

## Article

# Pyrolytic Valorization of *Polygonum multiflorum* Residues: Kinetic, Thermodynamic, and Product Distribution Analyses

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## Abstract

*Polygonum multiflorum* (PM) residues represent an underutilized biomass resource, with pyrolysis offering a promising route for valorizing its biomass into valuable chemicals and biochar. This study elucidated how the intrinsic physicochemical properties of PM residue governed its pyrolysis kinetics, thermodynamics, mechanisms, and product distribution across varying thermal regimes (slow pyrolysis at 20 °C/min vs. fast pyrolysis). The primary devolatilization stage (174–680 °C) dominated the pyrolysis process. Applying three model-free kinetic approaches (FWO, KAS, Starink) over  $0.1 < \alpha < 0.7$ , this study observed a dramatic shift in apparent activation energy (219.7–354.7 kJ/mol). Major gaseous pyrolysis products identified included alcohols, aldehydes, ketones, acids, aromatic hydrocarbons, phenolics, CO, and CO<sub>2</sub>. Ketones constituted the predominant fraction (23.80%), followed by acids (18.18%), phenolic derivatives (18.18%), N-containing compounds (14.28%), and furans (4.54%). The findings of this study contribute significant theoretical understanding and practical solutions for the effective pyrolysis and resource recovery from *Polygonum multiflorum* processing byproducts.

**Keywords:** *Polygonum multiflorum*; biomass; pyrolysis; thermogravimetric analysis; Py-GC/MS



Academic Editor: Albert Ratner

Received: 3 August 2025

Revised: 21 August 2025

Accepted: 23 August 2025

Published: 25 August 2025

**Citation:** Huang, J.; Chen, Y.; Chen, X.; Jia, D.; Evrendilek, F.; Liu, J. Pyrolytic Valorization of *Polygonum multiflorum* Residues: Kinetic, Thermodynamic, and Product Distribution Analyses. *Processes* **2025**, *13*, 2701. <https://doi.org/10.3390/pr13092701>

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## 1. Introduction

Fossil fuels are non-renewable resources underpinning societal development and economic activity; however, their intensive exploitation accelerates their depletion and precipitates severe ecological crises, such as climate change, land degradation, pollution, and ecosystem disruption [1]. These impacts challenge sustainable socioeconomic development. Currently, biomass provides approximately 10% of the worldwide energy supply, with the potential to reach 18–20% by mid-century contingent on robust policy support and continuous innovation [2]. Agricultural and forestry residues offer particular promise due to their C neutrality (typically achieving net-zero CO<sub>2</sub> emissions over their lifecycle), high calorific value, and low waste generation [3].

*Polygonum multiflorum* (PM), a medicinally valued Polygonaceae herb, exemplifies this potential. Its tuberous roots are used clinically to tonify the liver/kidneys, enrich essence/blood, and promote hair darkening, thus making PM a key raw material in pharmaceuticals and health products. Expanding cultivation driven by demand generates

substantial residues during planting, harvesting, and processing [4], primarily comprising pruned stems and post-extraction marc. In particular, bioactive constituent (e.g., anthraquinones and stilbene glycosides) extraction yields are only ~1% [5]; thus, approximately 99 kg of marc is produced per kg of extracted compounds. In China, annual plant-based medicine residue reaches ~70 million tons, with PM marc contributing tens of thousands of tons [4]. Valorizing this biomass could reduce fossil fuel dependence while generating economic and environmental benefits.

Current research on valorizing Chinese medicinal residues focuses on thermochemical pathways like pyrolysis. For instance, Zhao et al. [4] investigated changes in three-phase products of Chinese medicine residue pyrolysis and gasification under varying temperatures and oxygen contents (including PM as a component of mixed residues). Cho et al. [6] utilized red ginseng residue to improve the production of pyrolysis gas by maximizing the production of CO<sub>2</sub> in the synthesis gas. Chen et al. [7] applied a multi-technique approach (thermogravimetric–fourier-transform infrared spectroscopy–gas chromatography–mass spectrometry—TG-FTIR-GC/MS) to study the pyrolysis kinetics, real-time gas evolution, and condensable products of herbal tea and *Salvia miltiorrhiza* residues, providing mechanistic insights into their thermal decomposition. Despite the prevalence of PM residues in plant-based medicinal waste, they lack dedicated studies that correlate their unique physicochemical properties with pyrolytic behavior. In contrast, PM research has emphasized chemical constituent isolation, pharmacological validation, such as regenerative medicine [8] and processing techniques [9], with limited focus on its thermochemical conversion. While sporadic studies explore PM use in fertilizers or feed [10], systematic investigations of its pyrolytic kinetics, product yields, and volatile evolution pathways are lacking. Addressing this gap, this study aimed to (1) characterize pyrolytic mass loss of PM via TG analysis and volatile evolution and composition via TG-FTIR-GC/MS analyses; (2) identify bio-oil compounds via pyrolysis (Py)-GC/MS analysis; and (3) determine key kinetic and thermodynamic parameters via model-free methods.

## 2. Materials and Methods

### 2.1. Sample Preparation

Processed PM roots were commercially obtained from a herbal medicine supplier in Guangdong Province, China. Pretreatment involved drying, milling and sieving, and storage for analysis. Raw material was dried at 105 °C in a forced-air oven for 24 h until constant weight was achieved, ensuring complete moisture removal. Dried samples were pulverized using a high-speed grinder. The resulting powder was sieved through a 100-mesh sieve (particle size < 150 µm), and the sub-150 µm fraction was collected. The processed powder was sealed in aluminum foil bags and stored in a desiccator with silica gel desiccant at room temperature (25 ± 2 °C) to prevent moisture absorption prior to analysis.

### 2.2. Physicochemical Analyses

Proximate analysis of PM was performed according to Chinese National Standard GB/T 28731-2012 [11] (solid biofuels), determining moisture (M), ash (A), and volatile matter (VM) contents (wt%, air-dried basis). Fixed carbon content (FC, wt%, air-dried basis) was calculated as follows:

$$FC = 100 - M - A - VM$$

Ultimate analysis was employed to quantify C, H, N, and S contents (wt%, air-dried basis) via an elemental analyzer (Vario EL cube, Elementar Analysensysteme GmbH,

Langensfeld, Germany). Oxygen content (O, wt%, air-dried basis) was calculated by difference:

$$O = 100 - C - H - N - S - A - M$$

Higher heating value (HHV) was measured using a microprocessor-controlled oxygen bomb calorimeter (WZR-1T-CIL, Changsha Kaiyuan Instruments Co., Changsha, China).

### 2.3. TG-DTG Experiment

Pyrolysis was performed using a TG analyzer (TG 209 F1, Netzsch, Selb, Germany) under high-purity N<sub>2</sub> (99.999%) flowing at 50 mL/min. Experiments employed heating rates of 10, 20, and 40 °C/min with sample masses of 8.0 ± 0.20 mg lightly compacted in alumina crucibles, covering a temperature range of 25–1000 °C. This micro-scale configuration effectively minimized intraparticle heat and mass transfer limitations. The analyzer continuously recorded mass loss (TG) and derivative thermogravimetry (DTG) data as a function of temperature. System errors were corrected via blank baseline subtraction, and all analyses were performed in triplicate to ensure relative standard deviations (RSD) below 5%.

### 2.4. Pyrolysis Parameters and Performance Evaluation

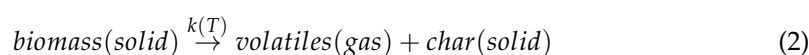
The following key parameters derived from TG analysis were used to assess PM pyrolysis performance: ignition temperature ( $T_i$ ), peak temperature ( $T_p$ ), maximum pyrolysis rate ( $-R_p, \max$ ), average mass loss rate ( $-R_v, \text{avg}$ ), and residual mass at the end of the reaction ( $R_e$ ). Also, the comprehensive pyrolysis index (CPI), a validated metric exhibiting feedstock reactivity and pyrolysis performance with a coefficient of determination ( $R^2$ ) of >0.98, was calculated as follows:

$$CPI = \frac{(-R_p) \times (-R_v) \times m_\infty}{T_i \times T_p \times \Delta T_{1/2}} \quad (1)$$

where ( $-R_p, \max$ ) is the maximum mass loss rate (%/min);  $\Delta W$  is the total mass loss over the main pyrolysis stage (wt%);  $T_p$  is the peak temperature (°C or K); and  $\Delta T_h$  is the temperature interval at half-maximum mass loss rate (°C or K).

### 2.5. Kinetic Analysis

Kinetic analysis decouples the synergistic effects of pyrolysis temperature and residence time on reaction pathways, enabling the prediction of biomass degradation behavior. While conventional models postulate reaction mechanisms a priori, inverse engineering from experimental data offers an alternative approach for identifying probable mechanistic frameworks [12]. Given the inherent complexity of biomass pyrolysis, characterized by competing endothermic/exothermic reactions, phase transitions, and mass transfer limitations, the one-step global reaction model provides a validated simplification for primary devolatilization kinetics [12]. Consistent with lignocellulosic decomposition studies, PM thermal degradation was described by the following reaction:



where the temperature-dependent rate constant  $k(T)$  follows the Arrhenius formalism as follows:

$$k(T) = Ae^{-\frac{E_\alpha}{RT}} \quad (3)$$

where  $E_\alpha$  is the activation energy (kJ·mol<sup>−1</sup>);  $A$  is the pre-exponential factor (s<sup>−1</sup>);  $R$  is the ideal gas constant (8.314 J·mol<sup>−1</sup>·K<sup>−1</sup>); and  $T$  is absolute temperature (K).

