectively. Notably, the apparent activation energy obtained from iso-conversional analysis is conversion-dependent and reflects the combined contribution of overlapping reactions occurring during biomass degradation[40]. Within the framework of Molecular Collision Theory (MCT), pyrolysis reactions are driven by energetic molecular interactions, with only collisions involving sufficiently energised molecules leading to chemical transformation [40]. These high-energy encounters disrupt stable bonds in the parent structure, initiating decomposition and the subsequent formation of new chemical species. The process involves a continuous cycle of bond dissociation and recombination, ultimately producing a range of volatile and solid products. Moreover, the ease with which a material undergoes pyrolysis is largely dictated by its activation energy, making it a key indicator of fuel reactivity. This parameter is critical to the efficient design and operation of

pyrolysis systems, as it influences energy requirements, reaction rates, and overall process performance [40]. At lower conversion levels (0.10-0.20), higher activation energies are observed. This behaviour is attributed to the initial decomposition of hemicellulose and the onset of cellulose degradation, which requires substantial energy to break strong chemical bonds and initiate devolatilization [9]. Moreover, as the conversion progresses (0.30-0.60), the activation energy stabilises and gradually decreases. This indicates that once the primary decomposition reactions are initiated, cellulose breakdown becomes more efficient due to the formation of reactive intermediates and enhanced heat transfer within the biomass matrix [9]. Additionally, the release of volatiles creates porous structures that facilitate further degradation. Also, at higher conversion levels (0.60-0.80), a noticeable decline in activation energy is observed across all models. For example, KAS decreases to 165.44 kJ/mol, while ST and LT exhibit similar downward trends. This stage corresponds to lignin decomposition and char formation, which are relatively slower but require less energy because they involve the progressive breakdown of already weakened structures [41]. The decreasing E_a suggests that secondary reactions such as char rearrangement dominate at this stage [41].

The average activation energy values obtained from different models show close agreement, confirming the reliability of the kinetic analysis. KAS, VZ and ST methods yield nearly identical average E_a values (171 kJ/mol), demonstrating their accuracy and consistency. This similarity arises because the methods use refined temperature-integral approximations, thereby minimising systematic errors [42]. The OFW and Advanced VZ methods provide slightly higher activation energies (181.61 and 187.43 kJ/mol), which are commonly reported in the literature due to their inherent approximations [42]. The DAEM model yields an average E_a of 176.41 kJ/mol, which is higher than KAS and ST but lower than OFW. This reflects DAEM's ability to account for the heterogeneous nature of biomass by considering a distribution of activation energies rather than a single value [39]. Since WMWS comprises components such as cellulose, hemicellulose, and lignin, the DAEM approach provides a more realistic representation of the pyrolysis process [39]. The Friedman method shows significant fluctuations in E_a (170.76-165.45 kJ/mol), highlighting its sensitivity to experimental noise and differential data. Unlike integral methods, FM directly depends on the conversion rate, making it more responsive to minor variations in experimental measurements. While this leads to less stable results, it provides valuable insight into reaction dynamics at specific conversion points [43]. The LT method yields

an average E_a of 172.98 kJ/mol, which closely aligns with the KAS and ST results. This indicates that LT is a reliable method with improved mathematical treatment and reduced approximation errors.

The pre-exponential factor (A) varies significantly across models, reflecting differences in reaction frequency and complexity (**Table 4 (a) and (b)**). The OFW and DAEM methods yield very high values, characteristic of complex reaction systems with multiple parallel pathways [44]. These high values indicate many effective collisions and active sites during pyrolysis. In contrast, the KAS and ST methods produce relatively moderate values, suggesting a more realistic representation of reaction kinetics (**Table 4(a)**) [42]. The gradual decrease in pre-exponential factor with increasing conversion indicates a reduction in reactive species and a shift from active devolatilization to slower char degradation. The Friedman method shows fluctuating pre-exponential factor values, consistent with its variable E_a results. This further confirms that differential methods capture instantaneous reaction behaviour but may lack overall stability [43]. The Li-Tang method shows a smooth, decreasing trend in the pre-exponential factor, indicating consistent reaction progression and improved model reliability. The variation in kinetic parameters across conversion levels clearly indicates that WMWS pyrolysis follows a multi-step reaction mechanism. The initial stage is dominated by hemicellulose decomposition, characterised by lower thermal stability and higher reactivity. This is followed by cellulose degradation, which contributes significantly to volatile release and energy demand. At higher temperatures and conversion levels, lignin decomposition becomes dominant. Lignin has a complex aromatic structure and decomposes over a broader temperature range, leading to gradual changes in activation energy. The final stage involves char formation and secondary reactions, which require less energy because the structure is already degraded. The agreement among different kinetic models confirms that the pyrolysis process cannot be described by a single reaction pathway. Instead, it involves overlapping reactions with varying activation energies, which supports the applicability of isoconversional and distributed energy models.

The variation of apparent average activation energy obtained from KAS, OFW, FM, DAEM, ST, LT, VZ and AVZ models with respect to conversion is illustrated in **Fig. 5**. The variation of activation energy (E_a) with conversion (0.10-0.80) for different kinetic models provides important insight into the thermal degradation behaviour of WMWS. All models exhibit a general trend of initially increasing E_a followed by a gradual decline at higher conversion levels,

confirming the multi-stage nature of biomass pyrolysis [42,43]. At low conversion (0.10-0.20), E_a increases sharply for all models, with OFW and AVZ showing the highest values. This stage corresponds to the decomposition of hemicellulose and the initiation of cellulose breakdown, which requires higher energy due to strong chemical bonds and structural complexity [9]. The rapid rise in E_a indicates the energy-intensive nature of initial devolatilization. In the intermediate conversion range (0.25-0.50), E_a shows a slight decreasing trend. Models such as KAS, ST, and LT exhibit consistent values, indicating steady cellulose decomposition. The reduced variation suggests improved heat transfer and the formation of reactive intermediates, which facilitate continuous degradation [42]. At higher conversion levels (0.50), E_a decreases gradually for most models. This is attributed to lignin degradation and char formation, which occur over a broader temperature range but require comparatively lower activation energy due to weakened molecular structures. The Friedman (FM) model shows significant fluctuations throughout the conversion range, reflecting its sensitivity to experimental noise. In contrast, KAS, ST, VZ, AVZ and LT exhibit smooth, consistent trends, indicating greater reliability. The results confirm that WMWS pyrolysis involves complex, overlapping reactions governed by varying activation energies.

