

Article

Co-Pyrolysis of Mushroom Residue Blended with Pine Sawdust/Wheat Straw for Sustainable Utilization of Biomass Wastes: Thermal Characteristics, Kinetic/Thermodynamic Analysis, and Structure Evolution of Co-Pyrolytic Char

Haiyu Meng ^{1,*}, Heng Yang ¹, Zhiqiang Wu ², Danting Li ¹, Zhe Wang ¹, Dongqi Wang ¹ , Hui Wang ¹ , Huaian Li ¹ and Jiake Li ^{1,*}

¹ Department of Municipal and Environmental Engineering, School of Water Resources and Hydro-Electric Engineering, Xi'an University of Technology, Xi'an 710048, China; 17629019398@163.com (H.Y.); 19891178388@163.com (D.L.); wangzhewater@xaut.edu.cn (Z.W.); wangdq@xaut.edu.cn (D.W.); wanghui306@xaut.edu.cn (H.W.); lhuaien@mail.xaut.edu.cn (H.L.)

² Shaanxi Key Laboratory of Energy Chemical Process Intensification, School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China; zhiqiang-wu@mail.xjtu.edu.cn

* Correspondence: hymeng321@163.com (H.M.); xaut_ljk@163.com (J.L.); Tel./Fax: +86-29-83239907 (H.M.)

Abstract: Co-pyrolysis technology is considered to be one of the most promising methods for the sustainable utilization of biomass wastes, as it can realize waste reduction and convert wastes into high-value-added products with little impact on the environment. The evaluation of thermal characteristics and product properties is necessary for understanding this technique. In this paper, thermal characteristics and kinetic and thermodynamic analysis during the co-pyrolysis of mushroom residue (MR) with pine sawdust (PS) or wheat straw (WS) were investigated in a TGA. The carbon structure and surface textures of co-pyrolytic char were explored using Raman spectroscopy and a scanning electron microscope. As the PS or WS mass ratio increased, the devolatilization index increased obviously, indicating that volatile release was promoted and concentrated. Weak interactions were observed between 250 and 400 °C during the co-pyrolysis process, which primarily affected the mass transfer, resulting in a change in the thermal decomposition temperatures and rates. The interactions had no prominent influence on the volatiles' yields. The non-additive performance of average activation energies for the blends was observed due to the interactions, and the lowest average activation energy was obtained when the PS or WS mass ratio was 50%. The lower average pre-exponential factor of the blends indicated the reduced complicity of the pyrolysis reaction. The relatively small deviation between the activation energy and enthalpy change (4.94–5.18 kJ·mol^{−1}) signified the energy sensitivity of product formation. PS promoted the formation of small aromatic rings (<6 fused rings) in co-pyrolytic chars, whereas WS favored the production of larger rings (≥6 fused rings). The surface textures of the co-pyrolytic chars became porous, and the greater fractal dimensions of the surface morphology for the co-pyrolytic chars indicated that the char surface became irregular and rough.

Keywords: sustainable utilization of biomass waste; co-pyrolysis; thermal characteristics; kinetic/thermodynamic analysis; char structure



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1. Introduction

Sustainable energy development, environmental contamination, and greenhouse gas reduction render it necessary to develop renewable energy for the partial substitution of fossil energy [1,2]. In this situation, biomass, the only renewable carbon resource with “zero carbon” characteristics, has been extensively researched for producing clean fuels, high-value chemicals, carbon-based functional materials, and so on [3–6]. Edible fungi residue (EFR), the primary by-product of edible fungi cultivation, is the spent cultivation

substrate after several mature edible fungi harvests. The production amount of wet EFR was approximately five times the quantity of edible fungi produced [7,8]. The cultivation substrates of edible fungi are predominantly composed of lignocellulose-based feedstocks such as straw, sawdust, bagasse, corncob, wood chips, etc. [9,10]. Thus, EFRs are regarded as secondary biomass resources because they have a certain amount of cellulose, hemicellulose, and lignin [11]. Nowadays, the Chinese edible fungi cultivation industry is the world's largest, and the total annual amount of EFR exceeds 13 million tons in China [12]. Presently, EFRs can be utilized as alternative fuels, animal feeds, fertilizers, cultivation substrates for new edible fungi, and bioremediation agents for the adsorption and degradation of contaminants [10,13]. However, due to various reasons, most of the EFRs are not appropriately treated (directly discarding, landfilling, open burning, or composting), which causes the waste of resources and secondary environmental problems [14,15]. Therefore, the need to develop reasonable and efficient technology for the resource utilization of EFRs is urgent, which is meaningful for environmental protection and fossil fuel substitution.

Pyrolysis technology has been considered to be one of the most promising pathways to generate high-value-added products including combustible gas, bio-oil, and porous char from biomass [4,16]. Many efforts have been devoted to exploring the pyrolysis characteristics of different kinds of EFRs [17,18]. Researchers found that the volatile product yield of spent mushroom substrate (SMS) pyrolysis was larger than 60%, and the produced bio-oil had a promising potential of energy resource [19–21]. Pyrolytic char derived from waste mushroom substrate contained abundant nutrients that could be used to sustain and improve the soil nutritional status, but the surface area of pyrolytic char produced at 400–700 °C was very small (1.05–4.04 m²·g^{−1}) [22]. The catalytic pyrolysis or microwave catalytic pyrolysis of EFR were also investigated, and the produced bio-oil had a high hydrocarbon content [11,23,24].

Recently, co-pyrolysis technology has received much attention because it can achieve the simultaneous disposal of multi-component feedstocks. Furthermore, the pyrolysis performance and product quality will probably be improved due to the interactions between different feedstocks [25,26]. Currently, co-pyrolysis technology is being extensively investigated with biomass and other carbon-based feedstocks such as coal, biomass, sludge, waste plastics, etc. [1,27]. Some investigations into the co-pyrolysis of EFRs with other feedstocks have been conducted. Li et al. found the existence of good interactions between mushroom residue and three kinds of waste plastics, and the activation energy of mushroom residue pyrolysis declined by 31.23–46.44% [14]. Wu et al. observed the occurrence of interactions promoting the generation of volatile products (by 9% at 50% EFR) for the co-pyrolysis of *Flammulina velutipes* residue with coal and obtained high-reactivity char containing more small aromatic ring structures (3–5 rings) [28]. Huang et al. found that there existed obvious interactions between SMS and textile dyeing sludge during the co-pyrolysis process, which promoted the volatile yield (obtaining the most significant effect at 30% SMS) and improved the aromatics content by 4.13% in the bio-oil [29]. Sewu et al. obtained a superior biochar with good adsorption performance by the co-pyrolysis of SMS blended with marine macroalgae (seaweed kelp), of which the adsorptive capacity was 2.2 times higher than that of SMS char [30]. Jiang et al. found that the co-pyrolysis of oil shale semi-coke and SMS can lead to an increase in bio-oil yield (obtaining the maximum yield of 8.59% at 50% SMS) and produced remarkable effects on the compositions of bio-oil [31]. The existing research indicates that the co-pyrolysis of EFR with some feedstocks (coal, waste plastics, sludge, macroalgae, and oil shale) indeed changes the pyrolysis performance and product quality, which results from the differences in the chemical components and structure of different feedstocks. As the main agricultural and forestry biomass, the co-pyrolysis of EFR with straw/wood is a convenient and widely adaptable method for the collaborative disposal of biomass waste, but no relevant research has been reported. There still exists a tremendous knowledge disparity in existing investigations about the thermal characteristics and interactions during the co-pyrolysis of EFR and wood or straw.

Furthermore, to gain a deeper understanding of this technique, the carbon structure and surface textures of co-pyrolytic char, two important factors affecting its application performance in the subsequent application scenarios, have also gained attention. It was reported that the surface textures of chars from EFR and coal mixtures became homogeneous [28], while the surface textures grew coarser and uneven during the co-pyrolysis process with marine macroalgae or textile dyeing sludge [29,30]. However, research on the carbon structure and surface textures of co-pyrolytic char from EFR and wood/straw blends has not been conducted. Compared to EFR char, the structure of co-pyrolytic char may be changed because of the different thermal characteristics of each component. Raman spectroscopy has been proved to be an appropriate method to investigate the carbon structure of pyrolytic chars from carbonaceous solid feedstocks (coal, biomass, etc.) [32,33]. Scanning electron microscopy (SEM) has been popularly applied to analyze the surface textures of pyrolytic chars. Further quantitative knowledge about surface textures can be obtained by the fractal analysis of micrographs, using the fractal dimension [34]. Consequently, obtaining knowledge about the carbon structure and surface textures of co-pyrolytic chars from EFR and wood/straw blends is necessary for the sake of deeply understanding the impact of possible interactions and evaluating the application performance of co-pyrolytic chars.

In this context, this research aims to explore the thermal characteristics, kinetic/thermodynamic analysis, and structure evolution of chars during the co-pyrolysis of EFR and wood/straw biomass. The influences of biomass type and blending ratio on the thermal characteristics were explored using a thermogravimetric analyzer, and the interactions between feedstocks were analyzed. The activation energies were computed using the iso-conversional method, and the thermodynamic parameters were calculated. The carbon microcrystalline structure of pyrolytic chars was measured applying Raman spectroscopy. The surface texture of residual chars was analyzed employing scanning electron microscopy and was quantitatively described by the fractal dimension. The results will provide useful knowledge about thermal characteristics and interactions during the co-pyrolysis of edible fungi residue and wood/straw biomass.

2. Experimental Section

2.1. Materials

The yield of mushrooms is the highest among edible fungi in China; thus, mushroom residue (MR) was chosen as the typical representative of EFR in this study. The MR was from an edible fungi (*Lentinus edodes*) cultivation base in Southern Shaanxi, China. As important forestry and agricultural biomass waste in China, pine sawdust (PS) and wheat straw (WS) were used to conduct the co-pyrolysis experiments. Air-dried samples were crushed by a crusher and then screened by a standard vibrating screen machine. Samples of less than 125 μm were selected to carry out the co-pyrolysis experiments. The blending ratios of MR were 30%, 50%, and 70%, which were marked as MRPS3-7, MRPS1-1, and MRPS7-3, respectively, for the MRPS blends. The MRWS blends were marked in the same way as the MRPS blends. The analysis results of the basic characteristics of the MR, PS, and WS are listed in Table 1. The proximate analysis of raw materials was carried out according to the GB/T 28731-2012 criterion. The MR showed a relatively high content of volatile matter, which was consistent with the spent cultivation substrates of other edible fungi [11,28]. Compared with previous research [26], the WS used in our study had a relatively high ash content, which probably affected the activation energies of the pyrolysis process.

Table 1. Proximate and ultimate analysis of MR and wood/straw biomass.

Material	MR	PS	WS
Proximate analysis/wt %, ad			
Moisture	8.24	7.86	7.15
Ash	7.79	1.40	17.12
Volatile matter	72.16	77.24	61.81
Fixed carbon	11.81	13.50	13.92
Ultimate analysis/wt %, daf			
Carbon	47.92	50.03	47.10
Hydrogen	5.05	5.37	5.20
Nitrogen	0.85	0.20	1.56
Sulfur	0.20	0.03	0.57
Oxygen ^c	45.98	44.37	45.57
H/C atomic ratio	1.26	1.29	1.32
Q _{gr,d} /MJ·kg ^{−1}	17.10	20.47	16.64

ad: air-dried; daf: dry ash-free; c: calculated by difference.

2.2. Pyrolysis Experiments

A thermogravimetric analyzer (STA2500, NETZSCH, Selb, Germany) was employed to explore the thermal characteristics of individual and blended samples. A sample of about 7 mg was used for each pyrolysis experiment. The purge gas and protective gas were high-purity nitrogen (99.999%), of which the flow rates were, respectively, 60 and 20 mL·min^{−1}. The purge gas mainly discharged volatile products from the instrument, and the protective gas played a role in protecting the balance. Thermogravimetric tests were executed from room temperature to 950 °C at heating rates of 10, 20, and 40 °C·min^{−1}. Each test was performed at least two times to assure the repeatability of the thermogravimetric analysis and the accuracy of the data. The pyrolytic chars produced at 10 °C·min^{−1} were collected and further analyzed.

To quantitatively describe the volatile releasing characteristics of the pyrolysis process, the devolatilization index (D_i) was calculated as follows [34,35]:

$$D_i = R_{max} / (T_{in} T_{max} \Delta T_{1/2}) \quad (1)$$

where R_{max} is the maximum weight loss rate, T_{in} refers to the initial devolatilization temperature, T_{max} represents the temperature of the maximum weight loss rate, and $\Delta T_{1/2}$ is the temperature interval when the instantaneous weight loss rate (R_d) is half of R_{max} . The T_{in} values were obtained from the thermogravimetric (TG) and differential thermogravimetric (DTG) profiles based on the TG-DTG graphing method [36]. The greater the D_i value is, the more easily and violently the volatile is discharged.

The interactions between the MR and PS/WS during the co-pyrolysis process were evaluated using the deviation (ΔW) between the experimental and calculated results. The computing formula of ΔW is as follows [37]:

$$\Delta W = W_{\text{Experimental}} - W_{\text{Calculated}} \quad (2)$$

where $W_{\text{Experimental}}$ is the experimental weight loss or weight loss rate of the blended sample. $W_{\text{Calculated}}$ is the calculated result based on the weighted-average sum of experimental values from independent pyrolysis. The $W_{\text{Calculated}}$ is calculated as follows:

$$W_{\text{Calculated}} = x_M W_M + x_B W_B \quad (3)$$

where x_M and x_B are the mass ratios of each component in the mixtures, and W_M and W_B are the weight losses or weight loss rates of individual feedstocks obtained under the same experimental conditions as those of MRPS or MRWS blends.

Moreover, the root mean square (RMS) of ΔW was used to evaluate the intensity of interactions. The larger the RMS is, the stronger the interactions are. The value of RMS

should be zero if there were no interactions. The RMS is calculated based on the following formula [38]:

$$RMS = \sqrt{\frac{\sum_{i=1}^n (W_{\text{Experimental}} - W_{\text{Calculated}})^2}{n}} \quad (4)$$

where n is the number of ΔW data points.