### 2.5.1. Model-Free Methods

Model-free isoconversional methods circumvent mechanistic assumptions to determine accurate apparent activation energy ( $E_\alpha$ ) values for solid-state reactions, eliminating errors from preselected reaction models [13]. This study employed three methodologies: (1) Kissinger–Akahira–Sunose (KAS); (2) Flynn–Wall–Ozawa (FWO), and (3) Starink. Reaction mechanism consistency was verified by examining  $E_\alpha$  dependence when  $\alpha = 0.1 - 0.9$ . Kinetic parameters were derived from multi-heating-rate TG profiles (10, 20, and 40 °C/min) via nonlinear regression [14]. For PM exhibiting multi-stage decomposition, reaction progress was quantified as follows:

$$\alpha = (m_0 - m_t) / (m_0 - m_f) \quad (4)$$

where  $m_0$ ,  $m_t$ , and  $m_f$  are the initial, instantaneous, and final sample masses (mg), respectively. The fundamental rate equation is as follows:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = Ae^{-\frac{E_\alpha}{RT}}f(\alpha) \quad (5)$$

where  $f(\alpha)$  is the reaction model. Given linear temperature ramping ( $\beta = dT/dt$ ), Equation (5) transforms to

$$\frac{d\alpha}{dt} = Ae^{-\frac{E_\alpha}{RT}}f(\alpha) \xrightarrow{\beta=dT/dt} \frac{d\alpha}{dT} = \frac{A}{\beta}e^{-\frac{E_\alpha}{RT}}f(\alpha) \quad (6)$$

When  $G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$ , integration yields

$$G(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \left(\frac{A}{\beta}\right) \int_0^T e^{(-\frac{E_\alpha}{RT})} \cdot dT \quad (7)$$

Under initial reaction conditions ( $\alpha \rightarrow 0$ ,  $T \rightarrow T_0$ ), Equation (7) simplifies to

$$G(\alpha) = \left(\frac{A}{\beta}\right) \int_{T_0}^T e^{(-\frac{E_\alpha}{RT})} \cdot dT \quad (8)$$

As a benchmark method for biomass kinetics [14], KAS is derived by logarithmically transforming Equation (7) and applying the Coats–Redfern approximation as follows:

$$\ln \frac{\beta}{T^2} = \ln \left( \frac{AE_\alpha}{RG(\alpha)} \right) - \frac{E_\alpha}{RT} \quad (9)$$

At a fixed conversion degree ( $\alpha$ ),  $G(\alpha)$  is constant. Plotting  $\ln(\beta/T^2)$  versus  $1/T$  yields a linear relationship where the slope  $m = -E_\alpha/R$  directly determines the activation energy.

Utilizing Doyle's approximation for the temperature integral, FWO kinetics is as follows [14]:

$$\ln \beta = \ln \left( \frac{AE_\alpha}{RG(\alpha)} \right) - 5.3305 - 1.052 \frac{E_\alpha}{RT} \quad (10)$$

For a constant value of  $\alpha$ , plotting  $\ln \beta$  versus  $1/T$  produces a linear fit. The activation energy is calculated from the slope  $m = -1.052 E_\alpha/R$ .

Synthesizing KAS and FWO approaches, Starink's equation achieves superior accuracy ( $\pm 1.5\%$  error) in  $E_\alpha$  determination:

$$\ln \frac{\beta}{T^{1.92}} = \text{Constant} - 1.0008 \left( \frac{E_\alpha}{RT} \right) \quad (11)$$

where  $C_s$  is a conversion-dependent constant. The plot of  $\ln(\beta/T^{1.92})$  versus  $1/T$  yields  $E_\alpha$  from the slope  $m = -1.0008 E_\alpha/R$ .

### 2.5.2. Master-Plots Method

The values of  $E_\alpha$  obtained via FWO, KAS, and Starink enable the determination of the most probable reaction mechanism through the master-plot method as follows [15]:

$$P(u) = \frac{\exp(-u)}{u \times (1.00198882u + 1.87391198)} \quad (12)$$

where  $u = E_\alpha / RT$ .

From Equation (7), the reaction model integral is expressed as follows:

$$G(\alpha) = \frac{AE_\alpha}{\beta R} P(u) \quad (13)$$

As a reference, when  $\alpha = 0.5$ , this becomes

$$G(0.5) = \frac{AE_\alpha}{\beta R} P(u_{0.5}) \quad (14)$$

where  $u_{0.5} = E_\alpha / RT_{0.5}$ , and  $T_{0.5}$  is the temperature when  $\alpha = 0.5$ .

The normalized master plot equation is derived by combining Equations (13) and (14):

$$\frac{G(\alpha)}{G(0.5)} = \frac{P(u)}{P(u_{0.5})} \quad (15)$$

The common dynamic models are shown in Table 1.

**Table 1.** Isoconversional kinetic models for solid-state decomposition, including reaction mechanisms and  $f(\alpha)$  (differential) and  $G(\alpha)$  (integral) functions.

| Symbol                  | Mechanism                       | $f(a)$                               | $G(a)$                      |
|-------------------------|---------------------------------|--------------------------------------|-----------------------------|
| Diffusion               |                                 |                                      |                             |
| D1                      | One-dimension diffusion         | $1/(2a)$                             | $a^2$                       |
| D2                      | Two-dimension diffusion         | $[-\ln(1-a)]^{-1}$                   | $(1-a)\ln(1-a) + a$         |
| D3                      | Three-dimension diffusion       | $[(3/2)(1-a)^{2/3}]/[1-(1-a)^{1/3}]$ | $[1-(1-a)^{1/3}]^2$         |
| D4                      | Four-dimension diffusion        | $[(3/2)(1-a)^{1/3}]/[1-(1-a)^{1/3}]$ | $(1-2a/3)-(1-a)^{2/3}$      |
| Geometrical contraction |                                 |                                      |                             |
| R2                      | Contracting cylinder            | $2(1-a)^{1/2}$                       | $1-(1-a)^{1/2}$             |
| R3                      | Contracting sphere              | $3(1-a)^{1/3}$                       | $1-(1-a)^{1/3}$             |
| Reaction order          |                                 |                                      |                             |
| F1                      | First-order reaction            | $1-a$                                | $-\ln(1-a)$                 |
| F2                      | Second-order reaction           | $(1-a)^2$                            | $(1-a)^{-1} - 1$            |
| F3                      | Third-order reaction            | $(1-a)^3$                            | $[(1-a)^{-2} - 1]/2$        |
| Fn                      | $n^{\text{th}}$ -order reaction | $(1-a)^n$                            | $[(1-a)^{(1-n)} - 1]/(n-1)$ |
| Power law               |                                 |                                      |                             |
| P2                      | One-power law                   | $2a^{1/2}$                           | $a^{1/2}$                   |
| P3                      | Two-power law                   | $3a^{1/3}$                           | $a^{1/3}$                   |
| P4                      | Three-power law                 | $4a^{1/4}$                           | $a^{1/4}$                   |
| Nucleation              |                                 |                                      |                             |
| A1.5                    | Avrami-Erofeev                  | $1.5(1-a)[- \ln(1-a)]^{1/3}$         | $[- \ln(1-a)]^{2/3}$        |
| A2                      | Avrami-Erofeev                  | $2(1-a)[- \ln(1-a)]^{1/2}$           | $[- \ln(1-a)]^{1/2}$        |
| A3                      | Avrami-Erofeev                  | $3(1-a)[- \ln(1-a)]^{2/3}$           | $[- \ln(1-a)]^{1/3}$        |
| An                      | Avrami-Erofeev                  | $n(1-a)[- \ln(1-a)]^{(n-1)/n}$       | $[- \ln(1-a)]^{1/n}$        |

## 2.6. Thermodynamic Parameter Estimation

The key thermodynamic parameters—pre-exponential factor ( $A$ ), enthalpy change ( $\Delta H$ ), Gibbs free energy change ( $\Delta G$ ), and entropy change ( $\Delta S$ )—were calculated as follows [16]:

$$A = \beta \cdot E_{\alpha} \cdot e^{\left(\frac{E_{\alpha}}{RT_P}\right)} / R \cdot T_P^2 \quad (16)$$

$$\Delta H = E_{\alpha} - RT \quad (17)$$

$$\Delta G = E_{\alpha} + R \cdot T_P \cdot \ln\left(\frac{K_B \cdot T_P}{h \cdot A}\right) \quad (18)$$

$$\Delta S = \frac{\Delta H - \Delta G}{T_P} \quad (19)$$

where  $K_B$  is the Boltzmann constant ( $1.381 \times 10^{-23}$  J/K);  $h$  is the Planck constant ( $6.626 \times 10^{-34}$  J·s);  $E_{\alpha}$  is apparent activation energy ( $\text{kJ} \cdot \text{mol}^{-1}$ );  $\beta$  is heating rate ( $^{\circ}\text{C} \cdot \text{min}^{-1}$ );  $T_P$  is peak temperature (K);  $T$  is absolute temperature (K) for  $\Delta H$ ; and  $R$  is universal gas constant ( $8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ ).

