

Copyrolysis of Waste Cartons and Polyolefin Plastics under Microwave Heating and Characterization of the Products

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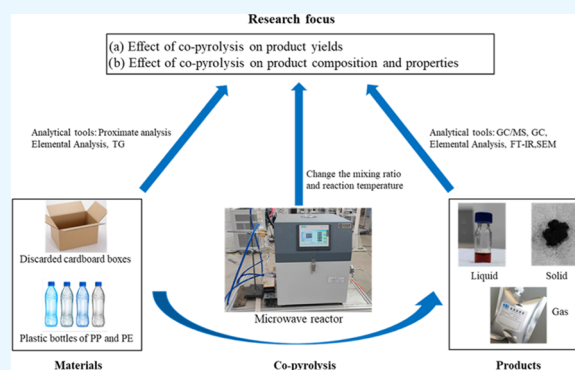
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ABSTRACT: Municipal organic solid waste contains many recoverable resources, including biomass materials and plastics. The high oxygen content and strong acidity of bio-oil limit its application in the energy field, and the oil quality is mainly improved by copyrolysis of biomass with plastics. Therefore, in this paper, a copyrolysis method was utilized to treat solid waste, namely, common waste cartons and waste plastic bottles (polypropylene (PP) and polyethylene (PE)) as raw materials. The products were analyzed by Fourier transform infrared (FT-IR) spectroscopy, elemental analysis, GC, and GC/MS to investigate the reaction pattern of the copyrolysis. The results show that the addition of plastics can reduce the residue content by about 3%, and the copyrolysis at 450 °C can increase the liquid yield by 3.78%. Compared with single waste carton pyrolysis, no new product appeared in the copyrolysis liquid products but the oxygen content of the liquid decreased from 65% to less than 8%. The content of CO₂ and CO in the copyrolysis gas product is 5–15% higher than the theoretical value; the O content of the solid products increased by about 5%. This indicates that waste plastics can promote the formation of L-glucose and small molecules aldehydes and ketones by providing H radicals and reduce the oxygen content in liquids. Thus, copyrolysis improves the reaction depth and product quality of waste cartons, which provides a certain theoretical reference for the industrial application of solid waste copyrolysis.



1. INTRODUCTION

The energy sources people currently use are mainly non-renewable, such as crude oil and coal, which are rapidly depleting and cannot be replenished. Municipal organic solid waste contains a large amount of renewable carbon resources and is a potential and abundant energy source. At present, global solid waste has exceeded 2 billion tons, and China produces nearly 300 million tons every year. If waste treatment is improper, it not only puts great pressure on the environment but also causes a waste of resources.^{1,2} Compared with landfill and incineration having the disadvantages of high pollution and carbon emissions, pyrolysis can convert solid wastes into fuels or chemicals cleanly and efficiently, which is one of the current research hotspots. In addition, pyrolysis can reduce carbon emissions by 50–60% compared with incineration.³

Municipal organic solid waste contains a large amount of biomass, and these biomass resources can be converted by pyrolysis into high-quality energy products, such as bio-oil.⁴ However, the high oxygen content and acidity of bio-oil limit its application in the energy sector.⁵ Copyrolysis not only reduces the oxygen content and acid value in bio-oil but also possibly eliminates some process problems in plastic pyrolysis.⁶ In

addition, copyrolysis can also reduce the separation time of organic solid waste in the preparation stage.⁷

The oxygen content of bio-oil is between 45 and 60%, while polyolefin plastic has no oxygen element, so adding plastic adjusts the carbon, hydrogen, and oxygen elements in bio-oil.^{8–10} The copyrolysis of agricultural wastes such as pine wood, corn stover, and bagasse with plastics has been extensively studied.^{11,12} Chen et al. explored the synergistic effect under the copyrolysis of vesicular and poly(ethylene terephthalate) (PET) in a solid bed and found that the synergistic effect reduced the gas yield and increased the coke and oil yields.¹³ Lu et al. investigated the effect of pine (PW) and plastic (PE and PVC) on coke and oil during copyrolysis.¹⁴ The results showed that, compared to the theoretical results, the oil yield under PW–PE copyrolysis is 3.7–4.4% higher, while that under PW–PVC is the opposite. In addition, the interaction between biomass and