2.3. Kinetic Method

The activation energy can be conveniently computed using the iso-conversional method since this method does not need to presume the reaction mechanism [39]. The activation energies at different conversions are acquired on the basis of thermogravimetric experimental data for at least three heating rates. The Kissinger-Akahira-Sunose (KAS) method was applied for the computation of activation energy in this paper. The formula is as follows [27,40]:

$$\ln \frac{\beta}{T_{\alpha}^2} = -\frac{E_{\alpha}}{RT_{\alpha}} + \ln \frac{AR}{E_{\alpha}G(\alpha)} \quad (5)$$

where β is the heating rate ($^{\circ}\text{C}\cdot\text{min}^{-1}$), α is the conversion of tested samples, T_{α} is the temperature corresponding to the conversion of α (K), R is the universal gas constant ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$), A is the pre-exponential factor (s^{-1}), E_{α} is the activation energy at each conversion ($\text{kJ}\cdot\text{mol}^{-1}$), and $G(\alpha)$ is the integration function of the reaction mechanism which is only determined by the conversion. The activation energy can be acquired from the slope of fitting a straight line between $\ln(\beta/T_{\alpha}^2)$ and $1/T_{\alpha}$.

The pre-exponential factor (A_{α}) at each conversion is computed based on the activation energies using the formula below [39]:

$$A_{\alpha} = \frac{\beta E_{\alpha} \exp(E_{\alpha}/RT_{\max})}{RT_{\max}^2} \quad (6)$$

where $T_{\max}$ refers to the temperature of the maximum weight loss rate (K).

2.4. Thermodynamic Parameter Calculation

The assessment of thermodynamic parameters can help to understand the pyrolysis process from this perspective of energy conversion. The thermodynamic parameters, enthalpy change (ΔH), Gibbs free energy (ΔG), and entropy change (ΔS), are computed following the formula below [41]:

$$\Delta H = E_{\alpha} - RT \quad (7)$$

$$\Delta G = E_{\alpha} + RT_{\max} \ln(K_B T_{\max}/hA) \quad (8)$$

$$\Delta S = (\Delta H - \Delta G)/T_{\max} \quad (9)$$

where E_{α} is calculated by the KAS method, and K_B and h are the Boltzmann constant ($1.381 \times 10^{-23} \text{ J}\cdot\text{K}^{-1}$) and Planck's constant ($6.626 \times 10^{-34} \text{ J}\cdot\text{s}^{-1}$), respectively.

2.5. Char Characterization

The Raman spectrum of pyrolytic chars was acquired employing a Raman spectrometer (InVia Qontor, Renishaw, Gloucestershire, UK). The spectrum in the first-order region ($800\text{--}1800 \text{ cm}^{-1}$) was curve-fitted with 10 Gaussian bands, according to the reported method [35,42]. A curve-fitting example of a Raman spectrum for co-pyrolytic char is presented in Figure 1. In this study, major bands (G_R , V_L , V_R , and D bands) were analyzed to understand the carbon microcrystalline structures of pyrolytic chars. The surface texture was measured using scanning electron microscopy (JEOL JSM-6700F) and quantitatively explored by the fractal analysis.

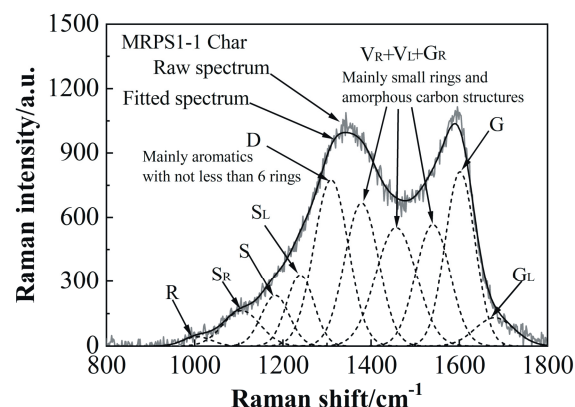


Figure 1. Curve fitting of the Raman spectrum for MRPS1-1 char.

3. Results and Discussion

3.1. Thermal Characteristics

3.1.1. Individual Feedstocks

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of the MR, PS, and WS at three heating rates are illustrated in Figure 2. The thermal decomposition of the MR mainly consisted of three steps. The first stage was from 50 °C to 210 °C due to the removal of free water and bound water from the MR [14]. The moisture removal process of the MR was held for a longer time duration, which was attributed to the existence of abundant capillary channels in MR particles. The water vapor generated surface tension in these channels when migrating from the inside of particles to the surface of particles, hindering the evaporation of moisture and extending the dehydration stage of the MR [19]. The second step from 210 °C to 540 °C was the main decomposition stage. The weight loss rate increased rapidly with the increase in temperature, and the maximum decomposition rate occurred in this stage. The most remarkable mass loss was primarily owing to the intense decomposition of cellulose, hemicellulose, and part of the lignin; meanwhile, a large amount of gaseous products was released, including CO₂, CO, and other hydrocarbon gas [21,28]. The DTG profile of the MR showed a shoulder in the weight loss peak of this stage. This phenomenon indicated that the thermal decomposition of MR components did not take place independently, and the decomposition of hemicellulose and cellulose partially overlapped. Previous research has also reported the same conclusions [19,20]. The MR exhibited a broad and blunt mass loss peak due to the longer duration of the lignin decomposition process. The third step was the continued decomposition of lignin and the carbonization stage from 540 °C to 950 °C accompanied by a slight mass reduction [40]. As the volatile substances were released continuously, the char was formed through polycondensation reactions. The DTG pattern of the MR illustrated two additional peaks in the temperature interval of 470–525 °C and 650–725 °C, which were probably caused by the dehydration of calcium hydroxide and the decomposition of calcium carbonate [18,20]. The observed thermal characteristics of the MR in this study were basically consistent with previous investigations on the pyrolysis characteristics of other spent mushroom substrates [14,19,21].

The thermal behavior of the PS and WS was different from that of the MR due to their different components. The pyrolysis process of the PS was composed of two stages, except the dewatering phase below 150 °C. In the first stage from 220 °C to 470 °C, the volatiles in the PS were primarily discharged because of the decomposition of hemicellulose, cellulose, and part of the lignin. The lignin decomposition and carbonization process mainly took place in the second stage above 500 °C. Hemicellulose and cellulose can basically complete the pyrolysis process in the temperature range of about 230–400 °C due to the high reactivity, while the decomposition of lignin started at a relatively high temperature and continued to the end of the pyrolysis process because of its cross-link structures [43]. As seen in Figure 2e–f, the evolution of the thermal behavior curves for the WS was different from

that of the PS. Although the decomposition process of the WS also consisted of two weight loss stages, the initial devolatilization temperature of the WS was lower than that of the PS, and the release of volatiles was more concentrated. The thermal characteristics of the PS and WS were consistent with previous reports [44,45]. With the increase in the heating rate, the mass loss rate increased significantly for these three samples, and the thermal behavior profiles shifted to a higher temperature region due to the increased delay in the heat and mass transfer at a higher heating rate [14]. Furthermore, it can be obviously found that the major pyrolysis stage of the MR partially overlapped with the main volatile releasing stage of the PS and WS, which was due to their similar lignocellulose structures.

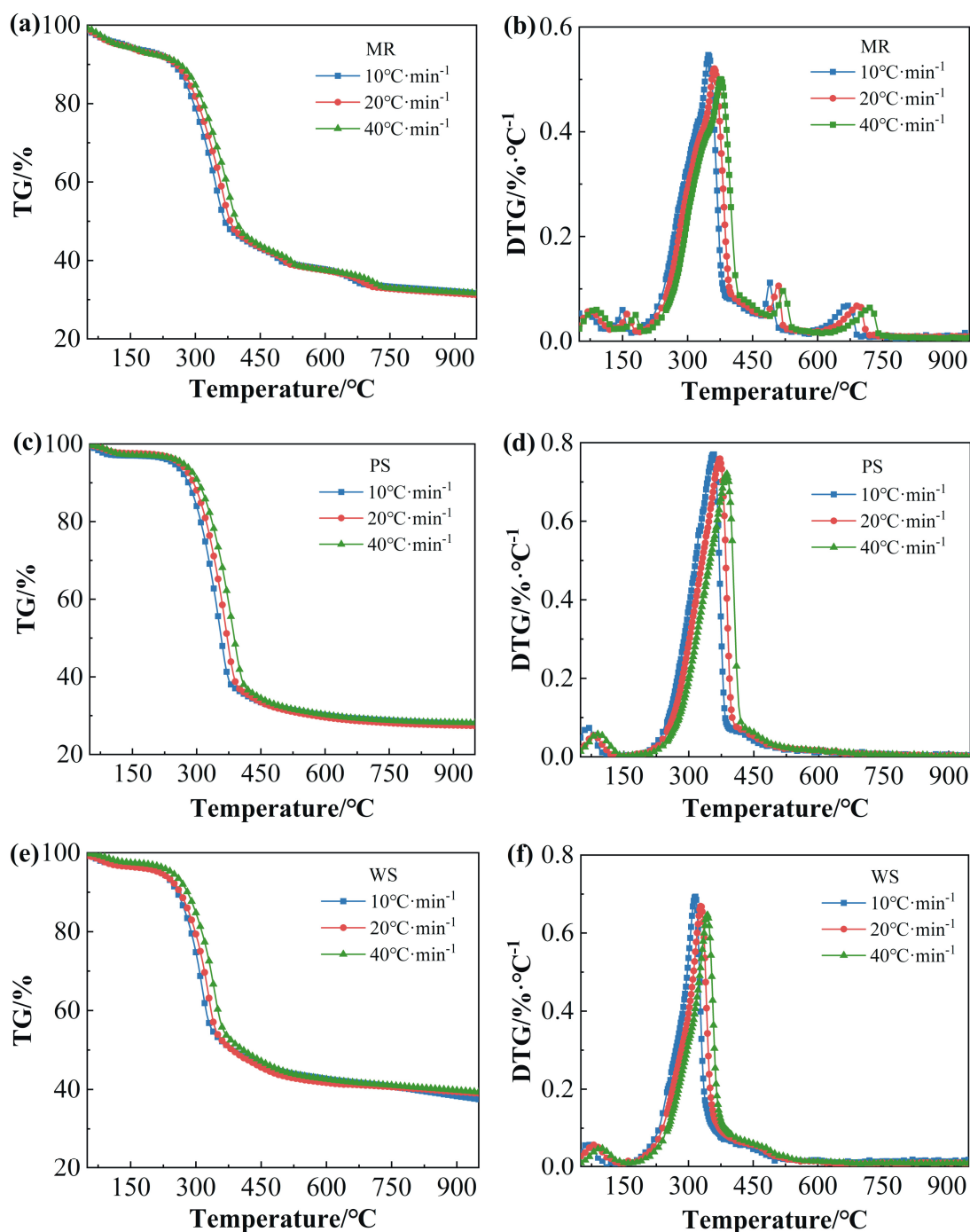


Figure 2. TG and DTG curves of MR, PS, and WS at three heating rates: (a) MR TG, (b) MR DTG, (c) PS TG, (d) PS DTG, (e) WS TG, and (f) WS DTG.

Several parameters for thermal characteristics are presented in Table 2. The initial devolatilization temperature of the MR was greater than that of the WS and lower than that of the PS. Compared to the PS and WS, the MR showed a lower maximum mass loss rate and larger temperature intervals of volatile release, which suggested that the MR had more temperature-resistant substances. The D_i values of the MR, PS, and WS were 10.85, 17.65, and 26.77, respectively. The characteristic parameters demonstrated that the thermal decomposition of the MR was relatively difficult. The char yields of the MR, PS, and WS were, respectively, 31.20%, 27.37%, and 39.04%. The higher char yield of the WS compared to the other two samples was attributed to its higher ash content.

Table 2. Thermal behavior parameters of the samples at $\beta = 20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

Parameters	MR	30% PS	50% PS	70% PS	PS	30% WS	50% WS	70% WS	WS
$T_{in}/^{\circ}\text{C}$	292	299	304	307	307	281	281	282	281
$T_1/^{\circ}\text{C}$	361	363	368	369	370	338	334	332	329
$R_1/\%\cdot\text{min}^{-1}$	10.41	11.93	12.82	13.69	15.24	10.19	10.69	12.21	13.61
$T_2/^{\circ}\text{C}$	508	507	505	504		502	500	475	
$R_2/\%\cdot\text{min}^{-1}$	2.19	1.53	1.21	1.01		1.60	1.35	1.17	
$T_3/^{\circ}\text{C}$	689	683	668	662		678	672	657	
$R_3/\%\cdot\text{min}^{-1}$	1.35	0.88	0.83	0.59		0.89	0.84	0.59	
$T_{max}/^{\circ}\text{C}$	361	363	368	369	370	338	334	332	329
$R_{max}/\%\cdot\text{min}^{-1}$	10.41	11.93	12.82	13.69	15.24	10.19	10.69	12.21	13.61
$\Delta T_{1/2}/^{\circ}\text{C}$	91	84	81	79	76	95	88	62	55
$D_i/10^{-7}\%\cdot\text{min}^{-1}\cdot^{\circ}\text{C}^{-3}$	10.85	13.09	14.15	15.30	17.65	11.29	12.94	21.03	26.77
Char yield/%	31.20	29.41	28.81	28.02	27.37	33.12	34.31	36.60	39.04

T_{in} : initial devolatilization temperature; T_1 : temperature of the first DTG peak; R_1 : weight loss rate of the first DTG peak; T_2 : temperature of the second DTG peak; R_2 : weight loss rate of the second DTG peak; T_3 : temperature of the third DTG peak; R_3 : weight loss rate of the third DTG peak; T_{max} : temperature of the maximum weight loss rate; R_{max} : maximum weight loss rate; $\Delta T_{1/2}$: temperature interval when $R_d/R_{max} = 1/2$; D_i : devolatilization index.

3.1.2. Blended Feedstocks

The thermal characteristic patterns of the MRPS mixtures and MRWS mixtures at β of 10, 20, and $40\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ are presented in Figure 3. It can be found that the pyrolysis characteristics of the mixtures presented the thermal behaviors of individual samples. The co-pyrolysis process of all the mixtures primarily consisted of three mass loss phases, which were the dehydration process, volatile releasing stage, and carbonization stage. These three stages were the result of the simultaneous thermal decomposition of the MR and PS/WS. Most of the volatiles were released in the second steps, and the weight loss rate was influenced by the blending ratio. As the MR blending ratio declined, the weight loss rate of the second phase increased, attributed to the higher pyrolysis rate of the PS/WS. However, the DTG peaks between 650 and $725\text{ }^{\circ}\text{C}$ caused by the decomposition of calcium carbonate in the MR were reduced significantly and almost disappeared with a 30% MR mass ratio. Moreover, the weight loss rate of the MRPS blends and MRWS blends increased with the increment in heating rates.