## 2.7. TG-FTIR-GC/MS Experiment

The thermal degradation behavior and volatile evolution of PM were monitored in real-time using a coupled TG-FTIR-GC/MS system. Approximately  $8.00 \pm 0.20$  mg of sample was loaded in an  $\text{Al}_2\text{O}_3$  crucible within a TG analyzer (TGA/DSC 3+, Mettler Toledo, Schwerzenbac, Switzerland) operated under high-purity  $\text{N}_2$  (99.999%) at  $50 \text{ mL/min}$ . The temperature program comprised heating from  $25^{\circ}\text{C}$  to  $302^{\circ}\text{C}$  at  $20^{\circ}\text{C/min}$  followed by a 10 min isothermal hold at  $302^{\circ}\text{C}$  to simulate slow pyrolysis conditions. Evolved volatiles were continuously transferred via heated transfer lines ( $230^{\circ}\text{C}$ ) to an FTIR (Nicolet iS 50, Thermo Fisher Scientific, Waltham, MA, USA) for functional group analysis and subsequently to a GC/MS system (GC: Trace 1300, MS: ISQ QD, Thermo Fisher Scientific, USA) for compound separation and identification. Liberated volatiles were transported through  $230^{\circ}\text{C}$  heated lines to an FTIR spectrometer (Thermo Fisher Nicolet iS 50) for functional group analysis ( $4000\text{--}500 \text{ cm}^{-1}$  range;  $4 \text{ cm}^{-1}$  resolution), and subsequently to a GC/MS system (Thermo Fisher Trace 1300 GC with ISQ QD MS) for compound separation/identification. Background signals were subtracted via blank tests. GC conditions included: initial oven temperature at  $40^{\circ}\text{C}$  (15 min), ramped at  $15^{\circ}\text{C/min}$  to  $250^{\circ}\text{C}$  (1 min hold),  $1 \text{ mL/min}$  injection flow, and  $5 \text{ mL/min}$  purge gas flow. MS operated at 70 eV ionization energy with a  $300^{\circ}\text{C}$  ion source. Spectra processing involved the use of OMNIC v9.0 software (FTIR) and NIST 2017 database matching (GC/MS).

## 2.8. Py-GC/MS Experiment

Fast pyrolysis products of PM were characterized using a pyrolyzer (PY-2020iD, Frontier Laboratories, Fukushima, Japan) coupled directly to a GC/MS (Trace Ultra-DSQ II, Thermo Scientific<sup>TM</sup>, Waltham, MA, USA). Approximately 1.00 mg of sample underwent pyrolysis under the high-purity He atmosphere at  $600^{\circ}\text{C}$ , maintaining a 24 s residence time at each target temperature. Evolved vapors were immediately transferred through a  $300^{\circ}\text{C}$ -heated transfer line (preventing condensation) to the GC inlet. Separation was achieved using an Rtx-5MS capillary column ( $30 \text{ m} \times 0.32 \text{ mm i.d.} \times 0.25 \mu\text{m}$  film thickness) with a temperature program (initial hold at  $45^{\circ}\text{C}$  for 2 min; ramp at  $4^{\circ}\text{C/min}$  to  $300^{\circ}\text{C}$ ; and final hold at  $300^{\circ}\text{C}$  for 10 min). Mass spectrometric detection employed electron ionization (70 eV). Compounds were identified by matching mass spectra against the NIST 2017 database, validated with retention indices and literature data. This technique enables qualitative identification and semi-quantitative analysis of individual components within pyrolytic vapors.

### 3. Results and Discussion

#### 3.1. Physicochemical Properties and Pyrolysis Suitability of PM Residues

Table 2 summarizes the proximate analysis, ultimate analysis, and higher heating value (HHV) of PM biomass. Its moisture content (4.10 wt%) was below the 10 wt% threshold optimal for pyrolysis [17], minimizing energy losses from water evaporation and volatile condensation. PM exhibited more volatile matter (69.83 wt% vs. 28.34 wt%), enhancing its devolatilization efficiency and ignition characteristics, but lower fixed carbon (20.81 wt% vs. 61.36 wt%) and reduced HHV, consistent with typical biomass fuels, than coal [18]. PM's fixed carbon content (20.81 wt%) exceeded that of corn stover (5.80 wt%) [19] and wheat straw (17.54 wt%) [20], suggesting its higher energy density. Elemental analysis revealed that PM's S content (0.03 wt%) was low, significantly reducing its SO<sub>x</sub> emission risks. Its N content (0.91 wt%) fell between those of corn stover (3.51 wt%) [21] and wheat straw (0.58 wt%) [20], indicating its NO<sub>x</sub> emission potential comparable to conventional biomass. Thus, this nitrogen content inherently translates into a potential for NO<sub>x</sub> emissions during the thermochemical conversion processes.

**Table 2.** Physicochemical fuel properties of *Polygonum multiflorum* residues on an air-dried basis.

| Sample | Proximate Analysis (wt%) |       |      |       | Ultimate Analysis (wt%) |      |      |       | HHV  |         |
|--------|--------------------------|-------|------|-------|-------------------------|------|------|-------|------|---------|
|        | M                        | V     | Ash  | FC    | C                       | H    | N    | O     | S    | (MJ/kg) |
| PM     | 4.10                     | 69.83 | 5.26 | 20.81 | 43.10                   | 6.07 | 0.91 | 44.63 | 0.03 | 16.69   |

O (wt%) = 100 – C – H – N – S – M – Ash; M, V, Ash, FC, and HHV refer to moisture, volatile matter, ash content, fixed carbon, and high calorific value, respectively.

The higher heating value of PM (16.69 MJ/kg) aligned with energy-dense herbaceous biomass, falling within the range of rice husk (14.81 MJ/kg) [22] and closely matching wheat straw (17.00 MJ/kg) [23]. In particular, PM's elemental composition revealed high C (43.10 wt%) and O (44.63 wt%) contents, indicating abundant oxygenated organic compounds that enhance thermal reactivity. Consequently, PM represents a viable pyrolysis feedstock with inherently lower SO<sub>x</sub> emission risks than conventional biomass or coal, while its NO<sub>x</sub> emission potential remains comparable to similar biomass.

#### 3.2. Thermal Decomposition Regime with Stage/Heating Rate-Specific Effects

The PM pyrolysis followed stage-specific decomposition: initial removal of adsorbed/crystalline water, followed by sequential degradation of hemicellulose (dehydration/depolymerization), cellulose (pyrolysis), and lignin (aromatization/fragmentation) [24]. This pathway was effectively modeled as superimposed reactions of the three primary components [25], with residual char undergoing further thermochemical conversion. Figure 1 reveals the TG and DTG curves, with stage-specific mass loss for PM. Using 20 °C/min as representative, PM pyrolysis exhibited three distinct stages [24,25]. Stage I (30–174 °C) resulted in 3.7 wt% loss from water evaporation and light extractives volatilization. Stage II (174–680 °C) was the dominant degradation phase (71.16 wt% loss, ~90% of total) with peak rate ( $-R_p$ , max) of 13.31%/min at 302.0 °C. Primary mechanisms included hemicellulose/cellulose depolymerization and partial lignin pyrolysis via bond scission, radical recombination, and oxygenated volatile formation [26]. Stage III (680–1000 °C) led to minimal mass loss (1.04 wt%) from lignin aromatization and mineral decomposition, yielding 24.1 wt% solid residue.