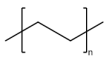
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Table 1. Structure and Composition of the Material

Material	WC	PP	PE
Component	Cellulose (60-70%) Hemicellulose (5-10%) Lignin (25-30%) ^{24, 25}		
Elemental analysis ^a (wt.%)			
C	39.3	85.2	84.3
H	5.9	13.7	14.1
O ^b	54.0	0.9	1.4
N	0.2	< 0.1	< 0.1
S	0.2	< 0.1	< 0.1
Proximate analysis ^a (wt.%)			
Volatile fraction	76.7	99.9	97.3
Moisture	7.4	-	-
Ash	6.4	0.1	0.1
Fixed Carbon ^b	9.5	0.1	2.6

^aDry basis. ^bCalculated by difference.

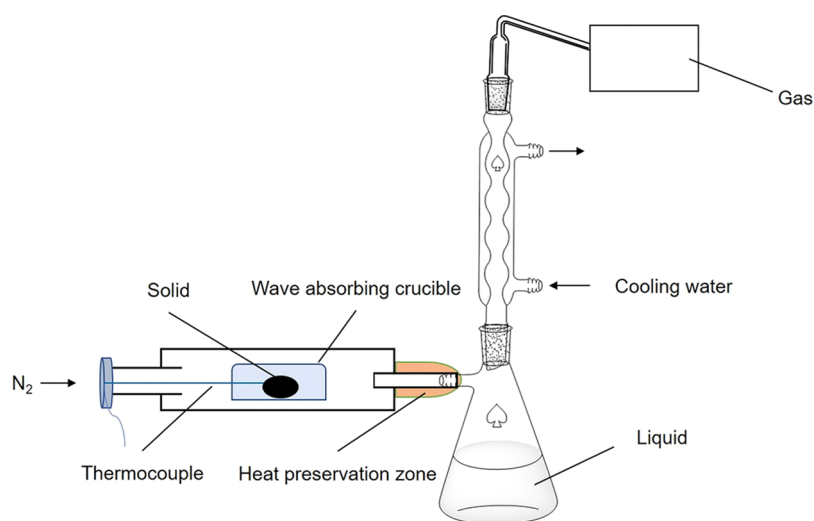


Figure 1. Microwave pyrolysis experimental setup.

plastic reduced the H/C atomic ratio of the semicoke and the O/C atomic ratio of the oil. Chen et al. studied the copyrolysis of old newspapers and polyethylene and found that the water content, total acid value, density, viscosity, and oxygen content of the oil were all lower than the theoretical values.¹⁵ However, waste cartons as a part of biomass-based resources are less studied, and the copyrolysis mechanism is not clear. This deficiency will be remedied by our best efforts.

The commonly used reactors for copyrolysis are currently fixed bed and fluidized bed.^{16,17} However, they have the disadvantage that heat is transferred from outside to inside and partial energy is lost in the heat transfer process, so the heating rate is also low.¹⁸ Microwaves generate heat through dielectric heating, and energy is transferred directly to the material through the interaction of molecules and electromagnetic fields, without wasting time heating the surrounding area.^{19,20} Compared with conventional heating, microwave heating has a higher heating rate, reducing the occurrence of secondary reactions.^{21,22} The microwave reactor also reduces the requirements for the shape and size of the feedstock.^{23–25} Therefore, the microwave reactor was used as the heat source in this study.

In this study, waste cartons and plastic bottles were subjected to microwave copyrolysis to investigate reaction laws and reaction products in copyrolysis. This study provides a reference for the development of clean and efficient waste treatment technologies.

2. EXPERIMENTAL SECTION

2.1. Materials. Waste cartons (WC) are used for courier packaging cartons and are mainly composed of cellulose and lignin; polypropylene (PP) and polyethylene (PE) both come from discarded plastic bottles. PP and PE plastic bottles were washed with water and dried naturally, and they were cut into squares of about 2 cm side length with scissors. The waste cartons were cut directly into squares of 2 cm side length. The structure and composition of the raw materials are shown in Table 1.