As shown in Table 2, the char yields of the MRPS blends declined with the PS addition because the PS had a higher volatile content and a lower ash content. As the PS blending ratio increased from 30% to 70%, the initial devolatilization temperatures of the MRPS mixtures increased by $7\text{--}15\text{ }^{\circ}\text{C}$. Meanwhile, the largest weight loss rate caused by volatile release increased from $11.93\%\cdot\text{min}^{-1}$ to $13.69\%\cdot\text{min}^{-1}$, and the peak temperature increased from $363\text{ }^{\circ}\text{C}$ to $369\text{ }^{\circ}\text{C}$. However, the dehydration rate of calcium hydroxide and the decomposition rate of calcium carbonate mainly caused by the MR were reduced with the increase in the PS mixing ratio, and the corresponding temperature declined synchronously. Co-pyrolysis with PS increased the initial devolatilization temperature and the peak temperature of volatile release but reduced the peak temperature of calcium hydroxide dehydration and carbonate decomposition. The D_i values of the MRPS blends increased gradually as the PS mass ratio increased, and the duration of volatile release was

reduced. The D_i values were, respectively, 13.09, 14.15, and 15.30 for MRPS7-3, MRPS1-1, and MRPS3-7 and basically linear with the PS mass ratio. Furthermore, the D_i values of the MRPS mixtures were greater than that of the MR, demonstrating that the releasing performance of volatile substances may be promoted by co-pyrolysis with PS.

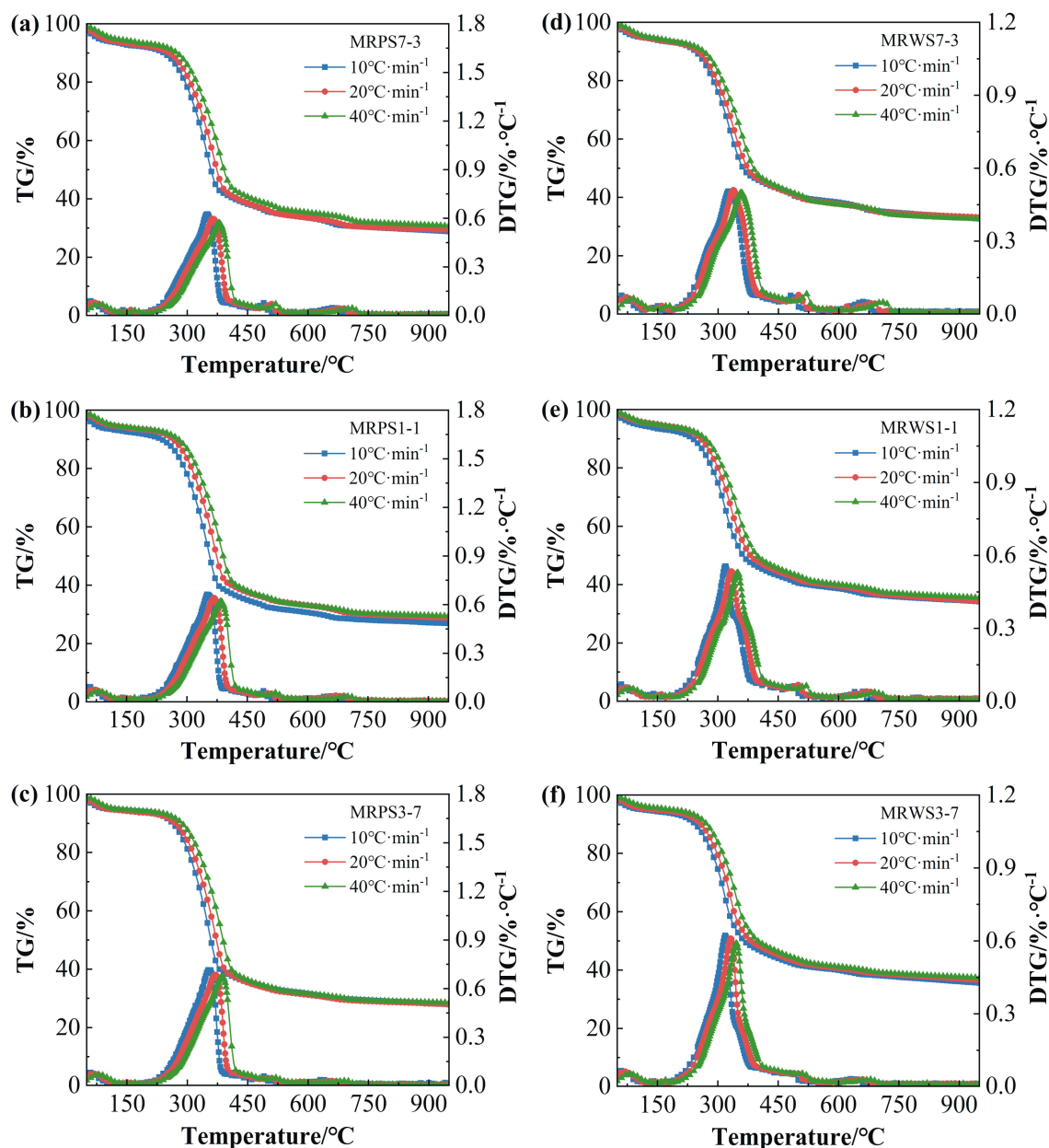


Figure 3. TG and DTG curves of MRPS and MRWS blends at three heating rates: (a) MRPS7-3, (b) MRPS1-1, (c) MRPS3-7, (d) MRWS7-3, (e) MRWS1-1, and (f) MRWS3-7.

The parameters for the thermal behavior of the MRWS blends showed a different variation trend from the MRPS blends. The char yields of the MRWS blends increased from 33.12% to 36.60% as the WS mass ratio was increased from 30% to 70%, which was because of the lower volatile content and higher ash content of the WS. With the increment in the WS blending ratio, the largest weight loss rate of volatile release increased slightly, whereas the initial devolatilization temperature, the peak temperature of the volatile releasing step, and the peak temperature of calcium hydroxide dehydration and carbonate decomposition declined obviously. The D_i of the MRWS blends also demonstrated higher values than that of the MR, increasing gradually from 11.29 to 21.03 as the WS mass ratio was increased from

30% to 70%. The addition of WS influenced the D_i values nonlinearly, and the D_i value of MRWS3-7 increased significantly due to the remarkable increment in the maximum weight loss rate and the obvious reduction in the volatile releasing duration.

In summary, co-pyrolysis with PS or WS significantly affected the thermal characteristics of the MR and boosted the volatile releasing performance of the MR. The observed changes in the thermal behavior parameters for the blends indicated that there probably existed some interactions during the co-pyrolytic process of MRPS blends and MRWS blends.

3.2. Interactions between MR and PS/WS

Figure 4 presents the comparative analysis of experimental and calculated results for the MRPS blends. It can be observed that the experimental weight losses at the final pyrolysis temperature showed no obvious difference from the calculated results, indicating that co-pyrolysis did not affect the pyrolysis reaction degree of the MRPS blends. To deeply analyze the influence of co-pyrolysis on the thermal characteristics, the deviations of the experimental and calculated results are presented in Figure 4d,e. The analysis results suggested that weak interactions occurred between the MR and PS during the co-pyrolysis process. The ΔW of weight loss below 210 °C was larger than zero, suggesting that the dehydration process was accelerated. The PS blending reduced the number of capillary channels in the samples; thus, the diffusion resistance of the water vapor was reduced, and the dehydration rate increased. The positive values of ΔW for DTG curves below 210 °C also proved this influence. As the temperature increased to the range of 270–400 °C, the ΔW of weight loss presented a variation trend of first declining and then improving, which was related to the change in the volatile releasing rate. In the meantime, the ΔW of DTG first showed smaller negative values and then became larger positive values, indicating that the experimental rate of volatile release first declined slightly and then increased obviously compared with the calculated rate. As the pyrolysis temperature continuing to increase, the ΔW values of weight loss kept a slight decreasing tendency until the pyrolysis reaction was completed, and the ΔW values of DTG were close to zero except the step of calcium hydroxide dehydration and calcium carbonate decomposition. In these two steps, the ΔW values of weight loss first increased slightly and then decreased, indicating that these two steps were advanced, which was consistent with the variation tendency of the thermal characteristic parameters. At the final pyrolysis temperature, the ΔW of weight loss for the MRPS blends was less than 1%. The RMS for the ΔW values of weight loss was, respectively, 1.493, 1.040, and 1.371 for MRPS7-3, MRPS1-1, and MRPS3-7. These values were further proof of the occurrence of weak interactions between the MR and PS during co-pyrolysis. The interactions mainly affected the performance of volatile release in the main weight loss step and the decomposition characteristics of inorganic minerals in the subsequent phase, resulting in the variation in characteristic temperatures and peak values of DTG curves, as described above. However, the interactions had no significant influence on the total volatile yields for the co-pyrolysis process of MRPS blends.

Figure 5 shows the comparative analysis of experimental and calculated results for the MRWS blends. Weak interactions also took place between the MR and WS during co-pyrolysis, while the impact of interactions on the volatile release was different from MRPS blends. When the temperature was in the range of 250–400 °C, the deviation curves of both the weight loss and DTG values showed a complicated variation tendency. Compared with the MR, the initial devolatilization temperature of the MRWS blends as well as the peak temperature of volatile release decreased rapidly, respectively, from 292 °C to 281–282 °C and from 361 °C to 332–338 °C. These temperatures were very close to those of the WS, suggesting that the volatile release of the MR was prominently increased with the addition of WS. Moreover, the interactions produced a more obvious influence on weight loss and DTG values for MRWS7-3. Similar to the MRPS blends, the calcium hydroxide dehydration and calcium carbonate decomposition steps were also advanced. When the pyrolysis reaction was completed, the ΔW values of weight loss for all the MRWS blends were also less than 1%, indicating that the volatile yields of the co-pyrolytic process were not

significantly promoted. The RMS for the ΔW values of weight loss was, respectively, 1.066, 0.485, and 0.471 for MRWS7-3, MRWS1-1, and MRWS3-7, demonstrating the relatively more remarkable interactions at a 30% WS blending ratio.

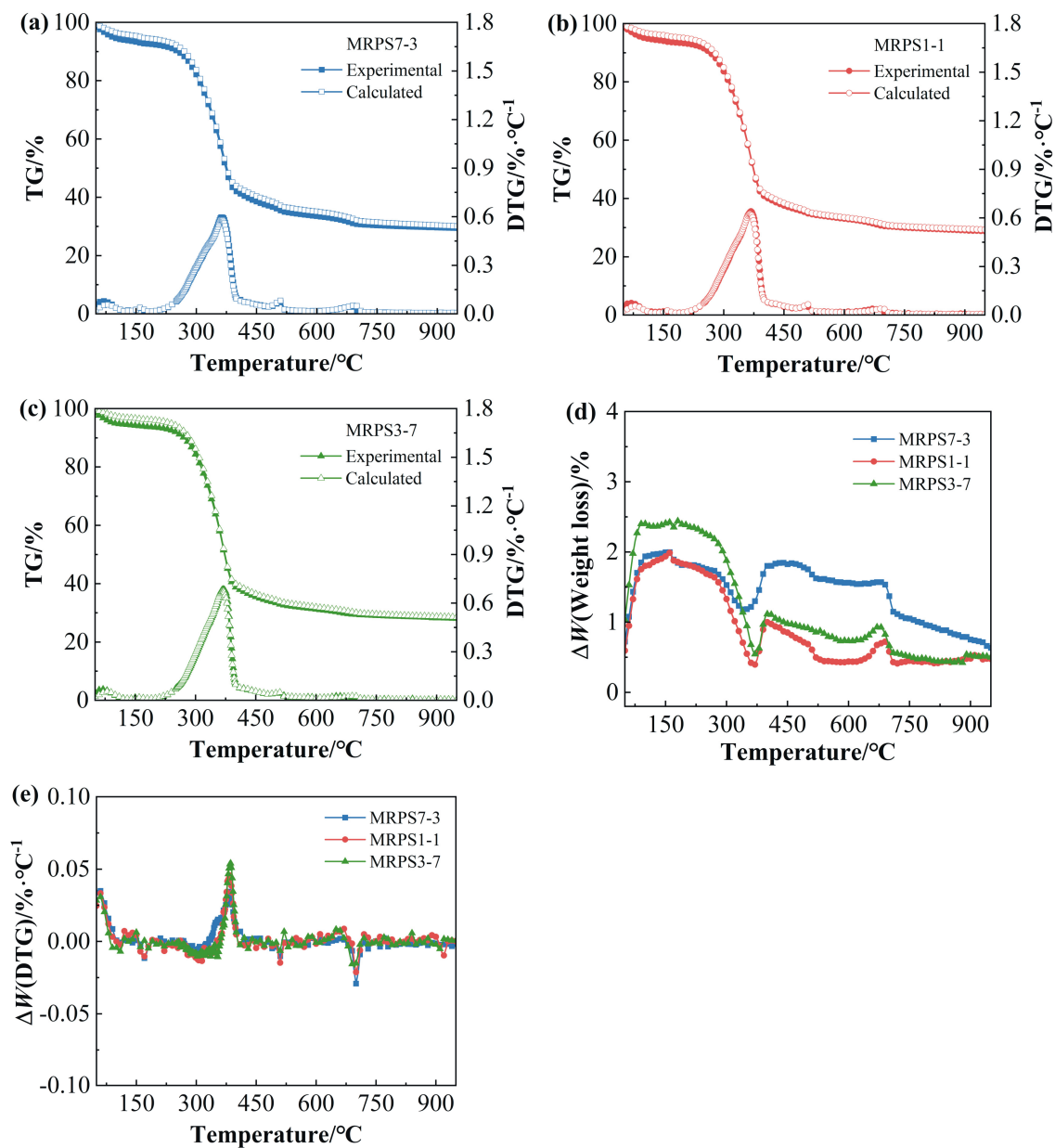


Figure 4. Comparative analysis of the experimental and calculated results for MRPS blends at $\beta = 20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$: (a) MRPS7-3, (b) MRPS1-1, (c) MRPS3-7, (d) ΔW of weight loss, and (e) ΔW of DTG.