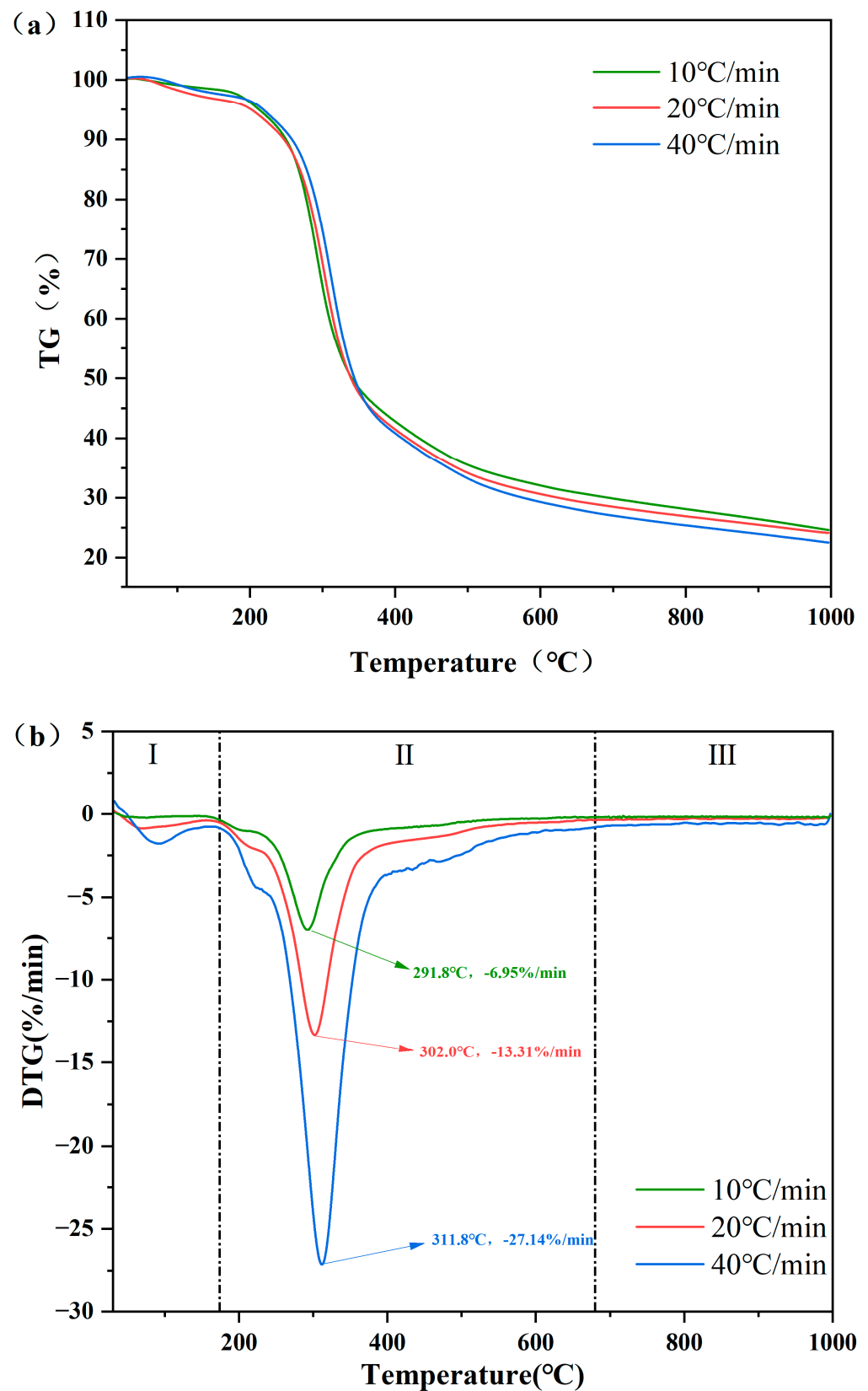


Figure 1. The (a) TG and (b) DTG curves of the PM pyrolysis at 10, 20, and 40 °C/min.

While the TG curve represents instantaneous sample mass, DTG characterizes the mass loss rate. Figure 1b reveals highly consistent DTG profile trends for the PM pyrolysis at 10, 20, and 40 °C/min, indicating heating-rate-independent reaction pathways. During the dominant Stage II decomposition, the DTG curves exhibited a single compos-

ite peak reflecting the overlapping decomposition of lignocellulosic constituents [27]. In particular, increasing heating rates from 10 to 40 °C/min amplified peak intensity ( $-R_p$ , max), shifted peak temperatures upward (292.1→312.2 °C), and reduced Stage II duration (97.5→22.5 min). These trends confirmed enhanced reaction intensity per unit time at the higher heating rates, attributed to thermal gradient lag effects and reaction kinetics. Specifically, the rapid heating induced internal heat transfer limitations, delaying the apparent peak decomposition temperature. Concurrently, the increased heating rates reduced the reaction time per temperature interval through Arrhenius kinetics, thus shifting the decomposition peaks to the higher temperatures [28]. In other words, the rapid heating induced internal heat transfer limitations, delaying peak decomposition temperatures [28]. Furthermore, Figure 2 shows increased Stage II mass loss and decreased solid residue yield with the elevated heating rates.

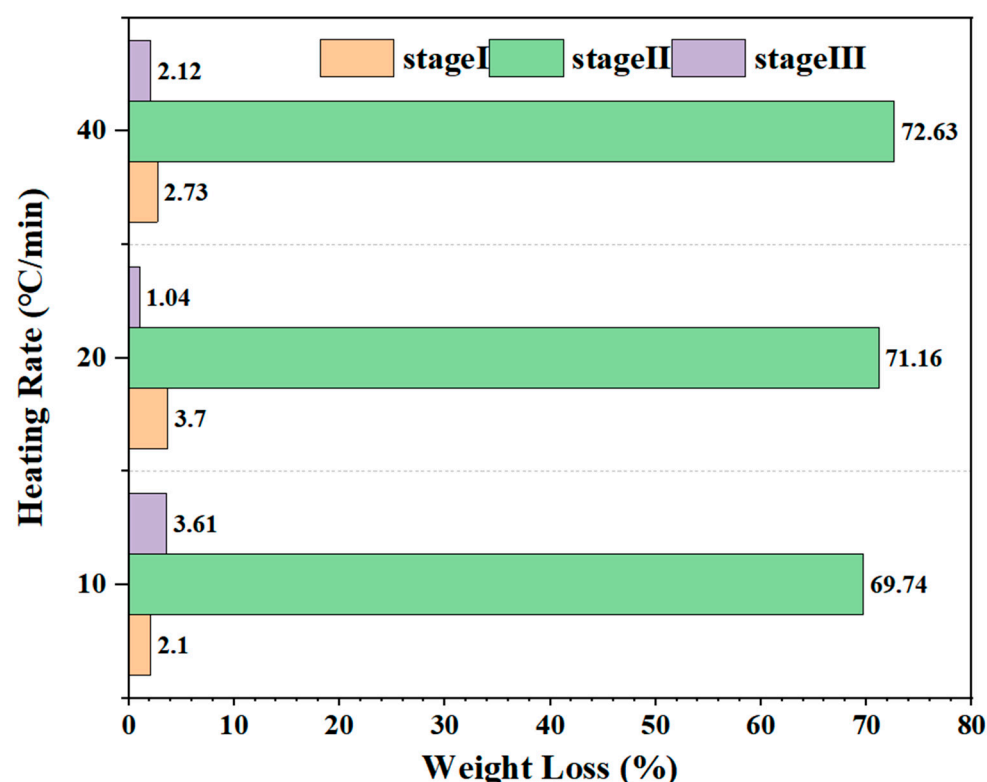


**Figure 2.** Stage-specific mass loss distributions of the PM pyrolysis at 10, 20, and 40 °C/min.

### 3.3. Key Pyrolysis Performance Indicators

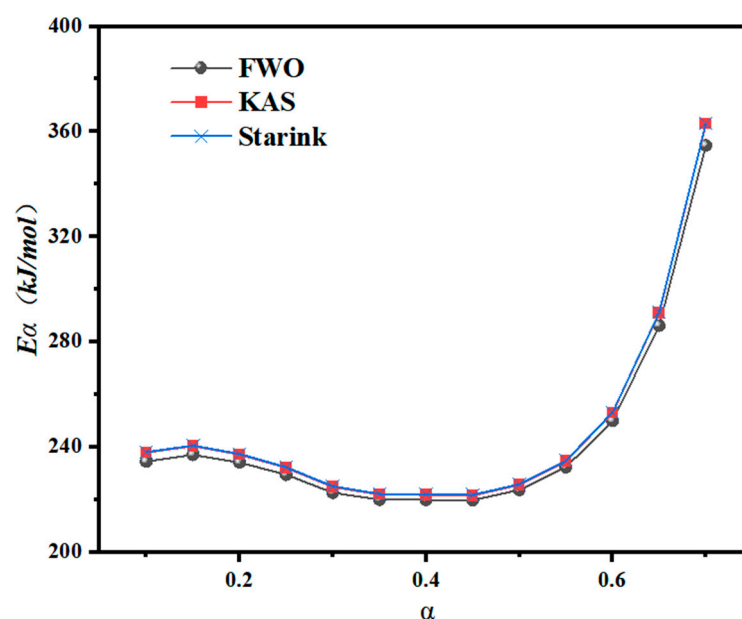
Key pyrolysis parameters for PM are summarized in Table 3. As the heating rate ( $\beta$ ) increased from 10 to 40 °C/min, ignition temperature ( $T_i$ ) and peak temperature ( $T_p$ ) significantly increased (292→312 °C), while total pyrolysis time decreased 8.1-fold from 182.8 to 22.5 min. Concurrently, maximum mass loss rate ( $-R_p$ , max) surged 3.9-fold (6.95→27.14%/min), while the CPI increased 12.7-fold from  $9.72 \times 10^{-5}$  to  $123.76 \times 10^{-5}$ . This behavior reflected competing thermal kinetics. Although Arrhenius kinetics predicted accelerated reactions at the elevated temperatures, PM thermal lag delayed temperature thresholds [29]. The observed CPI enhancement confirms superior reaction intensity and efficiency at higher heating rates. Final mass loss ( $m_\infty \approx 80\%$ ) aligns with PM's inherent high volatile matter (69.83 wt%) and ash (5.26 wt%) content, consistent with thermal conversion patterns observed in medicinal herb residues [29] and fungal substrates [30].