The apparent average activation energy (AAAE) estimated using the KAS, OFW, FM, DAEM, ST, LT, VZ and AVZ models was compared with the activation energy values reported for *Putranjiva roxburghii*, *Cassia fistula* [45], Switchgrass, *Cynodon dactylon* [46], sugarcane leaves [37], pine, sal, and areca nut sawdust [47]. The comparative results of apparent activation energy derived from KAS, OFW, FM, DAEM, ST, LT, VZ and AVZ models are presented in **Table 5**. A comparative evaluation of activation energy values revealed noticeable variations among the applied kinetic models. These differences arise primarily from the complex, heterogeneous nature of biomass, which decomposes over a broad temperature range [37]. Biomass is composed of distinct structural components such as hemicellulose, cellulose, and lignin, each exhibiting unique thermal stability and degradation behaviours, thereby contributing to the variation in activation energy [39]. In addition, the estimated activation energy is influenced by several factors, including fibre composition, type and origin of the feedstock, the mathematical approach adopted for kinetic calculations, and the operational conditions of pyrolysis, such as heating rate and temperature profile [9]. Furthermore, discrepancies among models can be attributed to differences in their underlying assumptions, numerical approximations, and sensitivity to experimental data. These factors collectively indicate that the activation energy is

not a single constant but a conversion-dependent parameter that reflects the multi-step, complex nature of biomass pyrolysis [13].

Table 4 (a). Kinetic analysis of WMWS using KAS, OFW, ST, FM, and DAEM.

Model	Conversion	E _a (KJ/mol	A (1/min)	R ²
KAS	0.10	159.54	9.58E+10	0.9796
	0.15	182.67	2.15E+12	0.9586
	0.20	177.52	2.61E+11	0.9874
	0.25	175.30	8.19E+10	0.9946
	0.30	173.81	3.51E+10	0.9969
	0.35	173.51	2.08E+10	0.9980
	0.40	173.87	1.46E+10	0.9986
	0.45	173.22	8.80E+09	0.9991
	0.50	172.34	5.31E+09	0.9996
	0.55	171.06	3.11E+09	0.9998
	0.60	169.33	1.74E+09	0.9999
	0.65	167.65	1.02E+09	0.9999
	0.70	166.59	6.86E+08	0.9999
	0.75	165.95	5.02E+08	1.0
	0.80	165.44	3.75E+08	1.0
	Average	171.18	1.79E+11	
OFW	0.10	168.71	2.15E+17	0.9510
	0.15	192.27	5.29E+18	0.9626
	0.20	187.38	6.78E+17	0.9887
	0.25	185.34	2.21E+17	0.9952
	0.30	184.00	9.75E+16	0.9973
	0.35	183.83	5.91E+16	0.9982
	0.40	184.31	4.26E+16	0.9988
	0.45	183.78	2.62E+16	0.9992
	0.50	183.00	1.61E+16	0.9997
	0.55	181.81	9.60E+15	0.9998

	0.60	180.16	5.47E+15	0.9999
	0.65	178.55	3.25E+15	0.9999
	0.70	177.57	2.21E+15	0.9999
	0.75	177.00	1.64E+15	1.0
	0.80	176.56	1.24E+15	1.0
	Average	181.61	4.45E+17	
ST	0.10	159.91	1.72E+11	0.9605
	0.15	183.05	3.87E+12	0.9588
	0.20	177.92	4.72E+11	0.9874
	0.25	175.70	1.48E+11	0.9946
	0.30	174.22	6.36E+10	0.9970
	0.35	173.92	3.76E+10	0.9980
	0.40	174.29	2.65E+10	0.9986
	0.45	173.65	1.60E+10	0.9991
	0.50	172.77	9.65E+09	0.9996
	0.55	171.49	5.65E+09	0.9998
	0.60	169.76	3.17E+09	0.9999
	0.65	168.08	1.86E+09	0.9999
	0.70	167.03	1.25E+09	0.9999
	0.75	166.39	9.15E+08	1.0
	0.80	165.89	6.83E+08	1.0
	Average	171.60	3.22E+11	
	0.10	164.13	1.44E+14	0.9506
	0.15	187.47	3.37E+15	0.9607
	0.20	182.45	4.21E+14	0.9881
	0.25	180.32	1.34E+14	0.9949
	0.30	178.90	5.85E+13	0.9971
	0.35	178.67	3.50E+13	0.9981
	0.40	179.09	2.49E+13	0.9987
	0.45	178.50	1.52E+13	0.9992

DAEM	0.50	177.67	9.26E+12	0.9997
	0.55	176.44	5.46E+12	0.9998
	0.60	174.74	3.09E+12	0.9999
	0.65	173.10	1.82E+12	0.9999
	0.70	172.08	1.23E+12	0.9999
	0.75	171.47	9.07E+11	1.0
	0.80	171.00	6.81E+11	1.0
	Average	176.41	2.82E+14	
FM	0.10	170.76	4.92E+14	0.9806
	0.15	186.86	4.57E+15	0.9899
	0.20	190.85	5.18E+15	0.9884
	0.25	161.02	8.78E+12	0.9989
	0.30	178.70	2.00E+14	0.9963
	0.35	161.24	4.91E+12	0.9995
	0.40	167.11	1.12E+13	0.9986
	0.45	176.34	4.80E+13	0.9984
	0.50	169.21	1.03E+13	0.9983
	0.55	157.68	1.03E+12	0.9984
	0.60	158.11	1.00E+12	0.9992
	0.65	154.69	4.82E+11	0.9984
	0.70	156.95	6.40E+11	0.9997
	0.75	169.34	5.01E+12	0.9997
	0.80	165.45	1.87E+12	0.9987
	Average	168.28	7.02E+14	
	0.10	165.20	1.00E+10	0.9800
	0.15	185.60	5.00E+09	0.9813
	0.20	181.30	3.33E+09	0.9827
	0.25	178.90	2.50E+09	0.9840
	0.30	176.80	2.00E+09	0.9853
	0.35	175.20	1.67E+09	0.9867