2.2. Microwave Pyrolysis Experiment. **2.2.1. Individual Pyrolysis Experiments.** The individual pyrolysis experiments of waste cartons were performed on the apparatus shown in Figure 1. The raw material with a mass of 4 g was raised to the set temperature (450, 500, and 550 °C) at a power of 400 W, then

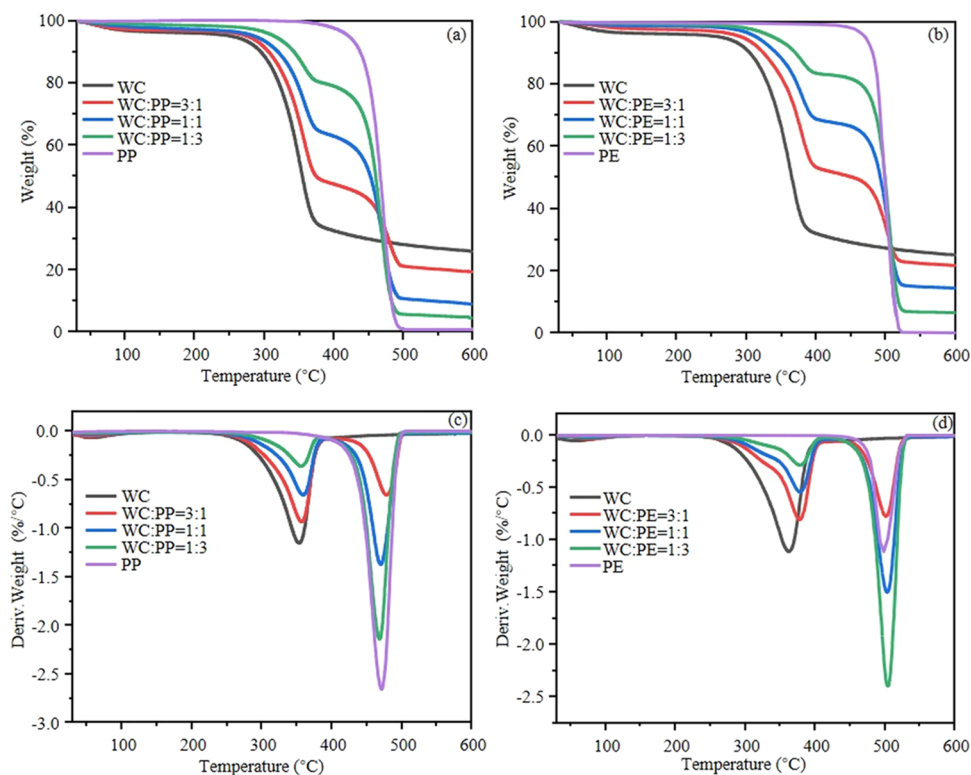


Figure 2. TG curves with different raw materials: (a) waste cartons and PP and (b) waste cartons and PE. DTG curves with different raw materials: (c) waste cartons and PP and (d) waste cartons and PE.

kept at a set temperature for 30 min, and finally dropped to ambient temperature naturally. The experimental conditions and procedures for PP and PE were consistent with those for waste cartons.

2.2.2. Copolyrolysis Experiments. Copolyrolysis experiments of waste cartons and PP were also carried out on the apparatus shown in Figure 1. The raw materials were the copolymer of waste cartons and PP in the ratios of 3:1, 1:1, and 1:3. The raw material with a mass of 4 g was raised to the set temperature (450, 500, and 550 °C) at a power of 400 W, then kept at the set temperature for 30 min, and finally dropped to ambient temperature naturally. The experimental methods and procedures for the copolyrolysis of waste cartons and PE were consistent with those for WC/PP.

2.3. Calculation Formula. The liquid product is condensed and collected in a conical flask, the gas is collected in a gas sampling bag, and the carbon solid is left in a wave absorbing crucible. The mass of liquid, gas, and solid is calculated by subtracting the difference, and the calculation formula is as follows

$$m_s = m_b - m_a \quad (1)$$

$$m_l = m_d - m_c \quad (2)$$

$$m_g = m_o - m_s - m_l \quad (3)$$

where m_s is the mass of the solid, m_a is the mass of the crucible, m_b is the sum of the masses of the crucible and the solid product after the reaction, m_l is the mass of the liquid product, m_c is the mass of the conical flask, m_d is the sum of the masses of the conical flask and the liquid product after the reaction, m_g is the mass of the gaseous product, and m_o is the quality of raw materials.