**Table 3.** Pyrolysis characteristic parameters of PM at the three heating rates.

| $\beta$<br>(°C/min) | $T_i$<br>(°C) | $T_p$<br>(°C) | $-R_p$<br>(%/min) | $-R_m$<br>(%/min) | $R_e$<br>(%) | $CPI$<br>( $10^{-5} \cdot \%^3 \cdot \text{min}^{-2} \cdot ^\circ\text{C}^{-3}$ ) |
|---------------------|---------------|---------------|-------------------|-------------------|--------------|-----------------------------------------------------------------------------------|
| 10                  | 254.0         | 291.8         | 6.95              | 0.79              | 24.36        | 9.72                                                                              |
| 20                  | 263.9         | 302.0         | 13.31             | 1.58              | 23.89        | 31.9                                                                              |
| 40                  | 270.0         | 311.8         | 27.14             | 3.26              | 22.27        | 124                                                                               |

### 3.4. Kinetic Analysis: Apparent Activation Energy Trends

FWO, KAS, and Starink were applied to determine the  $E_\alpha$  values of the PM pyrolysis during Stage II (174–680 °C) when  $0.1 < \alpha < 0.7$  at 0.05 intervals (Figure 3). The  $R^2$  values  $> 0.9$  (0.994–0.999) for all linear regressions for  $\ln\beta$  (FWO),  $\ln(\beta/T^2)$  (KAS), and  $\ln(\beta/T^{1.92})$  (Starink) vs.  $1/T$  (Table 4) confirmed method validity and estimation reliability. The  $E_\alpha$  profiles exhibited consistent conversion-dependent behaviors. During the low conversion ( $\alpha < 0.6$ ), stable  $E_\alpha$  values (FWO: 219–228 kJ/mol; KAS: 225–237 kJ/mol; Starink: 230–242 kJ/mol) reflected the decomposition of labile components (hemicellulose/extractives) requiring consistent energy input. When  $\alpha \approx 0.7$ ,  $E_\alpha$  sharply rose to 354.72 kJ/mol (FWO model), which corresponded to simultaneous cellulose depolymerization and lignin fragmentation. The  $E_\alpha$  values increased sharply when  $\alpha > 0.7$  and ranged from 354.72 to 627.99 kJ/mol. Therefore, the data when  $\alpha > 0.7$  were not analyzed in this study.

**Figure 3.** Variation in apparent activation energy ( $E_\alpha$ ) with conversion degree ( $\alpha$ ) for the PM pyrolysis at 20 °C/min determined by the FWO, KAS, and Starink methods.**Table 4.** Apparent activation energies ( $E_\alpha$ ) for the PM pyrolysis determined by the FWO, KAS, and Starink methods.

| $\alpha$ | FWO                 |       | KAS                 |       | Starink             |       |
|----------|---------------------|-------|---------------------|-------|---------------------|-------|
|          | $E_\alpha$ (kJ/mol) | $R^2$ | $E_\alpha$ (kJ/mol) | $R^2$ | $E_\alpha$ (kJ/mol) | $R^2$ |
| 0.10     | 234.38              | 0.999 | 237.87              | 0.999 | 238.03              | 0.999 |
| 0.15     | 236.99              | 0.997 | 240.36              | 0.997 | 240.52              | 0.997 |
| 0.20     | 234.07              | 0.998 | 237.12              | 0.998 | 237.29              | 0.998 |
| 0.25     | 229.41              | 0.999 | 232.09              | 0.999 | 232.27              | 0.999 |
| 0.30     | 222.60              | 0.999 | 224.81              | 0.999 | 225.01              | 0.999 |

Table 4. Cont.

| $\alpha$ | FWO                   |       | KAS                   |       | Starink               |       |
|----------|-----------------------|-------|-----------------------|-------|-----------------------|-------|
|          | $E_{\alpha}$ (kJ/mol) | $R^2$ | $E_{\alpha}$ (kJ/mol) | $R^2$ | $E_{\alpha}$ (kJ/mol) | $R^2$ |
| 0.35     | 219.93                | 0.999 | 221.92                | 0.999 | 222.12                | 0.999 |
| 0.40     | 219.84                | 0.999 | 221.74                | 0.999 | 221.95                | 0.999 |
| 0.45     | 219.70                | 0.999 | 221.51                | 0.999 | 221.72                | 0.999 |
| 0.50     | 223.67                | 0.999 | 225.60                | 0.999 | 225.81                | 0.999 |
| 0.55     | 232.29                | 0.999 | 234.57                | 0.999 | 234.77                | 0.999 |
| 0.60     | 249.89                | 0.999 | 252.97                | 0.999 | 253.17                | 0.999 |
| 0.65     | 286.16                | 0.997 | 290.98                | 0.997 | 291.15                | 0.997 |
| 0.70     | 354.72                | 0.994 | 362.91                | 0.994 | 363.03                | 0.994 |
| Average  | 243.36                | —     | 246.50                | —     | 246.68                | —     |

### 3.5. Thermal Decomposition Mechanisms

Model-free kinetic analysis yielded activation energies consistent with theoretical expectations, confirming that a single dominant reaction mechanism governed the PM pyrolysis. Given methodological consistency ( $E_{\alpha}$  differences < 5% across FWO/KAS/Starink) and FWO's superior regression quality ( $R^2 > 0.99$ ), we adopted FWO-derived  $E_{\alpha}$  for quantitative analysis. Figure 4a demonstrates heating-rate independence in the normalized master plot  $P(u)/P(u_{0.5})$  versus  $\alpha$ , confirming consistent reaction pathways across thermal regimes. Subsequent analysis, therefore, utilized the 20 °C/min profile. Figure 4b identifies the optimal reaction model by comparing experimental and theoretical master plots. The Fn (reaction-order) model family best described the kinetics, where the rate-determining step is chemical reaction control rather than diffusion. Specifically, the F8 model aligned with experimental data, evidenced by its integral form:  $G(\alpha) = ((1 - \alpha)^{-7} - 1)/7$  (Figure 4b). This eighth-order reaction model signified multi-step decomposition pathways during Stage II pyrolysis (174–680 °C).

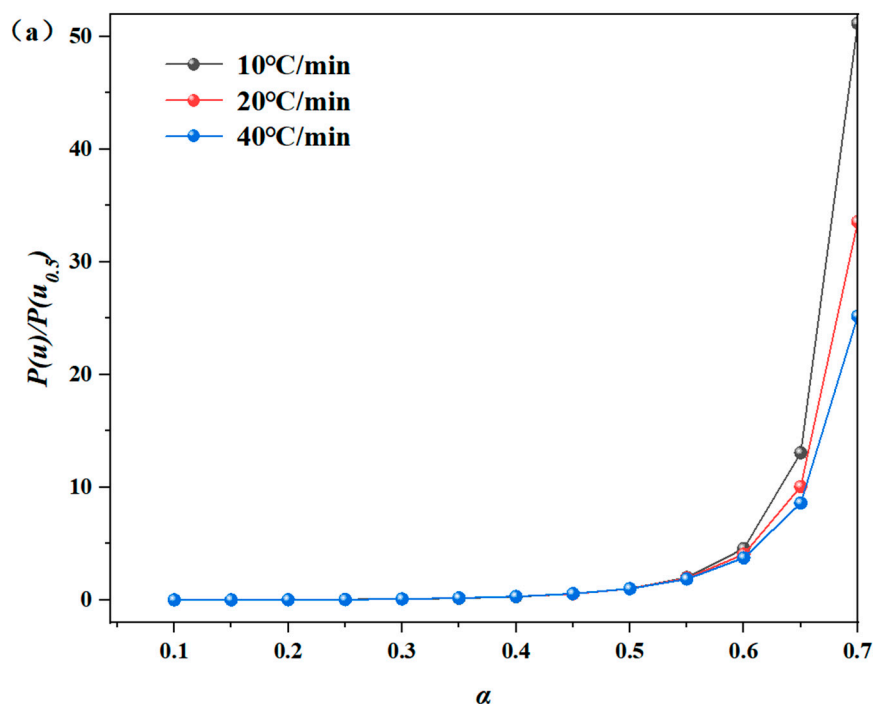


Figure 4. Cont.

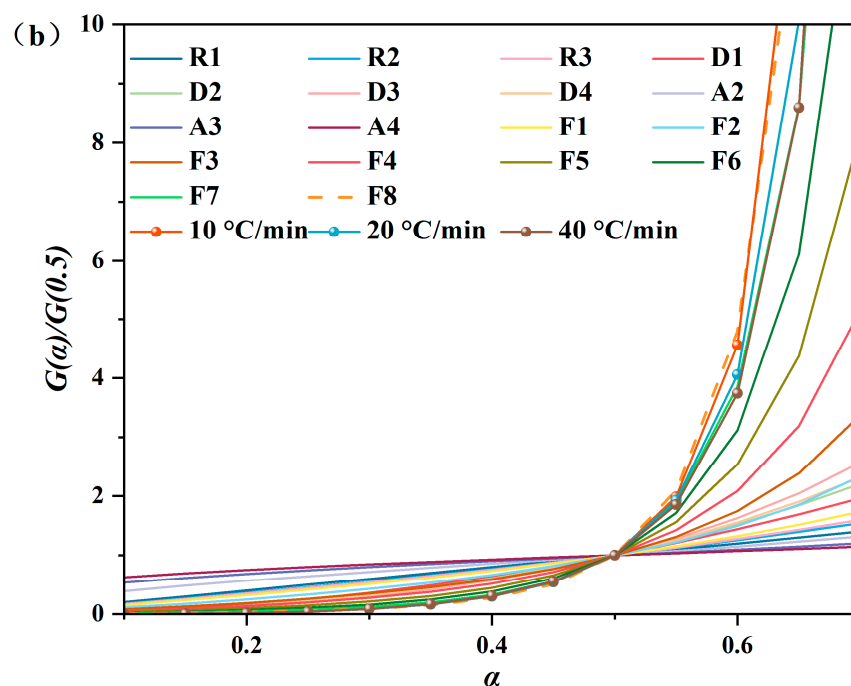


**Figure 4.** (a) Normalized master plots ( $P(u)/P(u_{0.5})$  vs.  $\alpha$ ) and (b) experimental vs. theoretical reaction models for mechanism identification for the PM pyrolysis at 10, 20, and 40 °C/min.