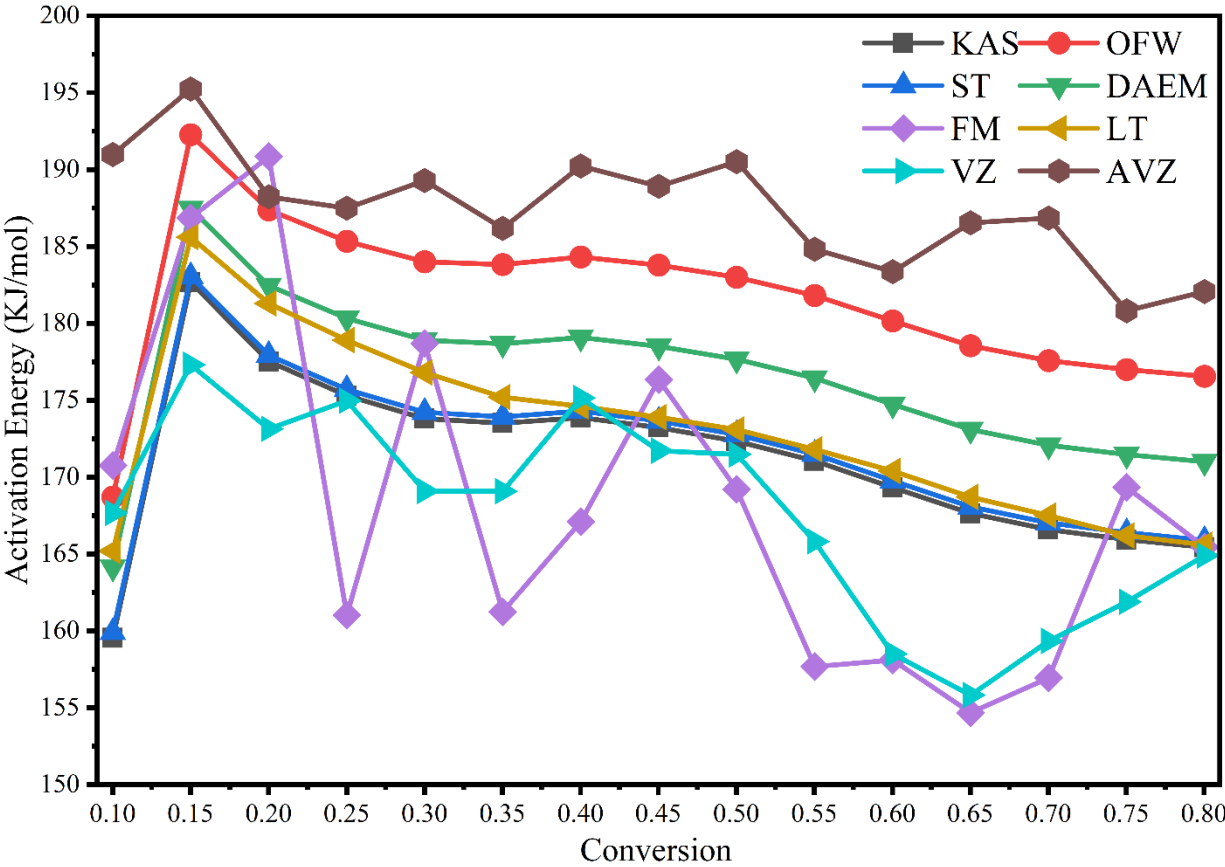
LT	0.40	174.60	1.43E+09	0.9880
	0.45	173.90	1.25E+09	0.9893
	0.50	173.10	1.11E+09	0.9907
	0.55	171.80	1.00E+09	0.9920
	0.60	170.40	9.09E+08	0.9933
	0.65	168.70	8.33E+08	0.9947
	0.70	167.50	7.69E+08	0.9960
	0.75	166.20	7.14E+08	0.9973
	0.80	165.60	6.67E+08	0.9987
	Average	172.98	2.212E+09	

440 Table 4(b). Kinetic analysis of WMWs using the Vyazovkin method and the Advanced Vyazovkin
441 method.

Conversion (α)	Vyazovkin method (VZ)		Advanced Vyazovkin method (AVZ)	
	Activation Energy (kJ/mol)	Error (RMSE)	Activation Energy (kJ/mol)	Error (RMSE)
0.10	159.54	0.2598	190.97	1.5700
0.15	182.67	0.1008	195.24	0.2900
0.20	177.52	0.0555	188.23	0.0860
0.25	175.3	0.0363	187.49	0.0400
0.30	173.81	0.0272	189.28	0.0170
0.35	173.51	0.0221	186.17	0.0230
0.40	173.87	0.0183	190.23	0.0130
0.45	173.22	0.0144	188.91	0.0036
0.50	172.34	0.0093	190.51	5e-05
0.55	171.06	0.0069	184.82	0.0054
0.60	169.33	0.0055	183.36	0.0016
0.65	167.65	0.0044	186.54	0.0075

0.70	166.59	0.0043	186.84	0.0260
0.75	165.95	0.0032	180.82	0.0099
0.80	165.44	0.0034	182.07	0.00023
Average	171.18		187.43	

442



443

444

Fig. 5. Variation of activation energy with respect to conversion.

445

446

447

448 Table 5. Comparison of average apparent energy activation against conversion value using model-free methods.

Biomass	Heating rate (°C/min)	KAS (kJ/mol)	OFW (kJ/mol)	ST (kJ/mol)	FM (kJ/mol)	LT (kJ/mol)	DAEM (kJ/mol)	VZ (kJ/mol)	AVZ (kJ/mol)	References
WMWS	10, 20, 30 and 40	171.18	181.61	171.60	168.28	172.98	176.41	171.18	187.43	Present Study
Putranjiva roxburghii	10, 25, 40, and 55	206.35	206.16	206.64	215.56	214.32	-	206.59	-	[45]
Cassia fistula	10, 25, 40, and 55	180.06	180.34	180.36	196.34	198.88	-	180.35	-	[45]
Switchgrass	10, 20 and 30	126.03	137.54	-	-	-	130.33	134.26	-	[13]
<i>Cynodon dactylon</i>	10, 30 and 50	216.45	220.43	-	-	-	214.28	-	-	[46]
Sugarcane leaves	5, 10, 15, 20, 30 and 40	226.75	226.97	226.94	239.58	-	-	215.11	214.89	[37]
Pine sawdust	5, 10, 15, 20 and 25	171.66	179.29	-			206.62	-	-	[36]
Sal sawdust	5, 10, 15, 20 and 25	148.44	156.58	-	-	-	171.63	-	-	[36]
Areca nut husk	5, 10, 15, 20 and 25	171.24	179.47	-	-	-	160.45	-	-	[36]