The yield of the product is calculated as follows

$$Y_s = \frac{m_s}{m_s + m_l + m_g} \quad (4)$$

$$Y_l = \frac{m_l}{m_s + m_l + m_g} \quad (5)$$

$$Y_g = \frac{m_g}{m_s + m_l + m_g} \quad (6)$$

where Y_s is the solid yield, Y_l is the liquid yield, and Y_g is the gas yield.

In this study, the effect of copolyrolysis on the yield and properties of the products was observed by calculating the difference between the experimental and theoretical values. The experimental value is obtained directly from the copolyrolysis experiment, and the theoretical value is calculated by the following equation

$$y = \alpha_1 \times \omega_1 + \alpha_2 \times \omega_2 \quad (7)$$

where α_1 and α_2 are the yields of each product from pyrolysis of biomass and plastic alone and ω_1 and ω_2 are the ratios of biomass and plastic to the total mass of raw materials, respectively, which follow the formula $\omega_1 + \omega_2 = 1$. Therefore, y is the product yield under theoretical conditions.²⁶

2.4. Characterization Methods. Waste cartons and PP were mixed in different ratios (1:0, 3:1, 1:1, 1:3, 0:1), and thermogravimetric analysis (TGA) was performed using a simultaneous Mettler–Toledo thermal analyzer. Under a N_2 atmosphere with a flow rate of 80 mL min^{-1} , the sample mass of 8–10 mg of raw materials was increased from 30 to 600 °C at a heating rate of 20 °C min^{-1} and then cooled down naturally. The TGA conditions for waste cartons and PE were the same as those for WC/PP.

The liquid was analyzed using the following methods: (1) the content of C, H, N, and S was analyzed using a Vario EL cube elemental analyzer with the detection method SN/T 3005-2011. (2) Fourier transform infrared (FT-IR) spectroscopy was performed using a Bruker Tensor II Fourier transform infrared spectrometer with a scan range of 4000–400 cm^{-1} , a resolution of 4 cm^{-1} , and 16 scans. (3) Gas chromatography–mass spectrometry (GC–MS) analysis was performed using an Agilent Model 6890 gas chromatograph with a column HP-5 and a carrier gas of helium at a split ratio of 50:1. The initial temperature of the column chamber was 35 $^{\circ}\text{C}$, maintained for 10 min and ramped up to 300 $^{\circ}\text{C}$ at 10 $^{\circ}\text{C min}^{-1}$. The mass spectra were identified by a NIST database with screening conditions match ≥ 800 .

The gas was chromatographed on an Agilent 7890 with argon as the carrier gas at a flow rate of 50 mL min^{-1} , using a TCD and FID with a detector temperature of 150 $^{\circ}\text{C}$.

The solid was analyzed for C, H, N, and S using a Vario EL cube type elemental analyzer. Fourier transform infrared (FT-IR) spectroscopy was performed using a Bruker Tensor II Fourier transform infrared spectrometer with a scan range of 4000–400 cm^{-1} , a resolution of 4 cm^{-1} , and 16 scans. Scanning electron microscopy (SEM) was used to characterize the morphology of the solids.

3. RESULTS AND DISCUSSION

3.1. Thermogravimetric Analysis. Thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG)

Table 2. Experimental and Theoretical Values of Solid Residues of WC/PP and WC/PE Blends in Thermogravimetric Analysis^a

material	content of solid residues (wt %)	
	Exp	The
waste carton (WC)	25.5	
PP	0	
PE	0	
WC/PP = 3:1	19.3	19.1
WC/PP = 1:1	9.1	12.8
WC/PP = 1:3	4.6	6.4
WC/PE = 3:1	20.7	19.1
WC/PE = 1:1	11.5	12.8
WC/PE = 1:3	5.7	6.4

^aExp: experimental yields under copyrolysis, The: theoretical yield under pyrolysis alone.