### 3.6. Thermodynamic Parameter Evolution

Figure 5a–d depicts the evolution of  $A$ ,  $\Delta H$ ,  $\Delta G$ , and  $\Delta S$  as a function of  $\alpha$  during the PM pyrolysis (see Table 5 for detailed data). The value of  $A$  reflects molecular collision frequency, where  $A > 10^9 \text{ s}^{-1}$  characterizes highly reactive systems [31].  $\ln A$  values ranged from 46.17 to 70.12 (corresponding to  $10^{20}$ – $10^{30} \text{ s}^{-1}$ ) when  $\alpha = 0.1$ – $0.7$ , confirming sustained high reactivity throughout the decomposition. In particular, a 51% increase in  $\ln A$  from 46.17 when  $\alpha = 0.1$  to 70.12 when  $\alpha = 0.7$  indicated accelerated thermal cracking driven by reaction front progression.

**Table 5.** Thermodynamic parameters of the PM pyrolysis at 20 °C/min when  $\alpha = 0.1$ – $0.7$ .

| $\alpha$ | $E_a$  | $A$<br>( $\text{s}^{-1}$ ) | $\Delta H$<br>( $\text{kJ/mol}$ ) | $\Delta G$<br>( $\text{kJ/mol}$ ) | $\Delta S$<br>( $\text{kJ/mol}$ ) |
|----------|--------|----------------------------|-----------------------------------|-----------------------------------|-----------------------------------|
| 0.1      | 234.38 | $5.52 \times 10^{23}$      | 230.04                            | 127.28                            | 0.20                              |
| 0.15     | 236.99 | $2.04 \times 10^{23}$      | 232.52                            | 131.35                            | 0.19                              |
| 0.2      | 234.07 | $3.77 \times 10^{22}$      | 229.51                            | 134.18                            | 0.17                              |
| 0.25     | 229.41 | $6.38 \times 10^{21}$      | 224.79                            | 136.37                            | 0.16                              |
| 0.3      | 222.60 | $8.08 \times 10^{20}$      | 217.92                            | 138.22                            | 0.14                              |
| 0.35     | 219.93 | $2.78 \times 10^{20}$      | 215.21                            | 139.79                            | 0.13                              |
| 0.4      | 219.84 | $1.76 \times 10^{20}$      | 215.08                            | 141.21                            | 0.13                              |
| 0.45     | 219.70 | $1.12 \times 10^{20}$      | 214.89                            | 142.57                            | 0.13                              |
| 0.5      | 223.67 | $1.69 \times 10^{20}$      | 218.82                            | 143.89                            | 0.13                              |
| 0.55     | 232.29 | $6.37 \times 10^{20}$      | 227.39                            | 145.28                            | 0.14                              |
| 0.6      | 249.89 | $1.37 \times 10^{22}$      | 244.94                            | 146.74                            | 0.16                              |
| 0.65     | 286.16 | $1.04 \times 10^{25}$      | 281.13                            | 148.34                            | 0.22                              |
| 0.7      | 354.72 | $2.80 \times 10^{30}$      | 349.60                            | 150.35                            | 0.32                              |

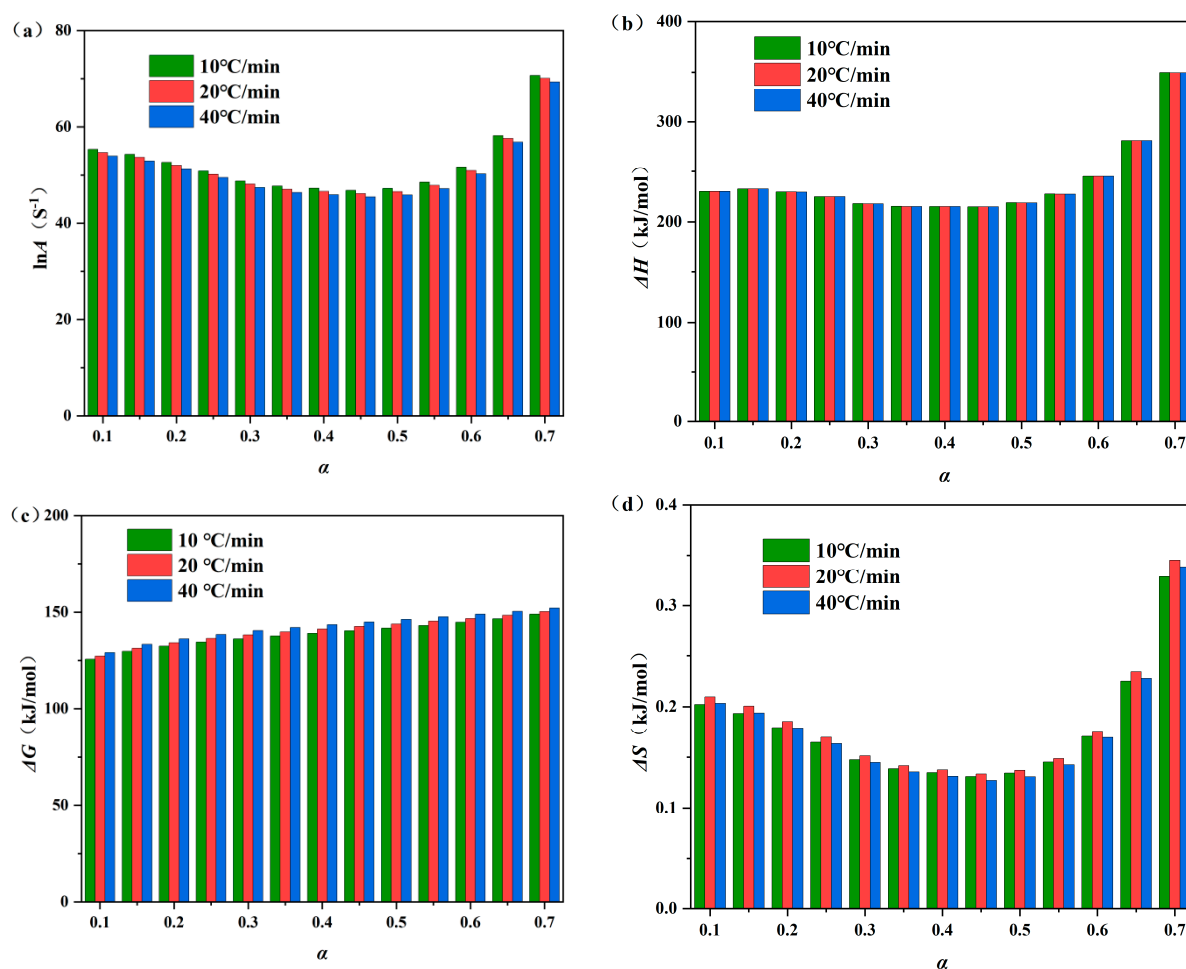


**Figure 5.** Evolution of the four thermodynamic parameters during the PM pyrolysis: (a)  $\ln A$ ; (b)  $\Delta H$ ; (c)  $\Delta G$ ; and (d)  $\Delta S$  as a function of conversion degree ( $\alpha$ ) and heating rate ( $\beta$ ).

Enthalpy change ( $\Delta H$ ), representing net energy absorption for bond cleavage during pyrolytic product formation [31], progressively increased from  $\alpha = 0.4$  to 0.7 (Figure 5b), peaking at 349.60 kJ/mol. This 163% increase reflected escalating energy barriers in the advanced conversion stages, corresponding to maximal endothermic demand preceding reaction completion. The minimum energy barrier ( $\Delta H - E_a$ ) [32] rose from 4.35 kJ/mol ( $\alpha = 0.4$ ) to 5.12 kJ/mol ( $\alpha = 0.7$ ) while remaining  $< 10$  kJ/mol, thus confirming PM's inherently facile pyrolytic conversion.

Gibbs free energy change ( $\Delta G$ ), governing pyrolysis spontaneity (Figure 5c), remained positive ( $139 \pm 11$  kJ/mol) when  $\alpha = 0.1$ –0.7, confirming non-spontaneous decomposition requiring continuous energy input. Its stability ( $\pm 2\%$  variation) indicated consistent thermodynamic driving forces across the stages. The heating-rate invariant values of  $\Delta G$  confirmed its state-function behavior under non-isothermal conditions. Entropy change ( $\Delta S$ ) remained positive across the decomposition (Figure 5d), reflecting increased disorder from volatile fragment generation.  $\Delta S$  rose monotonically from  $\alpha = 0.1$  to 0.7, peaking when  $\alpha = 0.7$  due to maximal molecular diversity during terminal carbohydrate depolymerization.