449

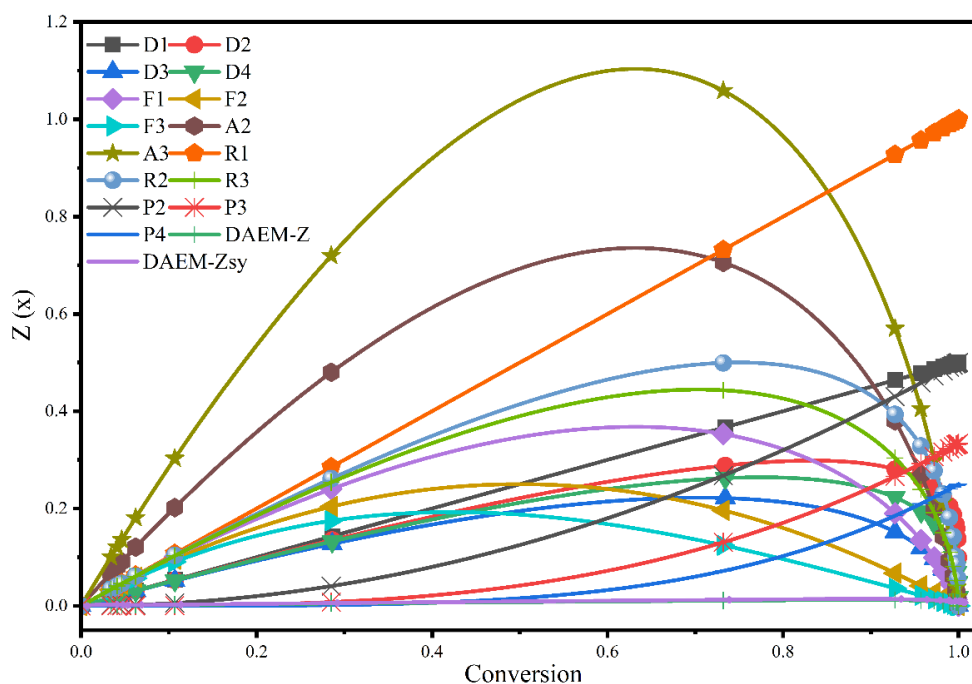
3.7 Master plot

The average activation energy obtained from the DAEM and VZ methods for WMWS was used to determine the thermal decomposition mechanism following the approach proposed by Criado et al. (1989) [12]. **Equation (19)** was employed to generate the theoretical reference (master) curves, which are derived from the $f(x)$ and $g(x)$ functions listed in **Table 1(b)**. These master curves were subsequently compared with the experimental data to identify the most appropriate solid-state reaction mechanism. According to **Table 1(b)**, the algebraic models are classified into five primary groups: F_n , D_n , R_n , A_n , and P_n . These groups represent different decomposition mechanisms, including nucleation and growth processes (F_n), diffusion-controlled mechanisms related to heat and mass transfer (D_n), phase-boundary or surface-reaction mechanisms (R_n), random nucleation processes (A_n), and power-law reactions (P_n). The experimental parameter $Z(\alpha)$ was calculated using a heating rate of 10 °C/min, while the theoretical $Z(x)$ values were determined using the activation energy derived from the DAEM and VZ model. The similarity between theoretical and experimental master plots facilitated the identification of the dominant reaction mechanism governing thermal degradation. The master plot analysis based on Criado's method provides valuable insight into the most probable reaction mechanism governing the sample's thermal decomposition. The plot compares the experimental curves (DAEM-Z and DAEM-Zsy) with theoretical master curves for different solid-state reaction models, including diffusion (D_1 - D_4), reaction order (F_n), phase boundary reactions (R_n), nucleation (A_n), and power-law models (P_n). The master plot of the conversion values against the activation energy derived from DAEM and VZ is presented in **Fig. 6(a) and 6(b)**. From **Fig. 6(a)**, the experimental curves (DAEM-Z and DAEM-Zsy) show the closest agreement with the diffusion-controlled models, particularly D_3 and D_4 , over a wide conversion range (0.20-0.80). This indicates that the decomposition process is predominantly governed by heat- and mass-transfer limitations within the solid matrix. In biomass pyrolysis, such behaviour is common due to the formation of a porous char layer, which restricts the outward diffusion of volatile products and inward heat transfer [8]. At lower conversion levels (<0.20), a slight deviation of the experimental curve from diffusion models suggests the contribution of nucleation mechanisms (A_n), in which initial bond breakage and active site formation dominate. As conversion increases, the overlap with diffusion models becomes more pronounced, confirming that internal diffusion resistance becomes the rate-limiting step. Furthermore, a divergence between the experimental and theoretical curves is

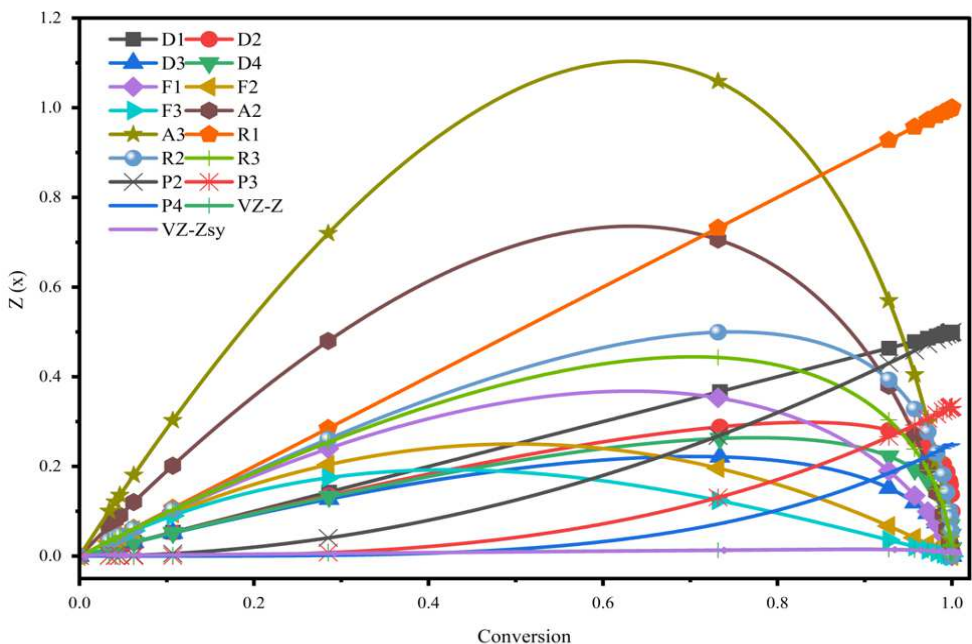
observed at a higher conversion level (0.80). This can be attributed to secondary reactions such as char rearrangement and structural collapse, which are not fully described by a single theoretical model [8]. The reaction order (F_n) and phase boundary (R_n) models show poor agreement with experimental data across most of the conversion range, indicating that surface reaction mechanisms are not dominant. The master plot analysis confirms that WMWS pyrolysis follows a diffusion-controlled mechanism with initial nucleation, highlighting the complex, multi-step nature of the thermal degradation process.

Criado master plot ($Z(\alpha)$ vs conversion) was used to identify the most probable solid-state reaction mechanism by comparing the experimental curve (VZ-Z and VZ-Zsy) with theoretical models (F_n , D_n , R_n , A_n , and P_n families) (**Fig. 6(b)**). The analysis reveals that the experimental curves agree best with diffusion-controlled models, particularly D_3 and D_4 , over a broad conversion range (0.20-0.75). This indicates that the thermal degradation process is primarily governed by internal heat and mass-transfer limitations. At the initial stage (0.20), the experimental curves slightly deviate from diffusion models and show partial alignment with nucleation models (A_2 and A_3). This suggests that decomposition begins with nucleation and growth mechanisms, during which active sites are formed, and bond cleavage is initiated. Such behaviour is typical of biomass materials, in which hemicellulose decomposes first due to its lower thermal stability [37]. In the intermediate region (0.30-0.70), the close overlap between the experimental and diffusion curves confirms that diffusion becomes the rate-limiting step. This is attributed to the formation of a char layer and an evolving pore structure, which restricts the escape of volatile products and slows heat transfer within the material matrix [13]. Moreover, at higher conversion levels (0.80), the experimental curves deviate from all theoretical models. This deviation is likely due to secondary reactions such as char rearrangement, cracking, and structural collapse, which cannot be accurately described by a single ideal model [13]. The poor agreement between the reaction-order (F_n) and phase-boundary (R_n) models suggests that surface reactions are not dominant in this system [8]. The results confirm that the pyrolysis process follows a multi-step mechanism, starting with nucleation and transitioning to diffusion-controlled degradation, highlighting the complex nature of thermal decomposition. The major difference between the two master plots lies in the behaviour of the experimental curves and the consistency of the model fits. In **Fig. 6(a)** (DAEM-based), the experimental curves exhibit stronger, more consistent overlap with the diffusion models (D_3 - D_4) over a wider conversion range, indicating a dominant diffusion-