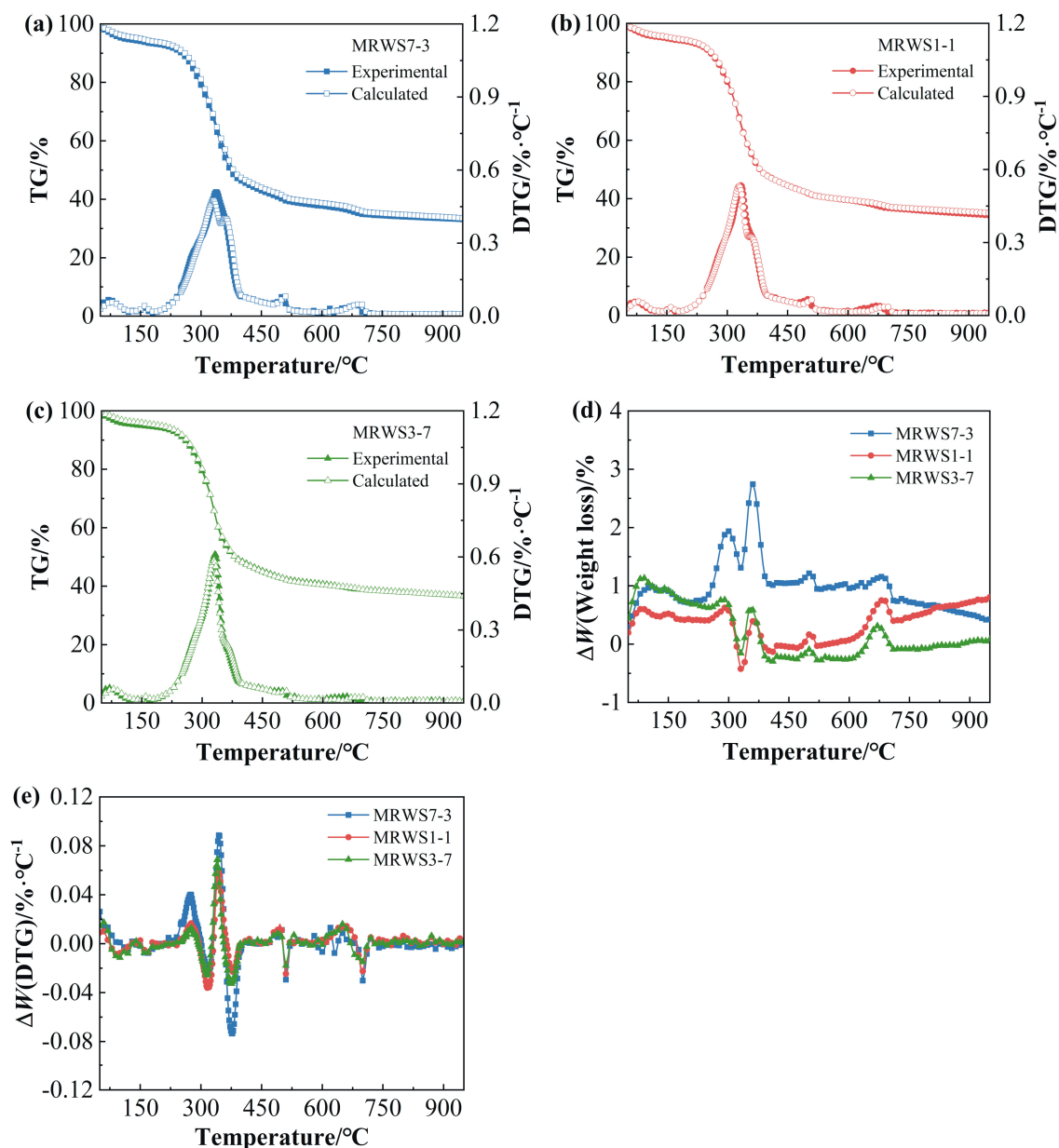


Figure 5. Comparative analysis of the experimental and calculated results for MRWS blends at $\beta = 20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$: (a) MRWS7-3, (b) MRWS1-1, (c) MRWS3-7, (d) ΔW of weight loss, and (e) ΔW of DTG.

The different influence of interactions on the thermal characteristics of the MRPS blends and MRWS blends could be due to the differences in pyrolysis characteristics between PS and WS. For these three samples, the order of the initial devolatilization temperature for individual pyrolysis is PS > MR > WS. For the co-pyrolysis of MRWS blends, the WS pyrolysis started first at the lower temperature. Compared to MR pyrolysis, intense volatile release caused by WS decomposition would create a large number of pores in the samples, which can promote the diffusion of volatiles produced by MR pyrolysis. Thus, the volatile release of the MRWS blends was advanced, resulting in the obvious diminution of the initial devolatilization temperatures and the peak temperatures of volatile release. In contrast, the MR pyrolysis began first for the co-pyrolysis of MRPS blends. Compared with PS pyrolysis, the volatile releasing rate of the MR was lower, and the diffusion of volatile matter to the outside of particles was relatively slow. Consequently, the macromolecular volatile substances produced by MR pyrolysis would adhere to the surface of PS particles

which restrained the further release and weakened the diffusion of volatiles produced by PS pyrolysis [29]. Moreover, as the pyrolysis temperature increased, the pyrolysis rate of the PS increased significantly, which accelerated the volatile release. At the same time, copious pores were formed in the samples. For both MRPS blends and MRWS blends, the decomposition and release of volatiles in the main weight loss stage produced a porous char structure, which advanced the diffusion of products generated by the calcium hydroxide dehydration and calcium carbonate decomposition. Many studies have found that the co-pyrolysis of coal with hydrogen-rich feedstocks (biomass, waste plastics, etc.) can accelerate the volatile yields attributed to the hydrogen transfer effect [35,46]. In the present study, due to the similar H/C atomic ratio of these three samples (shown in Table 1), the interactions promoting the volatile yields caused by the hydrogen transfer effect were not observed. Due to the lower initial devolatilization temperature and high volatile releasing rate, the WS pyrolysis produced many pore channels in the samples, promoting the release of volatiles at lower temperatures. Thus, compared with the MR, the initial devolatilization temperatures decreased by about 10 °C, and the temperatures of the maximum weight loss rate were reduced by 23–29 °C for the MRWS blends. On the contrary, in the initial stage of MRPS pyrolysis, the adhesion of MR pyrolysis substances on the PS particles would block part of the pore channels in the samples, delaying the volatile release of the blends. Furthermore, the volatile release was accelerated due to the PS pyrolysis at higher temperatures. Therefore, compared with the MR, the initial devolatilization temperatures increased by 7–15 °C, and the peak temperatures of volatile release increased by 2–8 °C for MRWS blends. In summary, the weak interactions between the MR and PS or WS were mainly caused by the formation or blocking of pore channels, primarily affecting the mass transfer of the co-pyrolysis process. Under the influence of these interactions, the thermal decomposition temperatures and rates of the blends changed, but the yields of volatile products showed no significant change.

3.3. Kinetic Analysis

The activation energies of the MR, PS, WS, and blends were computed using the KAS method, and the calculation results are listed in Tables 3 and 4. Most of the correlation coefficients (R^2) showed values higher than 0.9600, indicating that the fitting results were satisfactory and the calculation results of activation energies were reliable. The experimental data in the conversion scope of below 0.2 and above 0.8 were neglected because of the poor linearity for all the tested samples [35]. Figure 6 also presents the fitting straight lines between $\ln(\beta/T_\alpha^2)$ and $1/T_\alpha$.

Table 3. Kinetic parameters of MR, PS, and their blends calculated by KAS method.

Samples	α	$E_a/\text{kJ}\cdot\text{mol}^{-1}$	A_a/s^{-1}			R^2
			10 °C·min ^{−1}	20 °C·min ^{−1}	40 °C·min ^{−1}	
MR	0.2	190.72	1.02×10^{14}	9.75×10^{13}	8.07×10^{13}	0.9999
	0.3	186.76	4.64×10^{13}	4.51×10^{13}	3.79×10^{13}	0.9999
	0.4	180.38	1.30×10^{13}	1.30×10^{13}	1.12×10^{13}	0.9999
	0.5	174.20	3.81×10^{12}	3.88×10^{12}	3.45×10^{12}	0.9999
	0.6	174.96	4.44×10^{12}	4.50×10^{12}	3.99×10^{12}	0.9998
	0.7	169.19	1.41×10^{12}	1.46×10^{12}	1.33×10^{12}	0.9999
	0.8	379.73	1.50×10^{30}	7.20×10^{29}	2.60×10^{29}	0.9049
	Avg.	207.99	2.14×10^{29}	1.03×10^{29}	3.72×10^{28}	
MRPS7-3	0.2	164.54	5.27×10^{11}	5.29×10^{11}	4.69×10^{11}	0.9942
	0.3	162.99	3.87×10^{11}	3.91×10^{11}	3.49×10^{11}	0.9953
	0.4	159.41	1.90×10^{11}	1.94×10^{11}	1.76×10^{11}	0.9998
	0.5	160.91	2.56×10^{11}	2.60×10^{11}	2.35×10^{11}	0.9988
	0.6	161.22	2.72×10^{11}	2.77×10^{11}	2.49×10^{11}	0.9999
	0.7	155.41	8.55×10^{10}	8.89×10^{10}	8.22×10^{10}	0.9974
	0.8	196.15	2.81×10^{14}	2.48×10^{14}	1.90×10^{14}	0.9638
	Avg.	165.80	4.03×10^{13}	3.57×10^{13}	2.74×10^{13}	

Table 3. Cont.

Samples	α	$E_a/\text{kJ}\cdot\text{mol}^{-1}$	A_a/s^{-1}			R^2
			$10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$	$20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$	$40\text{ }^\circ\text{C}\cdot\text{min}^{-1}$	
MRPS1-1	0.2	144.87	9.93×10^9	8.98×10^9	8.44×10^9	0.9960
	0.3	151.37	3.63×10^{10}	3.18×10^{10}	2.89×10^{10}	0.9999
	0.4	147.68	1.74×10^{10}	1.55×10^{10}	1.44×10^{10}	0.9987
	0.5	155.50	8.27×10^{10}	7.08×10^{10}	6.32×10^{10}	0.9999
	0.6	149.69	2.60×10^{10}	2.29×10^{10}	2.11×10^{10}	0.9988
	0.7	155.77	8.72×10^{10}	7.46×10^{10}	6.66×10^{10}	0.9999
	0.8	157.25	1.17×10^{11}	9.94×10^{10}	8.81×10^{10}	0.9998
	Avg.	151.73	5.38×10^{10}	4.63×10^{10}	4.15×10^{10}	
MRPS3-7	0.2	178.80	5.99×10^{12}	6.09×10^{12}	4.63×10^{12}	0.9877
	0.3	167.00	5.88×10^{11}	6.24×10^{11}	5.03×10^{11}	0.9953
	0.4	161.58	2.02×10^{11}	2.19×10^{11}	1.81×10^{11}	0.9962
	0.5	156.09	6.85×10^{10}	7.56×10^{10}	6.45×10^{10}	0.9969
	0.6	156.22	7.03×10^{10}	7.75×10^{10}	6.61×10^{10}	0.9990
	0.7	155.77	6.43×10^{10}	7.11×10^{10}	6.07×10^{10}	0.9999
	0.8	161.93	2.17×10^{11}	2.34×10^{11}	1.94×10^{11}	0.9974
	Avg.	162.49	1.03×10^{12}	1.06×10^{12}	8.14×10^{11}	
PS	0.2	152.90	3.47×10^{10}	3.88×10^{10}	3.38×10^{10}	0.9998
	0.3	149.51	1.78×10^{10}	2.02×10^{10}	1.78×10^{10}	0.9998
	0.4	150.21	2.04×10^{10}	2.31×10^{10}	2.03×10^{10}	0.9987
	0.5	150.80	2.30×10^{10}	2.59×10^{10}	2.27×10^{10}	0.9998
	0.6	150.34	2.10×10^{10}	2.37×10^{10}	2.08×10^{10}	0.9999
	0.7	149.48	1.77×10^{10}	2.00×10^{10}	1.77×10^{10}	0.9998
	0.8	144.43	6.53×10^9	7.53×10^9	6.83×10^9	0.9998
	Avg.	149.67	2.02×10^{10}	2.27×10^{10}	2.00×10^{10}	

Table 4. Kinetic parameters of MR, WS, and their blends calculated by KAS method.

Samples	α	$E_a/\text{kJ}\cdot\text{mol}^{-1}$	A_a/s^{-1}			R^2
			$10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$	$20\text{ }^\circ\text{C}\cdot\text{min}^{-1}$	$40\text{ }^\circ\text{C}\cdot\text{min}^{-1}$	
MR	0.2	190.72	1.02×10^{14}	9.75×10^{13}	8.07×10^{13}	0.9999
	0.3	186.76	4.64×10^{13}	4.51×10^{13}	3.79×10^{13}	0.9999
	0.4	180.38	1.30×10^{13}	1.30×10^{13}	1.12×10^{13}	0.9999
	0.5	174.20	3.81×10^{12}	3.88×10^{12}	3.45×10^{12}	0.9999
	0.6	174.96	4.44×10^{12}	4.50×10^{12}	3.99×10^{12}	0.9998
	0.7	169.19	1.41×10^{12}	1.46×10^{12}	1.33×10^{12}	0.9999
	0.8	379.73	1.50×10^{30}	7.20×10^{29}	2.60×10^{29}	0.9049
	Avg.	207.99	2.14×10^{29}	1.03×10^{29}	3.72×10^{28}	
MRWS7-3	0.2	183.13	9.46×10^{13}	8.83×10^{13}	5.61×10^{13}	0.9845
	0.3	176.55	2.43×10^{13}	2.33×10^{13}	1.54×10^{13}	0.9709
	0.4	171.56	8.68×10^{12}	8.49×10^{12}	5.77×10^{12}	0.9761
	0.5	165.35	2.41×10^{12}	2.41×10^{12}	1.70×10^{12}	0.9802
	0.6	159.63	7.37×10^{11}	7.55×10^{11}	5.51×10^{11}	0.9834
	0.7	168.18	4.32×10^{12}	4.28×10^{12}	2.97×10^{12}	0.9833
	0.8	234.74	3.83×10^{18}	2.92×10^{18}	1.36×10^{18}	0.9195
	Avg.	179.88	5.47×10^{17}	4.17×10^{17}	1.95×10^{17}	
MRWS1-1	0.2	149.19	1.24×10^{11}	1.11×10^{11}	1.04×10^{11}	0.9955
	0.3	155.00	4.18×10^{11}	3.65×10^{11}	3.32×10^{11}	0.9985
	0.4	151.20	1.88×10^{11}	1.68×10^{11}	1.55×10^{11}	0.9986
	0.5	152.10	2.27×10^{11}	2.02×10^{11}	1.86×10^{11}	0.9998
	0.6	152.75	2.61×10^{11}	2.30×10^{11}	2.12×10^{11}	0.9987
	0.7	161.29	1.56×10^{12}	1.32×10^{12}	1.16×10^{12}	0.9935
	0.8	176.48	3.73×10^{13}	2.93×10^{13}	2.40×10^{13}	0.9213
	Avg.	156.86	5.73×10^{12}	4.53×10^{12}	3.74×10^{12}	

Table 4. Cont.