### 3.7. Real-Time Volatile Evolution During Slow Pyrolysis

Functional group evolution and gaseous product composition during the PM slow pyrolysis were analyzed via coupled FTIR and GC/MS. Figure 6 shows the FTIR spectrum at the DTG peak temperature (302.0 °C, 20 °C/min), revealing characteristic functional groups of the pyrolysis products. Table 6 details (i) identified functional groups with vibrational

modes and corresponding volatiles, and (ii) major pyrolysis compounds (GC/MS relative abundance > 1%) [33].

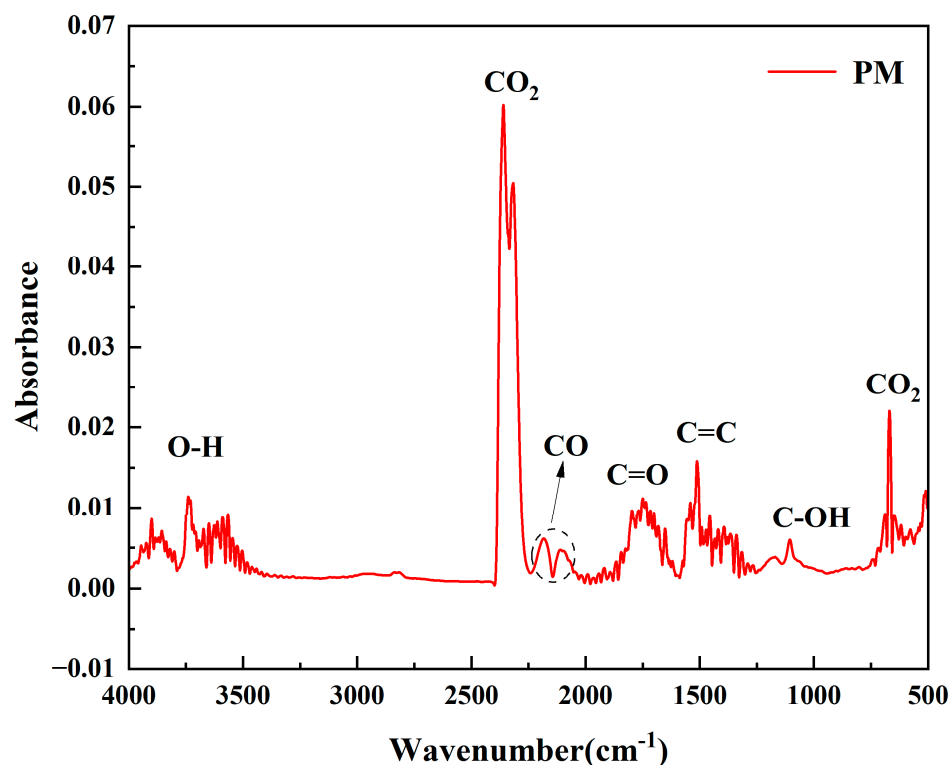


**Figure 6.** FTIR spectrum of volatile products from the PM slow pyrolysis at 302.0 °C.

**Table 6.** Assignment of FTIR absorption bands for volatile products from the PM Slow pyrolysis at 302 °C.

| Wavenumber (cm <sup>-1</sup> ) | Functional Group      | Possible Compounds                    |
|--------------------------------|-----------------------|---------------------------------------|
| 4000–3500                      | O-H                   | Water, alcohols, and carboxylic acids |
| 2400–2240                      | C=O                   | CO <sub>2</sub>                       |
| 2240–2020                      | C-O                   | CO                                    |
| 1900–1650                      | C=O                   | Aldehydes, ketones, acids             |
| 1650–1250                      | C=C, benzene skeleton | Aromatics                             |
| 1250–1000                      | C-O, O-H              | Ethers, alcohols                      |
| 750–500                        | C=O                   | CO <sub>2</sub>                       |

FTIR analysis of the PM pyrolysis products at 302 °C revealed key functional groups (Figure 6): O-H stretching (water release from mineral-bound/crystalline water and dehydration of oxygenated groups (180–530 °C)) between 4000 and 3500 cm<sup>-1</sup>; CO<sub>2</sub> antisymmetric stretching (primary gas from decarboxylation of hemicellulose/cellulose acetyl/carboxyl groups) between 2400 and 2240 cm<sup>-1</sup> + 670 cm<sup>-1</sup>; weak CO peak (carbonyl/ether bond degradation) between 2240 and 2020 cm<sup>-1</sup>; C=O stretching (aldehydes/ketones/acids; cellulose/hemicellulose markers [6]) between 1900 and 1650 cm<sup>-1</sup>; C=C aromatic vibration (phenolics; lignin pyrolysis signature) between 1650 and 1250 cm<sup>-1</sup>; and C-O/O-H stretching (alcohol formation) between 1250 and 1000 cm<sup>-1</sup>. GC/MS-identified high-value industrial precursors included benzene (C<sub>6</sub>H<sub>6</sub>) and 2,5-dimethylfuran (C<sub>6</sub>H<sub>8</sub>O) (Table 7). Products segregated into two classes: (1) Primary volatiles (174–680 °C): alcohols, aldehydes, phenols, toluene, and alkanes from direct hemicellulose/cellulose/lignin cracking.

(2) Secondary gases (initiating at  $\approx 300$  °C and dominating  $> 680$  °C): CO/CO<sub>2</sub> from decarboxylation of primary aldehydes.

**Table 7.** Major volatile compounds identified by GC/MS during the slow pyrolysis of PM at 302.0 °C.

| No | RT    | Area (%) | Substance                                        | Formula                                                         | MW  | Class        |
|----|-------|----------|--------------------------------------------------|-----------------------------------------------------------------|-----|--------------|
| 1  | 2.71  | 52.4     | 3-methyl-Furan                                   | C <sub>5</sub> H <sub>6</sub> O                                 | 82  | Furan        |
| 2  | 3.43  | 17.23    | Benzene                                          | C <sub>6</sub> H <sub>6</sub>                                   | 78  | Benzene      |
| 3  | 7.82  | 19.68    | Furfural                                         | C <sub>5</sub> H <sub>4</sub> O <sub>2</sub>                    | 96  | Aldehyde     |
| 4  | 9.09  | 5.02     | 4-[[[(4-methylphenyl)sulfonyl]oxy]-Cyclohexanone | C <sub>13</sub> H <sub>16</sub> O <sub>4</sub> S                | 268 | Ketones      |
| 5  | 9.71  | 1.32     | 2-(9,12-octadecadienyloxy)-, (Z,Z)-Ethanol       | C <sub>20</sub> H <sub>38</sub> O <sub>2</sub>                  | 310 | Alcohol      |
| 6  | 22.92 | 0.81     | 3-ethyl-5-(2-ethylbutyl)-Octadecane              | C <sub>26</sub> H <sub>54</sub>                                 | 366 | Hydrocarbons |
| 7  | 23.83 | 0.86     | Methyl glycocholate, 3TMS derivative             | C <sub>36</sub> H <sub>69</sub> NO <sub>6</sub> Si <sub>3</sub> | 695 | Ester        |
| 8  | 24.1  | 0.86     | 3-Desoxo-3,16-dihydroxy-12-desoxyphorbol         | C <sub>28</sub> H <sub>38</sub> O <sub>10</sub>                 | 534 | Ester        |
| 9  | 24.12 | 0.85     | 3,13,16,20-tetraacetate Withaferin A             | C <sub>28</sub> H <sub>38</sub> O <sub>6</sub>                  | 470 | Withaferin   |
| 10 | 25.49 | 1.17     | Oleic acid, 3-(octadecyloxy)propyl ester         | C <sub>39</sub> H <sub>76</sub> O <sub>3</sub>                  | 592 | Ester        |
| 11 | 26.88 | 0.49     | 3-acetoxy-7,8-Epoxy lanostan-11-ol               | C <sub>32</sub> H <sub>54</sub> O <sub>4</sub>                  | 502 | Alcohol      |

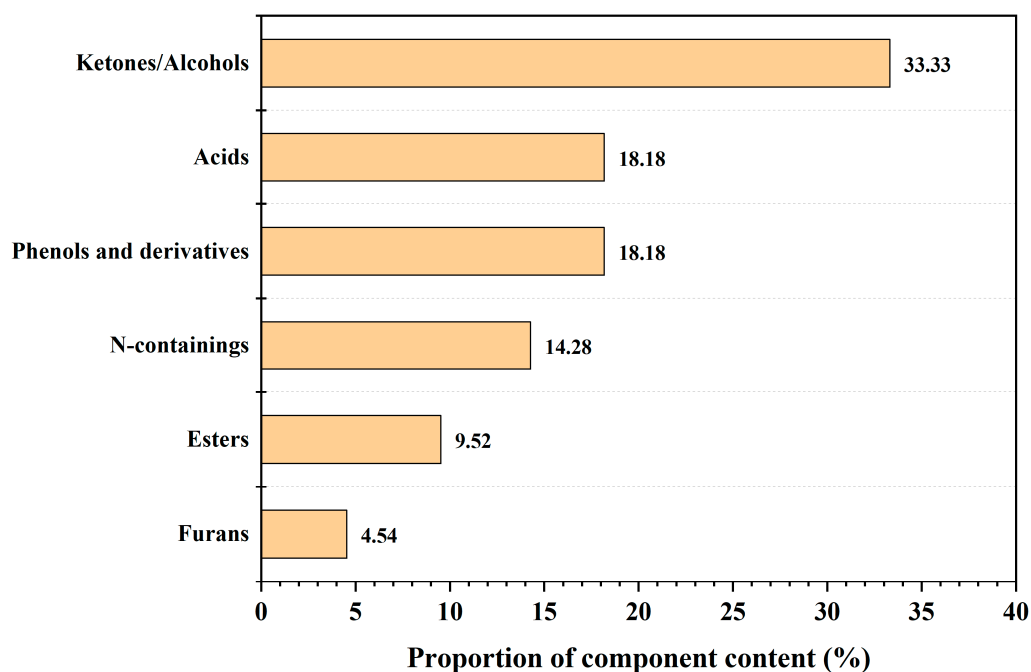
### 3.8. Fast-Pyrolysis Product Distribution