512 controlled mechanism. In contrast, **Fig. 6(b)** (VZ-based) shows slightly greater deviation and
513 dispersion, especially at higher conversions, suggesting a greater influence of secondary reactions
514 and structural changes. This difference arises because the DAEM approach better captures the
515 distributed nature of activation energies, whereas the VZ method is more sensitive to experimental
516 variations and simplifications.



(a)



(b)

Fig. 6. Master plot and experimental data obtained by the Criado method (a) DAEM and (b) VZ.

3.8. Thermodynamic analysis

Thermodynamic parameters (TD) are critical indicators for evaluating the suitability of biomass in thermochemical conversion processes. They play a vital role in selecting the most appropriate feedstock and are equally essential for the optimal design, scale-up, and efficient operation of pyrolysis reactors at industrial levels [48]. By providing insights into reaction feasibility, energy requirements, and system behaviour, these parameters significantly improve process performance and product yield. TD parameters of WMWS were evaluated at a heating rate of 10 °C/min and are presented in **Table 6**. The average activation energy (AAE), determined using the KAS, OFW, ST, VZ and DAEM methods, was employed to compute the thermodynamic parameters. These parameters include pre-exponential factor (A), enthalpy change (ΔH), Gibbs free energy (ΔG), and entropy change (ΔS), which collectively describe the energy requirement, feasibility, and reaction mechanism of the pyrolysis process. The enthalpy change (ΔH) represents the energy required to convert reactants into activated complexes and is closely related to activation energy. In the present study, ΔH values for WMWS show a fluctuation trend with increasing conversion (α) across all models. The enthalpy of the biomass increases from 154.15 kJ/mol ($\alpha = 0.10$) to 160.05 kJ/mol ($\alpha = 0.80$) using KAS, with an average value of 165.80 kJ/mol. A similar trend is observed for other models, including OFW (average: 176.23 kJ/mol), DAEM (171.01 kJ/mol), ST (166.22 kJ/mol), VZ (165.80 kJ/mol), and AVZ (182.04 kJ/mol). This gradual increase in ΔH suggests that as conversion progresses, slightly higher energy is required, which can be attributed to the transition from the decomposition of more reactive components (hemicellulose and cellulose) to more stable lignin structures [10]. At lower conversions (0.10-0.30), higher ΔH values are associated with the decomposition of hemicellulose and cellulose, which possess relatively stronger and more ordered structures. As conversion increases, lignin decomposition and char formation dominate, requiring comparatively lower energy due to weaker and more irregular bonds. The small difference between the activation energy (E) and ΔH suggests that the energy barrier for forming activated complexes is minimal, indicating efficient thermal conversion [10]. The moderate ΔH values confirm that WMWS is a suitable pyrolysis feedstock with manageable energy input requirements. The Gibbs free energy (ΔG) values range between 225.30 and 226.4 kJ/mol across all models and conversion levels. For example, KAS values vary

from 226.42 to 226.23 kJ/mol, while OFW ranges between 226.12 and 225.88 kJ/mol. The positive ΔG values clearly indicate that the pyrolysis process is non-spontaneous and requires continuous external heat input. The minimal variation in ΔG with conversion suggests a stable reaction pathway throughout the decomposition process, which is advantageous for reactor design and process predictability [10]. Additionally, the entropy change (ΔS) values are negative across all models, indicating a decrease in randomness during the formation of activated complexes. For example, ΔS values for KAS range from -111.51 to -102.10 J/mol.K (-92.96 J/mol.K), while those for OFW range from -96.90 to -84.41 J/mol.K. Similar negative trends are observed for DAEM (average: -84.66 J/mol.K), ST (-92.29 J/mol.K), VZ (-92.96 J/mol.K), and AVZ (-67.14 J/mol.K). These negative entropy values suggest that the activated complex is more ordered than the reactants, indicating a structured transition state and controlled reaction mechanism [37][49]. Furthermore, the pre-exponential factor (A) shows significant variation across models and conversion levels, reflecting the complex and multi-step nature of WMWS pyrolysis. The values range from 5.50×10^7 to $4.60 \times 10^9 \text{ s}^{-1}$ (KAS), 3.19×10^8 to $2.88 \times 10^{10} \text{ s}^{-1}$ (OFW), 5.90×10^7 to $4.95 \times 10^9 \text{ s}^{-1}$ (ST), 1.33×10^8 to $1.15 \times 10^{10} \text{ s}^{-1}$ (DAEM), 5.50×10^7 to $4.60 \times 10^9 \text{ s}^{-1}$ (VZ) and 2.25×10^9 to $4.10 \times 10^{10} \text{ s}^{-1}$ (AVZ) respectively. These variations indicate differences in collision frequency and reaction probability, confirming the heterogeneous and multi-component nature of biomass decomposition [50]. The thermodynamic parameters derived from multiple isothermal models provide a comprehensive understanding of WMWS pyrolysis. The process is characterised by moderate energy requirements, non-spontaneous behaviour, and increasing molecular disorder. The moderate enthalpy values suggest that WMWS is a viable pyrolysis feedstock that requires a reasonable energy input [49]. The increasing ΔH trend, stable ΔG values, and negative ΔS collectively indicate a controlled and energy-dependent reaction mechanism. Among the models, KAS, ST, and VZ yield closely aligned results, suggesting greater reliability, whereas OFW and AVZ exhibit relatively higher energy demand and system complexity. These insights are crucial for optimising pyrolysis conditions, improving reactor design, and enhancing product yield.

Table 6. Thermodynamic analysis of WMWS using KAS, OFW, ST, DAEM, VZ and AVZ models at 10 °C/min.