Samples	α	$E_a/\text{kJ}\cdot\text{mol}^{-1}$	A_a/s^{-1}			R^2
			$10^\circ\text{C}\cdot\text{min}^{-1}$	$20^\circ\text{C}\cdot\text{min}^{-1}$	$40^\circ\text{C}\cdot\text{min}^{-1}$	
MRWS3-7	0.2	157.07	6.44×10^{11}	6.22×10^{11}	5.87×10^{11}	0.9997
	0.3	161.54	1.64×10^{12}	1.56×10^{12}	1.44×10^{12}	0.9980
	0.4	155.97	5.12×10^{11}	4.96×10^{11}	4.70×10^{11}	0.9985
	0.5	156.17	5.34×10^{11}	5.17×10^{11}	4.90×10^{11}	0.9999
	0.6	162.13	1.86×10^{12}	1.75×10^{12}	1.62×10^{12}	0.9998
	0.7	186.60	3.08×10^{14}	2.62×10^{14}	2.16×10^{14}	0.9953
	0.8	287.37	3.68×10^{23}	2.01×10^{23}	1.06×10^{23}	0.9904
	Avg.	180.98	5.26×10^{22}	2.87×10^{22}	1.51×10^{22}	
WS	0.2	152.31	2.81×10^{11}	2.75×10^{11}	2.63×10^{11}	0.9638
	0.3	159.17	1.19×10^{12}	1.13×10^{12}	1.05×10^{12}	0.9901
	0.4	159.20	1.20×10^{12}	1.14×10^{12}	1.06×10^{12}	0.9853
	0.5	151.77	2.51×10^{11}	2.46×10^{11}	2.36×10^{11}	0.9878
	0.6	157.79	8.91×10^{11}	8.51×10^{11}	7.94×10^{11}	0.9962
	0.7	161.00	1.75×10^{12}	1.65×10^{12}	1.52×10^{12}	0.9748
	0.8	202.17	9.83×10^{15}	7.72×10^{15}	5.89×10^{15}	0.9920
	Avg.	163.35	1.41×10^{15}	1.10×10^{15}	8.42×10^{14}	

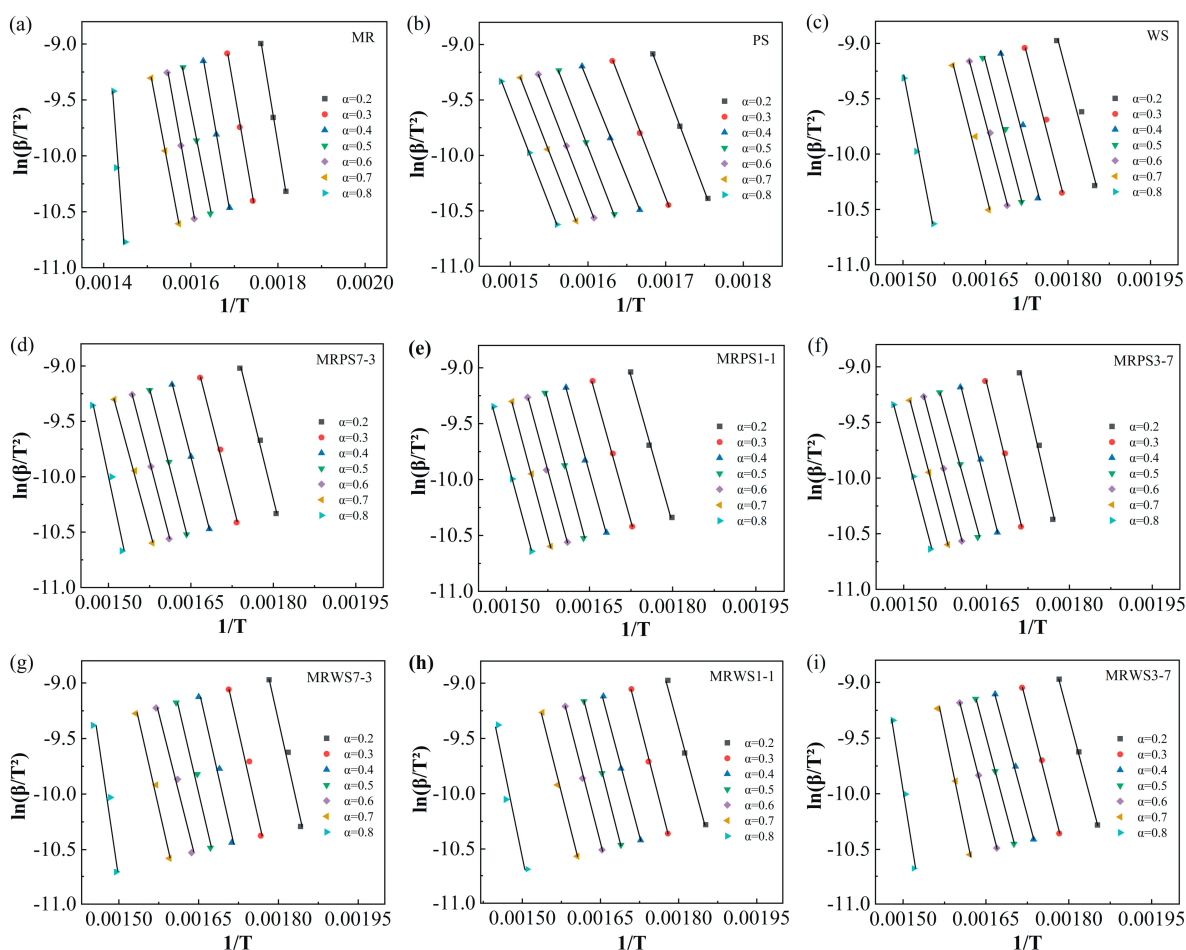


Figure 6. Linear relationship in the plot of $\ln(\beta/T_\alpha^2)$ versus $1/T_\alpha$: (a) MR, (b) PS, (c) WS, (d) MRPS7-3, (e) MRPS1-1, (f) MRPS3-7, (g) MRWS7-3, (h) MRWS1-1, and (i) MRWS3-7.

The activation energies versus the conversion for the MRPS blends and MRWS blends are illustrated in Figure 7. The activation energies changed with the conversion, indicating that the pyrolysis of individual and blended samples underwent multi-step kinetics in the various reaction stages [27]. With the increment in conversion, the activation energies of the MR first declined and then increased. However, the variation patterns of the PS and WS

were different. The activation energies of the PS were reduced slightly as the conversion was increased, while the activation energies of the WS showed a continuous and slight increasing trend. The increasing rates of activation energies were most conspicuous at $\alpha = 0.7$ for the MR and WS. The obvious changes in activation energies probably corresponded to the char formation phase in the presence of a high content of minerals, which had a negative impact on the diffusion of heat and the volatile release [47]. The average activation energy of the MR, PS and WS was 207.99, 149.67, and 163.35 $\text{kJ}\cdot\text{mol}^{-1}$, respectively. The similar change trend of activation energies with the conversion for MR has been reported, and the obtained average activation energy was almost the same as in previous research [17]. Jerzak et al. investigated the activation energies of oat straw pyrolysis using three iso-conversional methods (Friedman, Flynn-Wall-Ozawa, and Kissinger-Akahira-Sunose) [48]. It was found that the activation energies of oat straw increased slightly with the conversion and showed an obvious upward trend at a high conversion ($\alpha = 0.9$). The change trend of activation energies for WS pyrolysis in our study was basically consistent with oat straw pyrolysis.

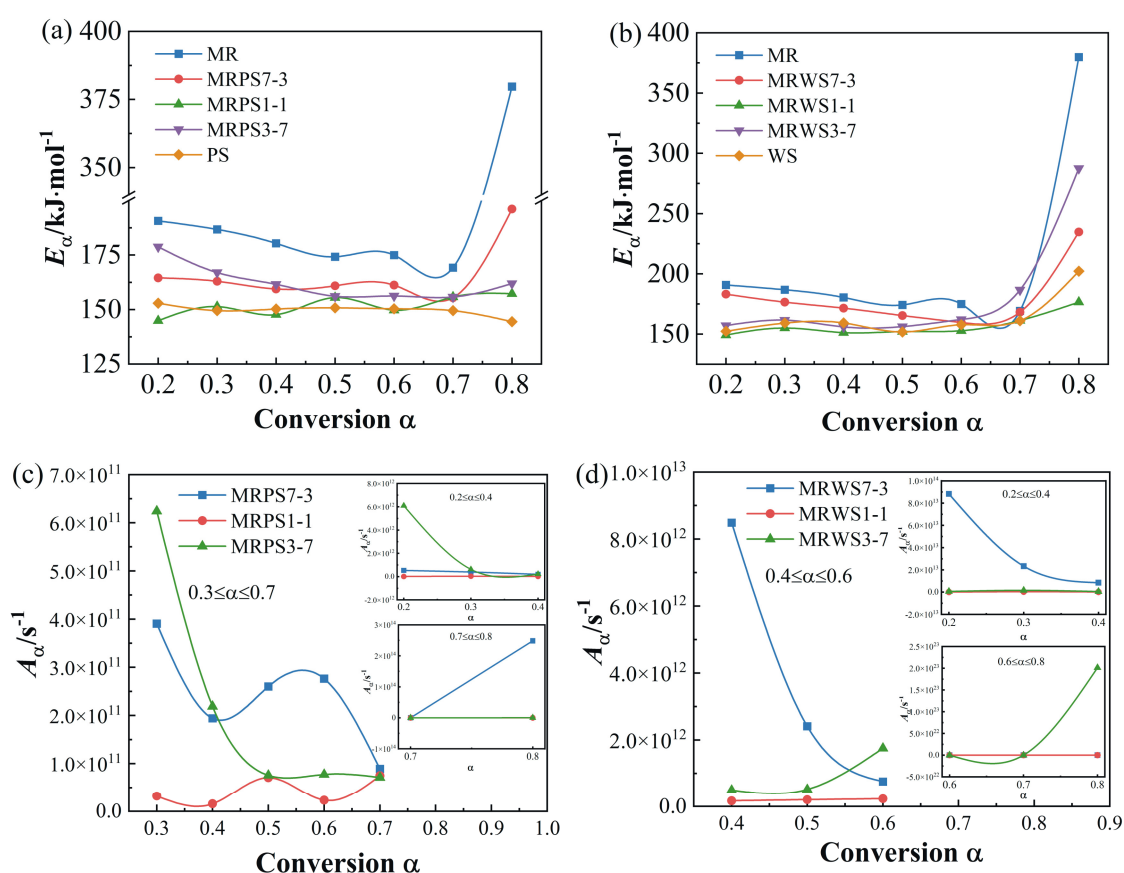


Figure 7. Variation in the kinetic parameters versus conversion for co-pyrolysis process: (a,c) E_α and A_α of MRPS blends and (b,d) E_α and A_α of MRWS blends.

The activation energies of the MRPS blends were less than those of the MR at different conversions and presented a change trend of first reducing and then rising with the increase in conversion. The average activation energy of MRPS7-3, MRPS1-1, and MRPS3-7 was, respectively, 165.80, 151.73, and 162.49 $\text{kJ}\cdot\text{mol}^{-1}$, indicating that PS blending lowered the average activation energy. The activation energies of MRWS7-3 first declined and then increased with the increment in conversion. However, the activation energies of MRWS1-1 and MRWS3-7 increased continuously with the increase in the conversion. The average activation energy of MRWS blends was also reduced compared to MR, respectively, 179.88, 156.86, and 180.98 $\text{kJ}\cdot\text{mol}^{-1}$ for MRWS7-3, MRWS1-1, and MRWS3-7. The average activation energies for both MRPS blends and MRWS blends first declined and then increased

with the increasing PS or WS blending ratio. The lowest average activation energy was found for MRPS1-1 and MRWS1-1. Furthermore, the predicted average activation energy of the blends was calculated by the weighted average based on the average activation energy of individual feedstocks and the blending ratio. It can be found that the average activation energies of MRPS blends and MRWS blends were lower than the predicted average activation energies. The non-additive performance on the average activation energies of MRPS blends and MRWS blends confirmed the existence of interactions between individual feedstocks during the co-pyrolysis process. A similar conclusion was obtained by previous research, which reported that the interactions between waste plastics and mushroom residue reduced the activation energies of the co-pyrolysis process [14].

The pre-exponential factor (A_α) was calculated based on Kissinger's method (Equation (6)), and the results are also presented in Tables 3 and 4. For the pyrolysis process, the pre-exponential factor was an indicator reflecting the complicity of a sample's surface structure or pyrolysis reaction [44,49]. Consequently, a larger value of the pre-exponential factor meant that the complexity of the reaction increased. It can be observed that the A_α values varied from 1.33×10^{12} to $1.50 \times 10^{30} \text{ s}^{-1}$ for the MR, 6.53×10^9 to $3.88 \times 10^{10} \text{ s}^{-1}$ for the PS, and 2.36×10^{11} to $9.83 \times 10^{15} \text{ s}^{-1}$ for the WS. The widely distributed values especially for the MR indicated the complicated composition of the mushroom residue and the complex reactions during the pyrolysis process. As seen from Figure 7c,d, the A_α values ranged from 8.22×10^{10} to $2.81 \times 10^{14} \text{ s}^{-1}$ for MRPS7-3, 8.44×10^9 to $1.17 \times 10^{11} \text{ s}^{-1}$ for MRPS1-1, and 6.07×10^{10} to $6.09 \times 10^{12} \text{ s}^{-1}$ for MRPS3-7. The values of A_α varied from 5.51×10^{11} to $3.83 \times 10^{18} \text{ s}^{-1}$ for MRWS7-3, $1.04 \times 10^{11} \text{ s}^{-1}$ to $3.73 \times 10^{13} \text{ s}^{-1}$ for MRWS1-1, and 4.70×10^{11} to $3.68 \times 10^{23} \text{ s}^{-1}$ for MRWS3-7. These results indicated that both individual and blended samples experienced sophisticated multiphasic degradation reactions at different conversions, and a range of parallel reactions constituted the overall pyrolysis process. For most samples, the highest value of A_α was observed at $\alpha = 0.8$, indicating that the reactions were most complicated in the final stage of the pyrolysis process. The average A_α value ranged from 3.72×10^{28} to $2.14 \times 10^{29} \text{ s}^{-1}$ for the MR, 2.00×10^{10} to $2.27 \times 10^{10} \text{ s}^{-1}$ for the PS, and 8.42×10^{14} to $1.41 \times 10^{15} \text{ s}^{-1}$ for the WS throughout the conversion scope of 0.2–0.8. The larger A_α values for the MR suggested the higher complexity of the pyrolysis reaction. In comparison with the MR, the average A_α values of both the MRPS blends and MRWS blends decreased significantly, signifying that the complicity of the pyrolysis reaction was reduced due to the addition of PS or WS.