GC/MS analysis of the PM fast pyrolysis products at 600 °C (Table 8) identified 21 compounds (relative abundance  $> 1\%$ ) spanning 11 chemical classes. Ketones dominated (23.8%), followed by acids and phenolic derivatives (both 18.18%), N-containing compounds (14.28%), and furans (4.54%) (Figure 7). Product formation mechanisms reflected biopolymer decomposition pathways. Cellulose underwent  $\beta$ -1,4-glycosidic bond cleavage to yield platform compounds including D-glucan and 5-hydroxymethylfurfural (5-HMF) [26]. Hemicellulose depolymerization and dehydration generated furfural, furfuryl alcohol, and derivatives. These carbohydrate fractions collectively contributed alcohols, aldehydes/ketones, and organic acids. Lignin depolymerization primarily produced phenolic compounds (phenol, guaiacol, cresols, and catechol) and aromatic hydrocarbons.

The product spectrum and yield of PM residues demonstrated competitive advantages for valorization compared to other medicinal herb residues and dedicated energy crops. For instance, the yield of furfural from PM slow pyrolysis (19.68% relative abundance, Table 7) was notably higher than that of *Salvia miltiorrhiza* residues (approximately 10–15% under similar conditions) [7]. This highlights PM's potential as a superior feedstock for producing this high-value chemical. Furthermore, the high abundance of phenolic compounds (18.18% in fast pyrolysis) was comparable to or exceeded that of many lignocellulosic energy crops, such as switchgrass (17.95%) [34]. High-value products included furfural, a platform chemical for resins and solvents [33], and hydroxyacetone, a demonstrated precursor for bio-based lactic acid synthesis [35]. Styrene and anthraquinone derivatives (notably 1,8-dihydroxy-3-methoxy-6-methylanthraquinone) were confirmed as PM-specific markers [36]. The presence of these specific compounds, particularly the anthraquinone derivatives, presents not only a challenge for downstream bio-oil fuel applications due to potential toxicity but also an opportunity for the recovery of high-value chemicals via an integrated biorefinery approach.

**Table 8.** Major products identified by Py-GC/MS during the fast pyrolysis of PM at 600 °C.

| No | RT    | Area (%) | Substance                                               | Formula                                                      | MW  | Class         |
|----|-------|----------|---------------------------------------------------------|--------------------------------------------------------------|-----|---------------|
| 1  | 1.49  | 5.54     | Carbamic acid, monoammonium salt                        | CH <sub>6</sub> N <sub>2</sub> O <sub>2</sub>                | 78  | Carbamates    |
| 2  | 1.97  | 1.17     | Ethenyl ester                                           | C <sub>4</sub> H <sub>6</sub> O <sub>2</sub>                 | 86  | Ester         |
| 3  | 2.02  | 2.22     | 3-Cyclopentene-1,2-diol, cis-                           | C <sub>5</sub> H <sub>8</sub> O <sub>2</sub>                 | 100 | Alcohols      |
| 4  | 2.26  | 9.22     | Acetic acid                                             | C <sub>2</sub> H <sub>4</sub> O <sub>2</sub>                 | 60  | Acids         |
| 5  | 2.48  | 12.3     | 2-Propanone, 1-hydroxy-                                 | C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>                 | 74  | Ketones       |
| 6  | 2.65  | 2.31     | Furan, 2,5-dimethyl-                                    | C <sub>6</sub> H <sub>8</sub> O                              | 96  | Furan         |
| 7  | 3.28  | 1.29     | Hydrazinecarboxylic acid, phenylmethyl ester            | C <sub>8</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> | 166 | Ester         |
| 8  | 3.56  | 3.05     | 3-Amino-2-oxazolidinone                                 | C <sub>3</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub>  | 102 | Ketones       |
| 9  | 4.44  | 9.49     | 2-Furanmethanol                                         | C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>                 | 98  | Alcohols      |
| 10 | 5.61  | 1.69     | 2-Cyclopenten-1-one, 2-hydroxy-                         | C <sub>5</sub> H <sub>6</sub> O <sub>2</sub>                 | 98  | Ketones       |
| 11 | 5.97  | 3.58     | 2-Furancarboxaldehyde, 5-methyl-                        | C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>                 | 110 | Aldehyde      |
| 12 | 6.36  | 12.81    | Phenol                                                  | C <sub>6</sub> H <sub>6</sub> O                              | 94  | Phenol        |
| 13 | 7.13  | 7.33     | 3-methyl-1,2-Cyclopentanedione                          | C <sub>6</sub> H <sub>8</sub> O <sub>2</sub>                 | 112 | Ketones       |
| 14 | 7.49  | 4.0      | o-Cresol                                                | C <sub>7</sub> H <sub>8</sub> O                              | 108 | Phenol        |
| 15 | 7.84  | 7.35     | p-Cresol                                                | C <sub>7</sub> H <sub>8</sub> O                              | 108 | Phenol        |
| 16 | 8.49  | 0.41     | 3-ethyl-2-hydroxy-2-Cyclopenten-1-one                   | C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>                | 126 | Ketones       |
| 17 | 9.66  | 1.93     | Dodecanoic acid, 3-hydroxy-                             | C <sub>12</sub> H <sub>24</sub> O <sub>3</sub>               | 216 | Acids         |
| 18 | 9.88  | 0.94     | Catechol                                                | C <sub>6</sub> H <sub>6</sub> O <sub>2</sub>                 | 110 | Phenol        |
| 19 | 18.8  | 6.41     | n-Hexadecanoic acid                                     | C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>               | 256 | Acids         |
| 20 | 20.49 | 2.77     | Oleic acid                                              | C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>               | 282 | Acids         |
| 21 | 24.78 | 4.20     | 9,10-Anthracenedione, 1,8-dihydroxy-3-methoxy-6-methyl- | C <sub>16</sub> H <sub>12</sub> O <sub>5</sub>               | 284 | Anthraquinone |

**Figure 7.** Relative abundance of chemical classes in the fast pyrolysis products of PM at 600 °C.

#### 4. Conclusions

In the N<sub>2</sub> atmosphere, the pyrolysis of root residues of PM proceeded through three stages: (1) dehydration below 174 °C involving moisture and light extractives release; (2) primary devolatilization (174–680 °C) accounting for 71.16 wt% mass loss through

lignocellulose decomposition; and (3) carbonization above 680 °C characterized by char formation with minimal mass change. Kinetic and thermodynamic analyses revealed exceptional pyrolysis performance, evidenced by apparent activation energies ranging from 219.7 to 354.72 kJ/mol (average  $R^2 > 0.994$  across FWO/KAS/Starink), consistently low energy barriers ( $\Delta H - E_a < 10$  kJ/mol), and high reactivity ( $\ln A = 46.17\text{--}70.12$  s<sup>−1</sup>). Product distribution varied with pyrolysis regime: slow pyrolysis favored 3-methylfuran (C<sub>5</sub>H<sub>6</sub>O, 23.8%), while fast pyrolysis at 600 °C yielded phenol (C<sub>6</sub>H<sub>6</sub>O) and 2-furanmethanol (C<sub>5</sub>H<sub>6</sub>O<sub>2</sub>) as co-dominant products (18.18% each). These findings demonstrated PM's dual-value potential through high bioenergy capacity ( $CPI = 123.76 \times 10^{-5}$  at 40 °C/min; volatile matter 69.83 wt%) and recoverable chemicals. This work establishes an efficient pyrolytic pathway for PM residue valorization within a circular bioeconomy framework, thus reducing environmental impact while maximizing resource recovery.

**Author Contributions:** J.H.: software, validation, data curation, formal analysis, investigation, writing—original draft, and writing—review and editing. Y.C.: methodology, software, validation, data curation, formal analysis, writing—original draft, and writing—review and editing. X.C.: formal analysis, writing—original draft, and writing—review and editing. D.J.: formal analysis, writing—original draft, and writing—review and editing. F.E.: conceptualization, data curation—optimization and modeling, and writing—review and editing. J.L.: investigation, resources, formal analysis, writing—review and editing, project administration, and funding acquisition. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research was funded by the Key Laboratory of Radioactive and Rare Scattered Minerals, Ministry of Natural Resources (2024-RRSM-02).

**Data Availability Statement:** The original contributions presented in this study are included in this article. Further inquiries can be directed to the corresponding author(s).

**Acknowledgments:** We are grateful to Yang at the Analysis and Testing Center of Guangdong University of Technology for her help with TG-FTIR-GC/MS analysis.

**Conflicts of Interest:** The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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