Model	Conversion	A (1/s)	H (KJ/mol)	G (KJ/mol)	S=J/mol.K
KAS	0.10	5.50E+07	154.15	226.42	-111.51

	0.15	4.60E+09	177.28	225.69	-74.70
	0.20	1.72E+09	172.13	225.85	-82.88
	0.25	1.13E+09	169.91	225.92	-86.41
	0.30	8.46E+08	168.42	225.96	-88.78
	0.35	7.99E+08	168.12	225.97	-89.26
	0.40	8.56E+08	168.48	225.96	-88.68
	0.45	7.56E+08	167.83	225.98	-89.72
	0.50	6.39E+08	166.95	226.01	-91.12
	0.55	5.00E+08	165.67	226.05	-93.15
	0.60	3.59E+08	163.94	226.10	-95.91
	0.65	2.60E+08	162.26	226.16	-98.58
	0.70	2.12E+08	161.20	226.19	-100.27
	0.75	1.88E+08	160.56	226.21	-101.29
	0.80	1.70E+08	160.05	226.23	-102.10
	Average	8.72E+08	165.80	226.05	-92.96
OFW	0.10	3.19E+08	163.32	226.12	-96.90
	0.15	2.88E+10	186.88	225.42	-59.46
	0.20	1.13E+10	181.99	225.56	-67.22
	0.25	7.67E+09	179.95	225.62	-70.46
	0.30	5.93E+09	178.61	225.65	-72.58
	0.35	5.75E+09	178.44	225.66	-72.85
	0.40	6.30E+09	178.92	225.65	-72.09
	0.45	5.69E+09	178.39	225.66	-72.93
	0.50	4.90E+09	177.61	225.68	-74.17
	0.55	3.91E+09	176.42	225.72	-76.06
	0.60	2.85E+09	174.77	225.77	-78.68
	0.65	2.09E+09	173.16	225.82	-81.24
	0.70	1.74E+09	172.18	225.85	-82.80
	0.75	1.56E+09	171.61	225.86	-83.71
	0.80	1.43E+09	171.17	225.88	-84.41

	Average	6.01E+09	176.23	225.73	-76.37
ST	0.10	5.90E+07	154.52	226.41	-110.92
	0.15	4.95E+09	177.66	225.68	-74.09
	0.20	1.86E+09	172.53	225.84	-82.24
	0.25	1.21E+09	170.31	225.90	-85.77
	0.30	9.15E+08	168.83	225.95	-88.13
	0.35	8.64E+08	168.53	225.96	-88.60
	0.40	9.27E+08	168.90	225.95	-88.02
	0.45	8.20E+08	168.26	225.97	-89.03
	0.50	6.93E+08	167.38	225.99	-90.43
	0.55	5.43E+08	166.10	226.03	-92.47
	0.60	3.90E+08	164.37	226.09	-95.22
	0.65	2.82E+08	162.69	226.14	-97.90
	0.70	2.31E+08	161.64	226.18	-99.57
	0.75	2.04E+08	161.00	226.20	-100.59
	0.80	1.86E+08	160.50	226.21	-101.39
	Average	9.42E+08	166.22	226.03	-92.29
DAEM	0.10	1.33E+08	158.74	226.27	-104.19
	0.15	1.15E+10	182.08	225.55	-67.07
	0.20	4.41E+09	177.06	225.70	-75.05
	0.25	2.94E+09	174.93	225.76	-78.43
	0.30	2.24E+09	173.51	225.81	-80.69
	0.35	2.14E+09	173.28	225.81	-81.05
	0.40	2.32E+09	173.70	225.80	-80.38
	0.45	2.07E+09	173.11	225.82	-81.32
	0.50	1.77E+09	172.28	225.84	-82.64
	0.55	1.40E+09	171.05	225.88	-84.60
	0.60	1.01E+09	169.35	225.93	-87.30
	0.65	7.39E+08	167.71	225.98	-89.91
	0.70	6.08E+08	166.69	226.02	-91.53

	0.75	5.41E+08	166.08	226.03	-92.50
	0.80	4.94E+08	165.61	226.05	-93.25
	Average	2.29E+09	171.01	225.88	-84.66
VZ	0.10	5.50E+07	154.15	226.42	-111.51
	0.15	4.60E+09	177.28	225.69	-74.70
	0.20	1.72E+09	172.13	225.85	-82.88
	0.25	1.13E+09	169.91	225.92	-86.41
	0.30	8.46E+08	168.42	225.96	-88.78
	0.35	7.99E+08	168.12	225.97	-89.26
	0.40	8.56E+08	168.48	225.96	-88.68
	0.45	7.56E+08	167.83	225.98	-89.72
	0.50	6.39E+08	166.95	226.01	-91.12
	0.55	5.00E+08	165.67	226.05	-93.15
	0.60	3.59E+08	163.94	226.10	-95.91
	0.65	2.60E+08	162.26	226.16	-98.58
	0.70	2.12E+08	161.20	226.19	-100.27
	0.75	1.88E+08	160.56	226.21	-101.29
	0.80	1.70E+08	160.05	226.23	-102.10
	Average	8.72E+08	165.80	226.05	-92.96
AVZ	0.10	2.25E+10	185.58	225.45	-61.52
	0.15	5.07E+10	189.85	225.33	-54.75
	0.20	1.33E+10	182.84	225.53	-65.87
	0.25	1.16E+10	182.10	225.55	-67.04
	0.30	1.63E+10	183.89	225.50	-64.20
	0.35	8.98E+09	180.78	225.59	-69.14
	0.40	1.95E+10	184.84	225.47	-62.69
	0.45	1.52E+10	183.52	225.51	-64.79
	0.50	2.06E+10	185.12	225.47	-62.25
	0.55	6.94E+09	179.43	225.63	-71.28
	0.60	5.25E+09	177.97	225.67	-73.60

	0.65	9.64E+09	181.15	225.58	-68.55
	0.70	1.02E+10	181.45	225.57	-68.07
	0.75	3.23E+09	175.43	225.75	-77.63
	0.80	4.10E+09	176.68	225.71	-75.65
	Average	1.45E+10	182.04	225.56	-67.14

4. Conclusions

The present study provides a comprehensive evaluation of waste-mixed wood sawdust (WMWS) as a viable feedstock for bioenergy production via pyrolysis. The physicochemical analysis confirmed that WMWS possesses favourable characteristics, including high volatile matter content, low ash content, and a relatively high calorific value, thereby enhancing its suitability for thermochemical conversion. Thermal analysis revealed a clear multi-stage degradation process, with significant mass loss occurring in the active pyrolysis zone due to the decomposition of hemicellulose and cellulose, followed by gradual lignin degradation. The kinetic analysis using various model-free approaches demonstrated that WMWS pyrolysis is a complex, multi-step process governed by conversion-dependent activation energy. The close agreement among different models validates the reliability of the results, while variations in activation energy highlight the heterogeneous nature of biomass. Furthermore, the influence of heating rate showed that higher rates enhance devolatilisation, which is critical for process optimisation. Thermodynamic parameters indicated that the process is endothermic and thermally feasible, requiring moderate energy input while maintaining reaction stability. The findings provide fundamental kinetic and thermal information that may support future reactor design and scale-up studies.