3.4. Thermodynamic Analysis

The thermodynamic parameters for the pyrolysis of the MR, PS, WS, and blends were computed according to Equations (7)–(9), respectively. The calculation results for the MRPS blends and MRWS blends are, respectively, demonstrated in Tables 5 and 6. The enthalpy change (ΔH) at different heating rates was very close, which suggested an ignorable influence of the heating rate on enthalpy change. However, the Gibbs free energy (ΔG) illustrated a slight increase with the increment in the heating rate.

Table 5. Thermodynamic parameters of MR, PS, and their blends at three heating rates.

Samples	α	10 °C·min ^{−1}			20 °C·min ^{−1}			40 °C·min ^{−1}		
		$\Delta H/$ kJ·mol ^{−1}	$\Delta G/$ kJ·mol ^{−1}	$\Delta S/$ J·mol ^{−1} ·K ^{−1}	$\Delta H/$ kJ·mol ^{−1}	$\Delta G/$ kJ·mol ^{−1}	$\Delta S/$ J·mol ^{−1} ·K ^{−1}	$\Delta H/$ kJ·mol ^{−1}	$\Delta G/$ kJ·mol ^{−1}	$\Delta S/$ J·mol ^{−1} ·K ^{−1}
MR	0.2	186.15	180.06	9.78	186.07	180.18	9.29	186.00	181.08	7.57
	0.3	181.99	180.17	2.92	181.90	180.29	2.54	181.82	181.19	0.97
	0.4	175.46	180.35	−7.86	175.37	180.48	−8.06	175.28	181.38	−9.41
	0.5	169.15	180.53	−18.30	169.05	180.66	−18.32	168.95	181.57	−19.45
	0.6	169.79	180.51	−17.23	169.69	180.64	−17.26	169.58	181.55	−18.43
	0.7	163.90	180.68	−26.97	163.79	180.81	−26.84	163.68	181.73	−27.81
	0.8	373.99	176.50	317.44	373.91	176.55	311.22	373.89	177.36	302.73
	Avg.	202.92	179.83	-	202.83	179.94	-	202.74	180.84	-

Table 5. Cont.

Samples	α	10 °C·min ^{−1}			20 °C·min ^{−1}			40 °C·min ^{−1}		
		$\Delta H/$ kJ·mol ^{−1}	$\Delta G/$ kJ·mol ^{−1}	$\Delta S/$ J·mol ^{−1} ·K ^{−1}	$\Delta H/$ kJ·mol ^{−1}	$\Delta G/$ kJ·mol ^{−1}	$\Delta S/$ J·mol ^{−1} ·K ^{−1}	$\Delta H/$ kJ·mol ^{−1}	$\Delta G/$ kJ·mol ^{−1}	$\Delta S/$ J·mol ^{−1} ·K ^{−1}
MRPS 7-3	0.2	159.93	181.14	−34.03	159.86	181.58	−34.15	159.76	182.79	−35.32
	0.3	158.19	181.19	−36.90	158.11	181.63	−36.98	158.00	182.85	−38.10
	0.4	154.47	181.30	−43.06	154.37	181.75	−43.04	154.26	182.97	−44.01
	0.5	155.85	181.26	−40.78	155.75	181.70	−40.80	155.63	182.92	−41.84
	0.6	156.06	181.25	−40.42	155.95	181.69	−40.46	155.83	182.90	−41.51
	0.7	150.15	181.44	−50.21	150.04	181.88	−50.06	149.91	183.10	−50.90
	0.8	190.70	180.23	16.79	190.63	180.65	15.68	190.50	181.84	13.27
	Avg.	160.76	181.12	-	160.67	181.55	-	160.56	182.77	-
MRPS 1-1	0.2	140.25	182.12	−67.08	140.14	183.81	−68.12	140.05	185.32	−68.79
	0.3	146.56	181.89	−56.61	146.46	183.58	−57.90	146.35	185.08	−58.85
	0.4	142.73	182.02	−62.94	142.62	183.71	−64.09	142.51	185.22	−64.89
	0.5	150.43	181.75	−50.18	150.32	183.43	−51.65	150.20	184.94	−52.77
	0.6	144.53	181.95	−59.95	144.40	183.64	−61.20	144.29	185.14	−62.08
	0.7	150.51	181.74	−50.04	150.39	183.43	−51.52	150.27	184.93	−52.66
	0.8	151.87	181.69	−47.78	151.75	183.38	−49.33	151.62	184.87	−50.52
	Avg.	146.70	181.88	-	146.58	183.57	-	146.47	185.07	-
MRPS 3-7	0.2	174.10	182.92	−13.99	174.04	183.00	−13.96	173.94	184.78	−16.43
	0.3	162.14	183.27	−33.53	162.06	183.37	−33.18	161.95	185.16	−35.15
	0.4	156.60	183.45	−42.60	156.51	183.54	−42.10	156.39	185.34	−43.85
	0.5	151.00	183.63	−51.77	150.90	183.73	−51.12	150.78	185.53	−52.64
	0.6	151.04	183.62	−51.71	150.93	183.72	−51.06	150.81	185.52	−52.59
	0.7	150.51	183.64	−52.58	150.39	183.74	−51.93	150.27	185.54	−53.43
	0.8	156.56	183.43	−42.65	156.45	183.53	−42.17	156.32	185.32	−43.94
	Avg.	157.42	183.42	-	157.33	183.52	-	157.21	185.31	-
PS	0.2	148.16	184.05	−56.87	148.06	184.15	−56.11	147.96	185.95	−57.45
	0.3	144.63	184.17	−62.65	144.52	184.27	−61.80	144.41	186.07	−63.01
	0.4	145.22	184.15	−61.67	145.11	184.24	−60.85	145.00	186.04	−62.08
	0.5	145.71	184.12	−60.86	145.60	184.22	−60.06	145.48	186.02	−61.32
	0.6	145.17	184.14	−61.75	145.05	184.24	−60.93	144.93	186.04	−62.18
	0.7	144.23	184.17	−63.28	144.11	184.27	−62.44	143.98	186.07	−63.66
	0.8	139.10	184.35	−71.70	138.97	184.45	−70.72	138.83	186.26	−71.73
	Avg.	144.60	184.16	-	144.49	184.26	-	144.37	186.06	-

Table 6. Thermodynamic parameters of MR, WS, and their blends at three heating rates.

Samples	α	10 °C·min ^{−1}			20 °C·min ^{−1}			40 °C·min ^{−1}		
		$\Delta H/$ kJ·mol ^{−1}	$\Delta G/$ kJ·mol ^{−1}	$\Delta S/$ J·mol ^{−1} ·K ^{−1}	$\Delta H/$ kJ·mol ^{−1}	$\Delta G/$ kJ·mol ^{−1}	$\Delta S/$ J·mol ^{−1} ·K ^{−1}	$\Delta H/$ kJ·mol ^{−1}	$\Delta G/$ kJ·mol ^{−1}	$\Delta S/$ J·mol ^{−1} ·K ^{−1}
MR	0.2	186.15	180.06	9.78	186.07	180.18	9.29	186.00	181.08	7.57
	0.3	181.99	180.17	2.92	181.90	180.29	2.54	181.82	181.19	0.97
	0.4	175.46	180.35	−7.86	175.37	180.48	−8.06	175.28	181.38	−9.41
	0.5	169.15	180.53	−18.30	169.05	180.66	−18.32	168.95	181.57	−19.45
	0.6	169.79	180.51	−17.23	169.69	180.64	−17.26	169.58	181.55	−18.43
	0.7	163.90	180.68	−26.97	163.79	180.81	−26.84	163.68	181.73	−27.81
	0.8	373.99	176.50	317.44	373.91	176.55	311.22	373.89	177.36	302.73
	Avg.	202.92	179.83	-	202.83	179.94	-	202.74	180.84	-
MRWS 7-3	0.2	178.62	173.04	9.30	178.56	173.29	8.62	178.47	175.53	4.66
	0.3	171.84	173.23	−2.31	171.79	173.48	−2.77	171.68	175.72	−6.41
	0.4	166.70	173.37	−11.12	166.64	173.62	−11.43	166.52	175.87	−14.83
	0.5	160.38	173.55	−21.99	160.30	173.81	−22.10	160.18	176.06	−25.21
	0.6	154.55	173.73	−32.01	154.47	173.99	−31.94	154.33	176.25	−34.77
	0.7	162.97	173.47	−17.53	162.88	173.72	−17.74	162.75	175.97	−20.98
	0.8	229.18	171.81	95.75	229.14	172.03	93.44	229.01	174.23	86.94
	Avg.	174.89	173.17	-	174.82	173.42	-	174.71	175.66	-
MRWS 1-1	0.2	144.70	171.86	−45.86	144.60	173.09	−46.93	144.52	174.16	−47.65
	0.3	150.33	171.67	−36.04	150.23	172.90	−37.34	150.14	173.96	−38.30
	0.4	146.39	171.79	−42.90	146.28	173.02	−44.05	146.18	174.09	−44.87
	0.5	147.18	171.76	−41.52	147.07	172.99	−42.70	146.96	174.06	−43.56
	0.6	147.72	171.74	−40.57	147.60	172.97	−41.78	147.50	174.04	−42.66
	0.7	156.11	171.47	−25.95	155.99	172.70	−27.53	155.89	173.76	−28.73
	0.8	170.98	171.03	−0.09	170.82	172.24	−2.35	170.76	173.29	−4.07
	Avg.	151.91	171.62	-	151.80	172.85	-	151.71	173.91	-

Table 6. Cont.

Samples	α	10 °C·min ^{−1}			20 °C·min ^{−1}			40 °C·min ^{−1}		
		$\Delta H/$ kJ·mol ^{−1}	$\Delta G/$ kJ·mol ^{−1}	$\Delta S/$ J·mol ^{−1} ·K ^{−1}	$\Delta H/$ kJ·mol ^{−1}	$\Delta G/$ kJ·mol ^{−1}	$\Delta S/$ J·mol ^{−1} ·K ^{−1}	$\Delta H/$ kJ·mol ^{−1}	$\Delta G/$ kJ·mol ^{−1}	$\Delta S/$ J·mol ^{−1} ·K ^{−1}
MRWS 3-7	0.2	152.58	171.60	−32.13	152.50	172.21	−32.58	152.41	172.98	−33.23
	0.3	156.88	171.47	−24.64	156.79	172.07	−25.25	156.69	172.84	−26.07
	0.4	151.18	171.64	−34.55	151.09	172.25	−34.96	150.98	173.02	−35.59
	0.5	151.28	171.63	−34.37	151.18	172.24	−34.80	151.07	173.01	−35.43
	0.6	157.15	171.45	−24.15	157.05	172.05	−24.79	156.94	172.82	−25.64
	0.7	181.47	170.76	18.09	181.39	171.35	16.59	181.28	172.09	14.83
	0.8	281.90	168.63	191.28	281.84	169.17	186.18	281.76	169.87	180.71
	Avg.	176.06	171.03	-	175.98	171.62	-	175.88	172.38	-
WS	0.2	147.81	170.81	−39.04	147.75	171.44	−39.33	147.64	172.23	−39.91
	0.3	154.52	170.60	−27.28	154.45	171.22	−27.85	154.34	172.00	−28.66
	0.4	154.44	170.59	−27.43	154.36	171.22	−27.99	154.24	172.00	−28.82
	0.5	146.92	170.83	−40.58	146.84	171.46	−40.88	146.72	172.24	−41.43
	0.6	152.87	170.64	−30.16	152.78	171.26	−30.70	152.66	172.05	−31.46
	0.7	155.98	170.54	−24.72	155.90	171.16	−25.34	155.77	171.94	−26.25
	0.8	196.82	169.42	46.51	196.72	170.02	44.33	196.63	170.78	41.97
	Avg.	158.48	170.49	-	158.40	171.11	-	158.29	171.89	-

To comprehend the pyrolysis process, the variation in the thermodynamic parameters versus the conversion for MRPS blends at 20 °C·min^{−1} is plotted in Figure 8. For the pyrolysis reaction system, the ΔH corresponded to the difference in total energy between the pyrolysis products and reactants. That is to say, ΔH represented the total energy expended for raw material decomposing into various solid, liquid, and gaseous products. As observed from Figure 8a, the ΔH presented positive values, demonstrating that the pyrolysis reactions of MR, PS, and their blends were endothermic. The variation in the ΔH values over conversion was because of the enhancement or abatement in endothermicity. The MR had a higher average ΔH value than that of the PS, indicating a higher energy requirement for the breakage of chemical bonds in reactants, which was probably due to the higher mineral content in MR. The minerals in feedstocks may obstruct the diffusion of heat and released volatiles during the pyrolysis process leading to more energy needed for the formation of products [39]. For the conversion varying from 0.2 to 0.8, the MRPS blends showed lower average ΔH values (160.67, 146.58, and 157.33 kJ·mol^{−1} for MRPS7-3, MRPS1-1, and MRPS3-7, respectively) than that of the MR (202.83 kJ·mol^{−1}), indicating the lower endothermicity for the co-pyrolysis of MRPS blends. The energy differences between reactants and products for the MRPS blends were smaller compared to MR. It was noteworthy that the change trends of ΔH with conversion were the same as those of the activation energies (Figure 7a). Similar trends have also been observed for the pyrolysis of wood sawdust and rice husk [27,39].

Figure 8b illustrates the intermediate energy barriers (EB , deviation between E_α and ΔH_α) versus conversion for MRPS blends. The EB represented the additional energy required for the generation of products from the reactants. For all the samples, the values of EB varied from 4.65 to 5.82 kJ·mol^{−1}. The EB values showed a slight increasing trend with the increment in conversion, indicating the increase in additional energy requirement with the pyrolysis reaction proceeding. Furthermore, the pyrolysis process of MR, PS, and MRPS blends showed relatively small values of EB (avg. EB = 5.13–5.18 kJ·mol^{−1}), implying that the formation of the activated complex required relatively low additional energy, and the generation of pyrolysis products from these feedstocks was easily impacted by energy [49].

The Gibbs free energy versus conversion for MRPS blends is presented in Figure 8c. The ΔG referred to the total energy increase in a system needed for the generation of products [50]. Positive values of ΔG suggested non-spontaneous reactions that could happen with the input of external energy. For MR, PS, and their blends, the ΔG showed positive values and remained almost unchanged throughout the entire conversion process. These values implied that the pyrolysis reaction was a non-spontaneous process, which can be promoted by providing sufficient energy [49]. Furthermore, the degree of disorder of

the pyrolysis system was evaluated by entropy change (ΔS). Negative changes in entropy demonstrated the reduction in the disorder degree of the reaction system. Small or negative values of ΔS implied the achievement of thermodynamic equilibrium of the pyrolysis reaction system, whereas positive values of ΔS indicated that the reaction system did not reach its thermodynamic equilibrium. The ΔS of MR presented negative values exclusive of the initial ($0.2 \leq \alpha \leq 0.3$) and final ($\alpha = 0.8$) stages of the pyrolysis reaction. The ΔS values of MRPS7-3 were negative except at the conversion of 0.8. However, the ΔS always showed negative values with the increase in conversion for PS, MRPS3-7, and MRPS1-1. These random changes in ΔS signified the complicity of reactions that happened during the pyrolysis of biomass waste into various products. For the pyrolysis system with a negative ΔS , the ΔG demonstrated larger values than the ΔH , which signified that partial heat energy fed to the system was superfluous. The ΔS values of MRPS blends were more negative than positive, demonstrating that the degree of disorder of the pyrolysis system declined compared to the initial state of the system during the co-pyrolysis process [41].

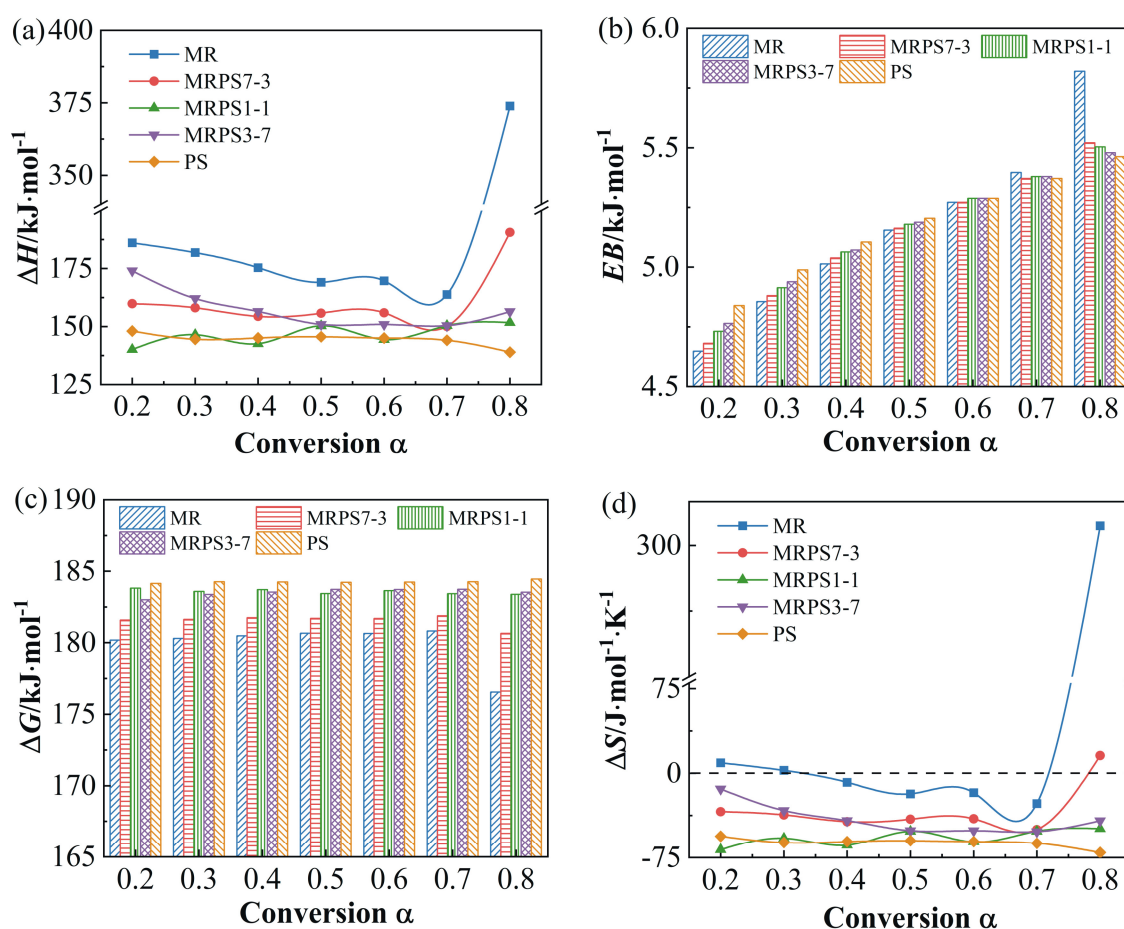


Figure 8. Variation in (a) ΔH versus conversion, (b) energy barrier versus conversion, (c) ΔG versus conversion, and (d) ΔS versus conversion for co-pyrolysis process of MRPS blends at $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

The variation in the thermodynamic parameters versus conversion for the MRWS blends at $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ is illustrated in Figure 9. The ΔH , EB , and ΔG presented similar change patterns to those of MRPS blends, whereas the variation in ΔS was slightly different. The ΔS showed positive values at specific conversion for MRWS7-3 ($\alpha = 0.1$ and 0.8) and MRWS3-7 ($\alpha = 0.7$ and 0.8), yet the ΔS values always showed negative values for MRWS1-1. The ΔS values of MRWS blends were also more negative than positive, signifying the reduction in the disorder degree of the system after the pyrolysis reaction.

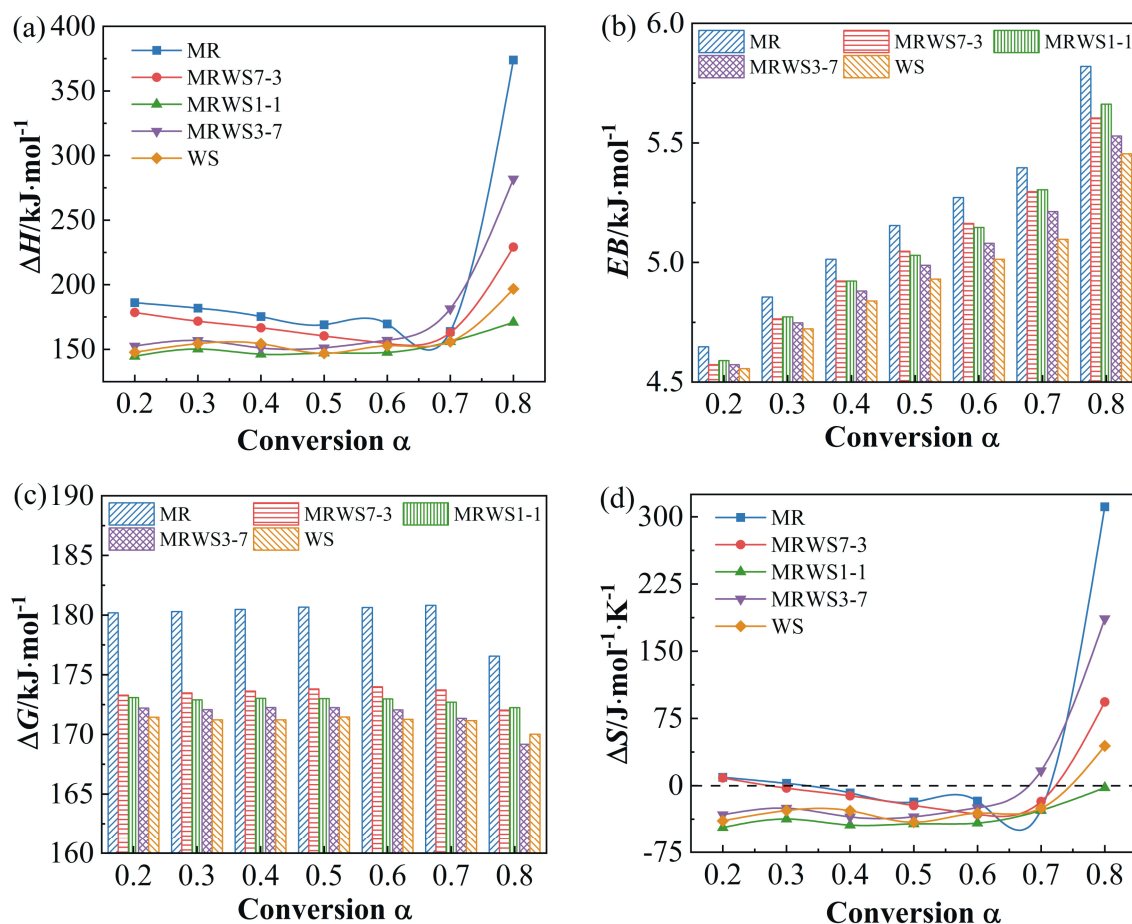


Figure 9. Variation in (a) ΔH versus conversion, (b) energy barrier versus conversion, (c) ΔG versus conversion, and (d) ΔS versus conversion for co-pyrolysis process of MRWS blends at $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

3.5. Structure Properties of Co-Pyrolytic Chars

3.5.1. Carbon Microcrystalline Structure

The Raman spectrums of pyrolytic chars produced at different blending ratios are presented in Figure 10. The spectrums of all the char samples illustrated two evident peaks at about 1590 cm^{-1} and 1360 cm^{-1} . The total Raman area, the integral area of the spectrum between 800 and 1800 cm^{-1} , was used to express the Raman peak intensity of pyrolytic chars. The Raman intensity of pyrolytic chars from carbon-based materials was primarily impacted by the Raman scattering ability, the light absorptivity, and oxygen-containing structures [32]. The total Raman intensity can be enhanced by oxygen-containing structures owing to the resonance effect between oxygen and aromatic rings. On the contrary, the condensed aromatic rings in chars resulted in the reduction in the total Raman intensity owing to the high light absorption ability.

Figure 11 illustrates the total Raman area versus blending ratio for MRPS chars and MRWS chars. The total Raman area of MRPS chars increased as the PS blending ratio increased from 30% to 70%. The enlargement in the total Raman area for MRPS chars was probably caused by the increment in oxygen-containing structures or the decreased light absorption ability. As seen from Figure 11c, the area ratio of small aromatic rings to larger ones for MRPS7-3 char was smaller, suggesting a higher amount of condensed aromatic rings, which reduced the Raman intensity. As the PS mass ratio increased, the reduction in the condensed aromatic rings decreased the light absorptivity, resulting in the increase in Raman intensity. Consequently, the change in the total Raman area for MRPS chars was primarily influenced by the amount of condensed aromatic rings. It can be observed from Figure 11b that the total Raman area of MRWS chars illustrated a reduction trend as the

WS blending ratio was increased from 30% to 70%. As presented in Figure 11d, the area ratio of small aromatic rings to larger ones for MRWS chars declined with the increase in the WS mass ratio, signifying that the increase in large aromatic rings would reduce the Raman intensity, consistent with the reduction in Figure 11b. Therefore, the increased light absorption ability caused by the enlargement of large aromatic rings was also probably the principal reason leading to the decrease in the total Raman area for MRWS chars. To sum up, due to the similar oxygen content of these three feedstocks, the difference in the small and large aromatic ring structures was the primary reason for the change in the Raman intensity of co-pyrolytic chars in this study.

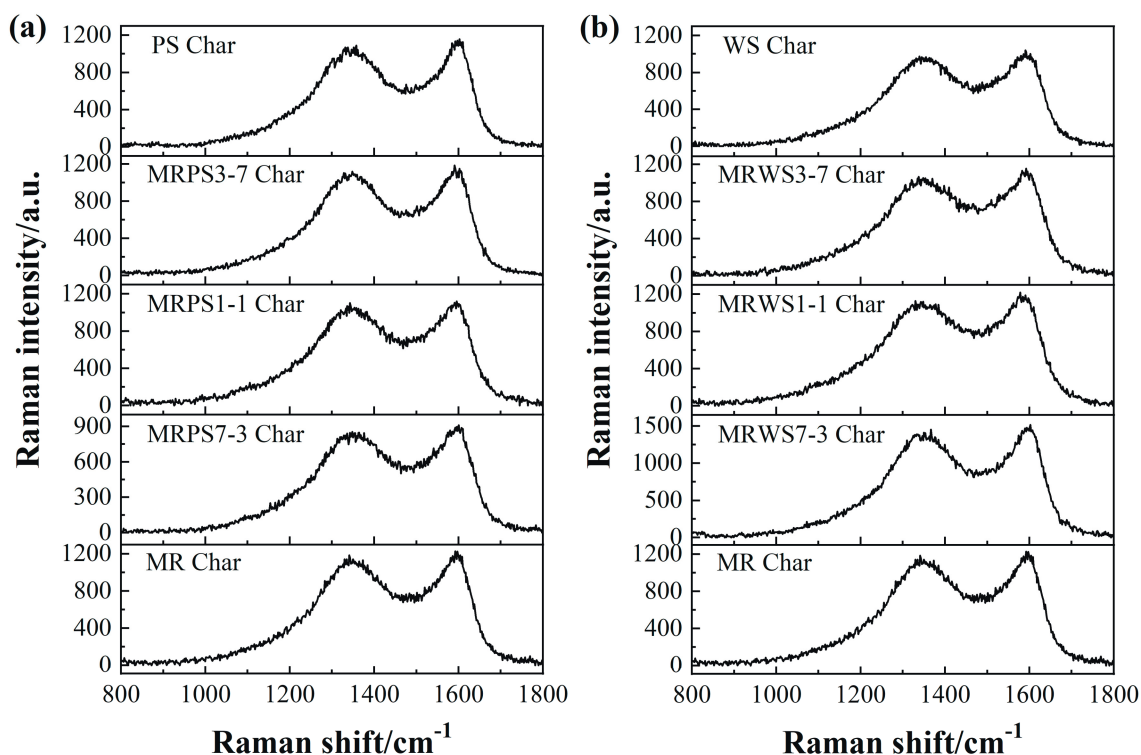


Figure 10. Raman spectrum of co-pyrolytic chars: (a) MRPS char and (b) MRWS char.

The changes in the area ratio between major Raman bands are also displayed in Figure 11. The three bands (G_R , V_L , and V_R) represented the small aromatic structures with <6 fused benzene rings, and D band mainly corresponded to the large aromatic structures with not less than 6 fused benzene rings. The area ratio of small aromatic rings to larger ones ($A_{(G_R+V_L+V_R)}/A_D$) can be employed to describe the evolution of aromatic structures. Analyzing the changes in the relative content of small and large rings was significant for understanding the reaction pathways of the co-pyrolysis process.