Acknowledgements

The author would like to thank the Biomass, Bioenergy and Bioproducts (3B) Lab and 3B Analytical Lab, School of Civil and Chemical Engineering, Manipal Institute of Technology, Manipal, Karnataka, for providing all necessary facilities.

Author contributions

Sonal Vithoba Tarkar: Conceptualization, Methodology, Writing original draft; **Deepraj Sarkar:** Conceptualization, Methodology, Validation, Writing original draft, Visualization; **Jyothi Acharya:** Methodology, Investigation, Writing original draft; **Ranjeet Kumar Mishra:**

Data collection and interpretation; conceptualisation, data curation, investigation, experimentation, visualisation, reviewing-original draft, review, and editing; **Srinivas Kini**: data curation, investigation, experimentation, visualisation, and editing.

Funding

The authors have no relevant financial or non-financial interests to disclose.

Availability of data and materials

The datasets generated during and/or analysed during the current study are available from the corresponding author upon reasonable request.

References

1. Perera, F. Pollution from fossil-fuel combustion is the leading environmental threat to global pediatric health and equity: Solutions exist. *Int. J. Environ. Res. Public Health* **15**, 16 (2018).
2. Agnihotri, N., Gupta, G. K. & Mondal, M. K. Thermo-kinetic analysis, thermodynamic parameters and comprehensive pyrolysis index of Melia azedarach sawdust as a genesis of bioenergy. *Biomass Convers. Biorefin.* **14**, 1863–1880 (2024).
3. Mishra, R. K. Co-pyrolysis of low-value wood sawdust and non-recyclable plastics into char: effect of plastic loading on char yield and its properties. *RSC Sustainability* **3**, 1774–1787 (2025).
4. Mishra, R. K. *et al.* Recent progress in post-modified biochar-based material for supercapacitor applications: a review. *Mater. Renew. Sustain. Energy* **14**, 63 (2025).
5. Trivedi, Y. *et al.* Biochar potential for pollutant removal during wastewater treatment: A comprehensive review of separation mechanisms, technological integration, and process analysis. *Desalination* **600**, 118509 (2025).
6. Pahnla, M., Koskela, A., Sulasalmi, P. & Fabritius, T. A review of pyrolysis technologies and the effect of process parameters on biocarbon properties. *Energies (Basel)*. **16**, 6936 (2023).
7. Ikegwu, U. M., Ozonoh, M. & Daramola, M. O. Kinetic Study of the Isothermal Degradation of Pine Sawdust during Torrefaction Process. *ACS Omega* **6**, 10759–10769 (2021).
8. Poletto, M., Zattera, A. J. & Santana, R. M. C. Thermal decomposition of wood: kinetics and degradation mechanisms. *Bioresour. Technol.* **126**, 7–12 (2012).
9. Ceylan, S. & Topçu, Y. Pyrolysis kinetics of hazelnut husk using thermogravimetric analysis. *Bioresour. Technol.* **156**, 182–188 (2014).

- 634 10. Kumar, M., Shukla, S. K., Upadhyay, S. N. & Mishra, P. K. Analysis of thermal
635 degradation of banana (*Musa balbisiana*) trunk biomass waste using iso-conversional
636 models. *Bioresour. Technol.* **310**, 123393 (2020).
- 637 11. Arumugam, D. B. & Ganesan, M. C. Catalytic co-pyrolysis of bauhinia purpurea seed and
638 waste medical plastics for sustainable biofuel production: kinetic analysis and prediction
639 modeling. *Process Safety and Environmental Protection* **189**, 374–386 (2024).
- 640 12. Criado, J. M., Malek, J. & Ortega, A. Applicability of the master plots in kinetic analysis
641 of non-isothermal data. *Thermochim. Acta* **147**, 377–385 (1989).
- 642 13. Kumar Mishra, R. Pyrolysis of low-value waste switchgrass: Physicochemical
643 characterization, kinetic investigation, and online characterization of hot pyrolysis
644 vapours. *Bioresour. Technol.* **347**, 126720 (2022).
- 645 14. Sakulkit, P., Palamanit, A., Dejchanchaiwong, R. & Reubroycharoen, P. Characteristics of
646 pyrolysis products from pyrolysis and co-pyrolysis of rubber wood and oil palm trunk
647 biomass for biofuel and value-added applications. *J. Environ. Chem. Eng.* **8**, 104561
648 (2020).
- 649 15. Varma, A. K., Thakur, L. S., Shankar, R. & Mondal, P. Pyrolysis of wood sawdust:
650 Effects of process parameters on products yield and characterization of products. *Waste*
651 *Management* **89**, 224–235 (2019).
- 652 16. Elhenawy, Y., Fouad, K., Bassyouni, M., Al-Qabandi, O. A. & Majozi, T. Yield and
653 energy outputs analysis of sawdust biomass pyrolysis. *Energy Conversion and*
654 *Management: X* **22**, 100583 (2024).
- 655 17. Ungureanu, N., Vlăduț, N.-V., Biriș, S.-Ștefan, Gheorghiță, N.-E. & Ionescu, M. Biomass
656 pyrolysis pathways for renewable energy and sustainable resource recovery: a critical
657 review of processes, parameters, and product valorization. *Sustainability* **17**, 7806 (2025).
- 658 18. Noh, Y.-H. *et al.* Ashless herbaceous biomass for slagging and fouling reduction in solid-
659 fuel boiler: Combustion and ash fusion characterizations. *Fuel* **379**, 132957 (2025).
- 660 19. Basu, P. *Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory*.
661 (Academic press, 2018).
- 662 20. Singh, G., Mishra, R. K. & Kumar, N. Pyrolysis behaviours and kinetics study of corn
663 ethanol industry co-product towards its bioenergy potential. *RSC Adv.* **15**, 43487–43503
664 (2025).
- 665 21. Jomantas, G., Buinevičius, K. & Štreika, J. Sulfur Emission Dependence on Various
666 Factors During Biomass Combustion. *Energies (Basel)*. **18**, 1701 (2025).
- 667 22. Parvari, E., Mahajan, D. & Hewitt, E. L. A Review of Biomass Pyrolysis for Production
668 of Fuels: Chemistry, Processing, and Techno-Economic Analysis. *Biomass* **5**, 54 (2025).