As observed from Figure 11c, MRPS chars with different blending ratios showed different $A_{(G_R+V_L+V_R)}/A_D$ values, indicating that the pyrolysis reaction pathways were different. For MRPS chars, the ratios illustrated a growing trend with the increase in the PS mass ratio. It was suggested that PS blending reduced the large aromatic rings and/or increased the small rings. A possible reason was that PS might enhance the release of oxygen-containing structures. The decomposition of oxygen-containing groups would probably promote the large oxygen-containing aromatic rings into small rings [32]. In addition, PS pyrolysis would generate more volatiles, which enhanced the volatile–char interactions. Thus, more small aromatic rings were generated in MRPS chars attributed to the accumulation of small molecule volatiles on the char surface [35]. These two impacts interpreted the increment in small aromatic rings during co-pyrolysis with PS. Furthermore, the change in small and large aromatic rings would influence the observed Raman intensity

from different aromatic rings. The A_T in Figure 11c represented the total Raman area, as previously described. The $A_{(GR+VL+VR)}/A_T$ and A_D/A_T , respectively, referred to the relative proportion of the observed Raman intensity from small aromatic rings and large aromatic rings. It can be observed that the $A_{(GR+VL+VR)}/A_T$ illustrated an increasing trend with the increase in the PS blending ratio, supporting the increase in small aromatic rings at a high PS blending ratio. The $A_{(GR+VL+VR)}/A_T$ was higher than A_D/A_T , indicating that the small aromatic rings contributed more to the observed total Raman area of MRPS chars.

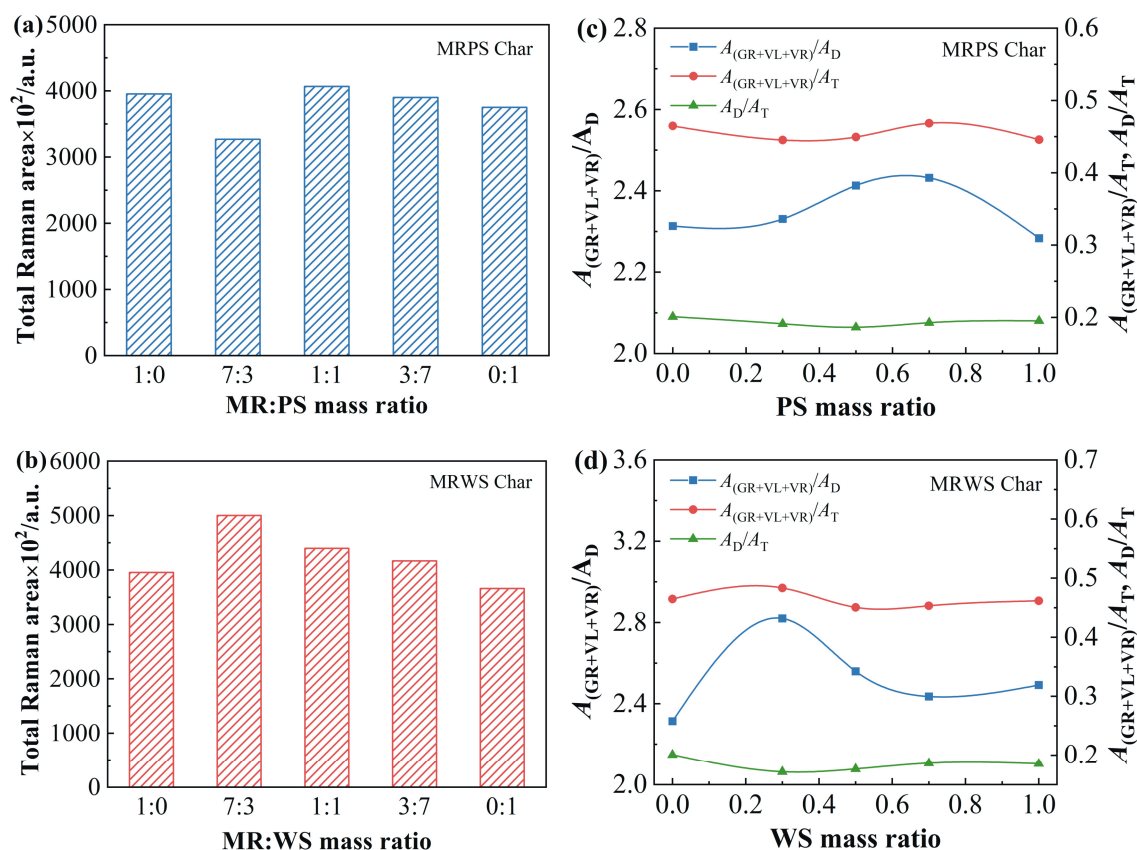


Figure 11. Total Raman area and major band area ratios versus blending ratio for co-pyrolytic chars: (a,c) MRPS char and (b,d) MRWS char.

As seen from Figure 11d, the $A_{(GR+VL+VR)}/A_D$ of MRWS chars declined obviously with the increment in the WS blending ratio. It was implied that WS blending reduced the small aromatic rings and/or increased the larger ones, which was probably due to the high mineral content of the WS. During the pyrolysis process, the alkali and alkaline-earth metal (AAEM) species in the WS can accelerate the breakage of weak bonds and enhance the generation of stronger bonds, thus increasing the large aromatic ring structures [51]. As shown in Figure 11d, the $A_{(GR+VL+VR)}/A_T$ decreased and the A_D/A_T increased with the increase in the WS mass ratio, confirming the conversion of small aromatic rings to larger rings. It was also found that the small aromatic rings contributed more to the observed total Raman area of MRWS chars. Generally speaking, the conclusion can be drawn that the formation of small or large aromatic rings during the co-pyrolysis process was impacted by the feedstock types and blending ratios.

3.5.2. Surface Texture

The surface textures of pyrolytic chars from MR, PS, WS, and their blends are shown in Figure 12. No obvious cavities were observed on the surface of MR char. The pyrolytic char of coprinus comatus fungi residue also showed similar surface textures [12]. Compared to the MR char, the PS char and WS char contained more porous and fibrous structures, which

were attributed to the larger releasing rate of volatiles. A previous investigation has also reported similar morphological features for residual chars from wood biomass [45]. The surface of the MR and WS char showed more bright and agglomerated white substances than that of PS, which was because the inorganic substance content of the MR and WS was higher. As the PS mass ratio was improved, the surface morphology of MRPS chars became porous, and the fibrous structural substances increased significantly. The surface characteristics of MRWS chars became more fragmented with the WS addition. The addition of PS or WS made the char surface coarser, and a similar surface morphology was observed for the co-pyrolytic char from spent mushroom substrate and marine macroalgae [30]. Various pyrolytic chars with diverse surface characteristics can be acquired from the co-pyrolysis of MR with different biomasses by adjusting the blending ratios.

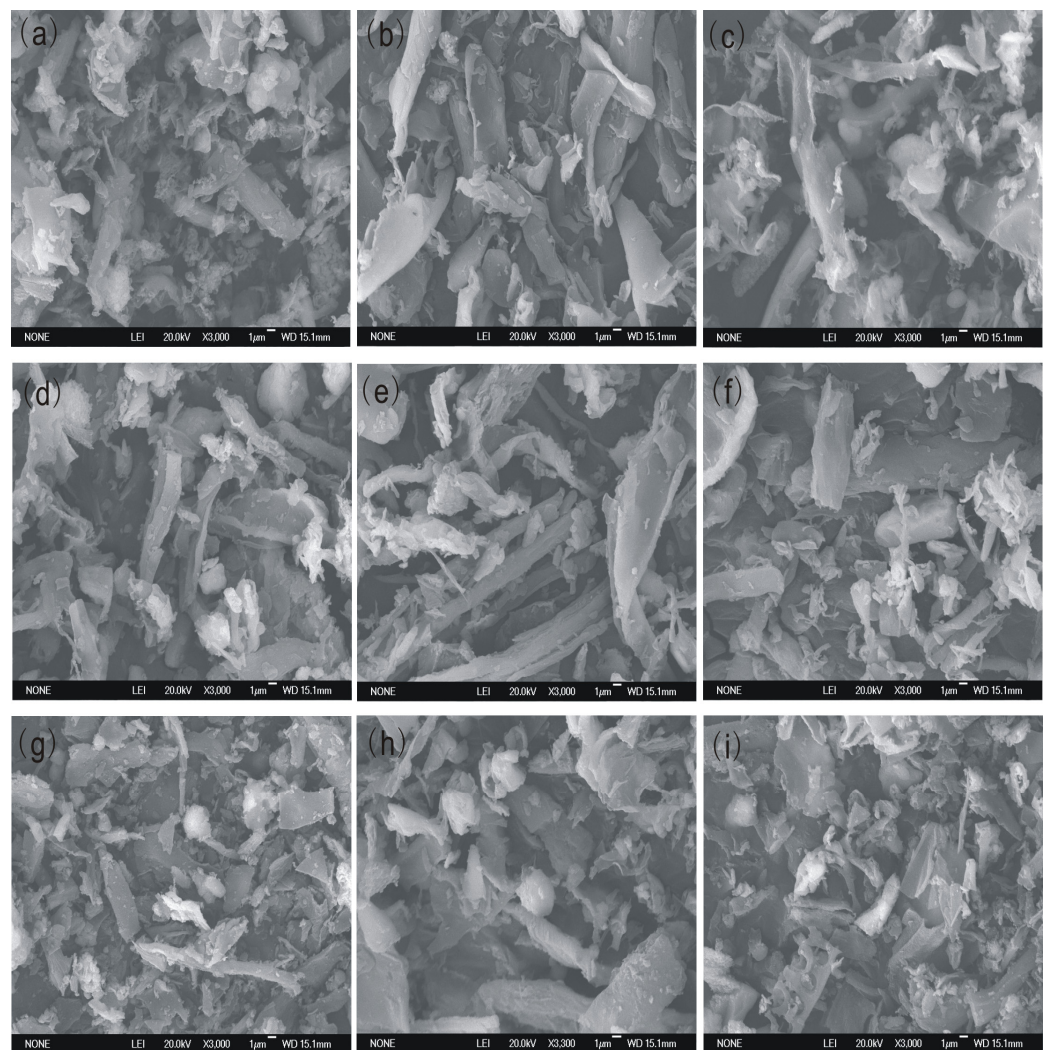


Figure 12. SEM micrographs of the pyrolytic chars: (a) MR char, (b) PS char, (c) WS char, (d) MRPS7-3 char, (e) MRPS1-1 char, (f) MRPS3-7 char, (g) MRWS7-3 char, (h) MRWS1-1 char, and (i) MRWS3-7 char.

The surface texture of pyrolytic chars was quantitatively explored by the fractal dimension (D_s) on the basis of fractal theory. The value of D_s can be calculated according to the following formula:

$$D_s = \frac{\ln(N_r)}{\ln(1/r)} \quad (10)$$

where r is the selected ruler, and N_r is the measurement results from the determinate ruler. Detailed information of the computational method was described in previous research [34].

The higher the D_s was, the more irregular and coarser the char surface was. Table 7 presents the fractal dimensions of surface morphology for pyrolytic chars from individual and blended samples. The correlation coefficients were higher than 0.99, suggesting the high reliability of the results. The fractal dimensions of the MR char, PS char, and WS char were 1.68, 1.65, and 1.67, respectively. It was observed that the fractal dimensions of MRPS chars and MRWS chars were higher than those of isolated chars, demonstrating that the surface textures of co-pyrolytic chars were obviously affected by the interactions between MR and PS or WS. The increase in the fractal dimension suggested that PS or WS blending promoted the char surface towards more irregular and rough structures, which would probably affect the reactivity of residual chars. The surface morphology of co-pyrolytic char from spent mushroom substrate and textile dyeing sludge was also reported to become rough and uneven due to the interactions [29].

Table 7. Fractal dimension of pyrolytic chars from individual and blended samples.

MR Blending Ratio	MRPS Char		MRWS Char	
	D_s	R^2	D_s	R^2
1	1.68	0.9921	1.68	0.9921
0.7	1.69	0.9921	1.83	0.9915
0.5	1.69	0.9921	1.63	0.9924
0.3	1.74	0.9918	1.76	0.9918
0	1.65	0.9923	1.67	0.9921

It can be concluded that the carbon structure of MRPS chars and MRWS chars was mainly composed of small aromatic rings. The pyrolytic chars with a high content of small aromatic rings were easier to combust or gasify due to their higher reactivity [35]. In addition, the co-pyrolytic chars were porous, which was conducive to the diffusion and adsorption of substances. Therefore, co-pyrolytic chars from MRPS blends or MRWS blends may be used as clean solid fuels, adsorption materials, catalysts, soil conditioners, etc. Further study should emphasize the application performance of co-pyrolytic chars from the blends of MR and wood/straw biomass.

4. Conclusions

Thermal characteristics and kinetic and thermodynamic analysis during the co-pyrolysis of mushroom residue (MR) and pine sawdust (PS) or wheat straw (WS), as well as the carbon microcrystalline structure and surface textures of co-pyrolytic chars, were investigated. The pyrolytic process of the blends consisted of three phases: the dehydration phase, volatile releasing phase, and carbonization phase. With an increase in the PS or WS blending ratio from 30% to 70%, the devolatilization index increased from 13.09 to 15.30 for MRPS blends and from 11.29 to 21.03 for MRWS blends, indicating that the volatile release was promoted and concentrated. Weak interactions were observed for the blends, which were affected by pyrolysis temperatures and blending ratios. The interactions mainly affected the thermal decomposition temperatures and rates in the stage of volatile release between 250 °C and 400 °C but had no prominent influence on the volatile yields for the co-pyrolysis process. The average activation energies of the blends (151.73–180.98 kJ·mol^{−1}) were smaller than that of MR (207.99 kJ·mol^{−1}) and presented non-additive performance owing to the interactions between individual components. The lowest average activation energy was obtained when the PS or WS mass ratio was 50%. The lower average pre-exponential factor of the blends indicated the reduced complicacy of the pyrolysis reaction. All the blends presented positive average ΔH and ΔG , and the relatively small deviation between E_a and ΔH_a (4.94–5.18 kJ·mol^{−1}) signified the energy sensitivity of product formation from the pyrolysis of these feedstocks. The observed trends of Raman intensity of co-pyrolytic chars were dependent on the difference in the small and large aromatic ring structures. As the PS or WS blending ratio increased, the PS promoted the generation of small aromatic rings, whereas the WS favored the production of larger rings. The surface textures of co-pyrolytic chars became porous, and the increased

fractal dimensions (1.69–1.83) indicated the promotion of surface irregularity and roughness. The results of this investigation can provide some valuable knowledge for developing the co-pyrolysis technology of edible fungi residue with wood/straw biomass.

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