- 669 23. Basu, S., Chinnam, S., Mishra, R. K. & Kini, M. S. Co-pyrolysis behaviour and kinetic
670 analysis of waste mango seeds and low-density polyethylene for their bioenergy potential.
671 *Bioresour. Technol. Rep.* 102514 (2025).
- 672 24. Chen, D. *et al.* Insight into biomass pyrolysis mechanism based on cellulose,
673 hemicellulose, and lignin: Evolution of volatiles and kinetics, elucidation of reaction
674 pathways, and characterization of gas, biochar and bio-oil. *Combust. Flame* **242**, 112142
675 (2022).
- 676 25. Giudicianni, P. *et al.* Inherent Metal Elements in Biomass Pyrolysis: A Review. *Energy &*
677 *Fuels* **35**, 5407–5478 (2021).
- 678 26. Dong, J. *et al.* Effect of CaO addition on fast pyrolysis behavior of solid waste
679 components using Py GC/MS. *J. Anal. Appl. Pyrolysis* **188**, 107055 (2025).
- 680 27. Lee, J., Lee, S., Kim, C., Yoo, J. S. & Moon, J. H. High-efficiency electrochemical
681 methane conversion using Fe₂O₃-based catalysts assisted by thermochemical active
682 oxygen. *Applied Catalysis B: Environment and Energy* **344**, 123633 (2024).
- 683 28. Puri, L., Hu, Y. & Naterer, G. Critical review of the role of ash content and composition in
684 biomass pyrolysis. *Frontiers in Fuels* **2**, (2024).
- 685 29. Qu, B. *et al.* Catalysis and absorption behaviors of the shelled-hollow CaO-MgO
686 microspheres on product distributions and desulfurization during waste tire fast pyrolysis.
687 *Fuel* **387**, 134232 (2025).
- 688 30. Yao, X., Xu, K. & Liang, Y. Comparative analysis of the physical and chemical properties
689 of different biomass ashes produced from various combustion conditions. *Bioresources*
690 **12**, 3222–3235 (2017).
- 691 31. Kumar, M., Mishra, P. K. & Upadhyay, S. N. Pyrolysis of Saccharum munja:
692 Optimization of process parameters using response surface methodology (RSM) and
693 evaluation of kinetic parameters. *Bioresour. Technol. Rep.* **8**, 100332 (2019).
- 694 32. Bhardwaj, G., Kumar, M., Mishra, P. K. & Upadhyay, S. N. Kinetic analysis of the slow
695 pyrolysis of paper wastes. *Biomass Convers. Biorefin.* **13**, 3087–3100 (2023).
- 696 33. El-Sayed, S. A. & Mostafa, M. E. Pyrolysis characteristics and kinetic parameters
697 determination of biomass fuel powders by differential thermal gravimetric analysis
698 (TGA/DTG). *Energy Convers. Manag.* **85**, 165–172 (2014).
- 699 34. Hosseinzai, B. *et al.* Pyrolysis of pistachio shell, orange peel and saffron petals for
700 bioenergy production. *Bioresour. Technol. Rep.* **19**, 101209 (2022).
- 701 35. Kumar, M., Rai, D., Bhardwaj, G., Upadhyay, S. N. & Mishra, P. K. Pyrolysis of peanut
702 shell: Kinetic analysis and optimization of thermal degradation process. *Ind. Crops Prod.*
703 **174**, 114128 (2021).

- 704 36. Mishra, R. K. & Mohanty, K. Pyrolysis kinetics and thermal behavior of waste sawdust
705 biomass using thermogravimetric analysis. *Bioresour. Technol.* **251**, 63–74 (2018).
- 706 37. Kumar, M., Sabbarwal, S., Mishra, P. K. & Upadhyay, S. N. Thermal degradation kinetics
707 of sugarcane leaves (*Saccharum officinarum* L) using thermo-gravimetric and differential
708 scanning calorimetric studies. *Bioresour. Technol.* **279**, 262–270 (2019).
- 709 38. Mishra, R. K., Chinnam, S. & Sharma, A. Catalytic co-pyrolysis behaviour and kinetics
710 study of waste lignocellulosic non-edible seeds and Covid-19 plastic over Al₂O₃ catalyst.
711 *Bioresour. Technol. Rep.* **27**, 101899 (2024).
- 712 39. Aslan, D. I., Özoğul, B., Ceylan, S. & Geyikçi, F. Thermokinetic analysis and product
713 characterization of Medium Density Fiberboard pyrolysis. *Bioresour. Technol.* **258**, 105–
714 110 (2018).
- 715 40. White W. James; Legendre Benjamin L., J. E. ; C. Biomass pyrolysis kinetics: A
716 comparative critical review with relevant agricultural residue case studies. *J. Anal. Appl.*
717 *Pyrolysis* **91**, 1–33 (2011).
- 718 41. Zhan, W. *et al.* Thermal conversion studies of lignin pyrolysis and the catalytic effect of
719 Fe: A reactive molecular dynamics study. *Journal of the Energy Institute* **117**, 101795
720 (2024).
- 721 42. Vyazovkin, S. *et al.* ICTAC Kinetics Committee recommendations for analysis of multi-
722 step kinetics. *Thermochim. Acta* **689**, 178597 (2020).
- 723 43. Heydari, M., Rahman, M. & Gupta, R. Kinetic study and thermal decomposition behavior
724 of lignite coal. *International Journal of Chemical Engineering* **2015**, 481739 (2015).
- 725 44. Gesese, T. N., Getahun, E. & Getahun, A. A. Investigation of Thermal Degradation
726 Properties and Chemical Kinetic Characteristics of Biomass Pyrolysis via TG/DTG and
727 FTIR Techniques: Sesame Stalks as Potential Source of Bioenergy in Ethiopia. *Int. J.*
728 *Energy Res.* **2024**, (2024).
- 729 45. Sahoo, A., Kumar, S. & Mohanty, K. Kinetic and thermodynamic analysis of Putranjiva
730 roxburghii (putranjiva) and Cassia fistula (amaltas) non-edible oilseeds using
731 thermogravimetric analyzer. *Renew. Energy* **165**, 261–277 (2021).
- 732 46. Mishra, R. K., Lu, Q. & Mohanty, K. Thermal behaviour, kinetics and fast pyrolysis of
733 Cynodon dactylon grass using Py-GC/MS and Py-FTIR analyser. *J. Anal. Appl. Pyrolysis*
734 **150**, 104887 (2020).
- 735 47. Mishra, R. K. & Mohanty, K. Kinetic analysis and pyrolysis behaviour of waste biomass
736 towards its bioenergy potential. *Bioresour. Technol.* **311**, (2020).
- 737 48. Sher, F., Iqbal, S. Z., Liu, H., Imran, M. & Snape, C. E. Thermal and kinetic analysis of
738 diverse biomass fuels under different reaction environment: A way forward to renewable
739 energy sources. *Energy Convers. Manag.* **203**, 112266 (2020).

- 740 49. El-Sayed, S. A. & Mostafa, M. E. Kinetics, thermodynamics, and combustion
741 characteristics of Poinciana pods using TG/DTG/DTA techniques. *Biomass Convers.*
742 *Biorefin.* **13**, 11583–11607 (2023).
- 743 50. Mabuda, A. I., Mamphweli, N. S. & Meyer, E. L. Model free kinetic analysis of
744 biomass/sorbent blends for gasification purposes. *Renewable and Sustainable Energy*
745 *Reviews* **53**, 1656–1664 (2016).

746

747

748

749