curves of different materials are shown in Figure 2. During single-material pyrolysis, the degradation of waste cartons is divided into three stages: moisture volatilization, rapid polymer degradation, and slow removal of light components. The rapid degradation of waste cartons occurs at 280–380 $^{\circ}\text{C}$, with a maximum decomposition rate at 350 $^{\circ}\text{C}$ and a residual of 25% at 600 $^{\circ}\text{C}$.²⁷ In contrast, there is only one process for the pyrolysis of PP and PE. PP is mainly degraded at 400–500 $^{\circ}\text{C}$, and the maximum decomposition rate is around 470 $^{\circ}\text{C}$; PE is decomposed at 450–520 $^{\circ}\text{C}$, and the maximum decomposition rate is 500 $^{\circ}\text{C}$. The weight loss is nearly 100%, which indicates that PP and PE can be completely pyrolyzed and converted without any coking products. Therefore, the solids of copyrolysis are all from waste cartons.

From Figure 2a,b, it can be seen that the addition of plastic reduced the yield of residues, which is mainly because the

pyrolysis process of plastic does not produce solids. Figure 2c,d shows that the degradation temperatures of plastic and waste cartons in copyrolysis do not change, which indicates that the pyrolysis processes of both are still relatively independent and may only change the reaction rate. Table 2 shows the experimental and theoretical values of the solid residue content in copyrolysis. It can be seen that the synergistic effect reduces the residue content compared to the theoretical value, the current explanation is that the free radicals from plastics triggering the fracture of the polymer in the biomass.²⁸ When the ratio of WC/PP is 1:3, the residue content is 2.8% less than the theoretical value. The effect of PP and PE on the waste carton is different. The residue content of the waste carton with PP in the ratio of 1:1 is 9.1% and the waste carton with PE is 11.5%. It can be seen that the residue content of waste cartons and PE is higher than that of WC/PP, which is due to the fact that PP containing branched chains has more reactive end groups, thus promoting the degradation of waste cartons.

3.2. Microwave Pyrolysis Product Yield. Figure 3 represents the yields of copyrolysis products, and it can be seen that the addition of plastic increased the liquid yield and decreased the solid yield. When the ratio of the waste carton and plastic was 3:1, the liquid yield was in the range of 45–50% and the solid yield was 20–25%; when the ratio was 1:3, the liquid yield was in the range of 65–70% and the solid yield was 8–10%. The synergistic effect was further analyzed by comparing the differences between experimental and theoretical values of product yields. The synergy is most favorable for liquids when the pyrolysis temperature of waste cartons and PP is 450 $^{\circ}\text{C}$, and the yield exceeds the theoretical value by 3–4%. This may be due to the fact that the long-chain hydrocarbons produced by plastics at lower temperatures inhibit the secondary degradation of polymers in waste cartons and hinder the release of gases, thus facilitating the formation of high-molecular-weight liquids.^{29,30} When the temperature rises to 550 $^{\circ}\text{C}$, the liquid yield is flat or even lower than the theoretical value, and the gas yield exceeds 3% of the theoretical value. This may be due to the fact that the small-molecule hydrocarbons produced by plastics at higher temperatures are more likely to induce ring-opening of glucose and bond breaking of long-chain oxygenated compounds, which are the reactions that accompany CO_2 and CO during the pyrolysis of waste cartons.³¹ PP and PE are completely converted to liquid and gas by pyrolysis. When the temperature is high enough to decompose the plastic material, the plastic does not increase the solid yield but decreases it due to the presence of the synergy. So, the positive synergistic effect of copyrolysis increases the yield of lighter products such as liquids or gases, prompting the conversion of more raw materials into liquids or gases. The copyrolysis of waste cartons and PE is basically the same as that of WC/PP. But, the pyrolysis temperature of PE is higher than that of PP, and PE cannot be completely degraded at 450 $^{\circ}\text{C}$ and partly left in the solid, so we need to increase the pyrolysis temperature to get a similar effect as WC/PP.

3.3. Analysis of the Liquid. Table 3 shows the compounds of the liquid determined by GC/MS; the compound content is also based only on the calculation of the peak area and not on the mass yield of the compound. We ignored some substances with small content, not easy to confirm. In addition, some long-chain hydrocarbons from PP and PE and oligomers from waste cartons, which are high-molecular-weight substances, could not be detected, so we only listed substances with high content and the type that can be accurately determined. As can be seen from

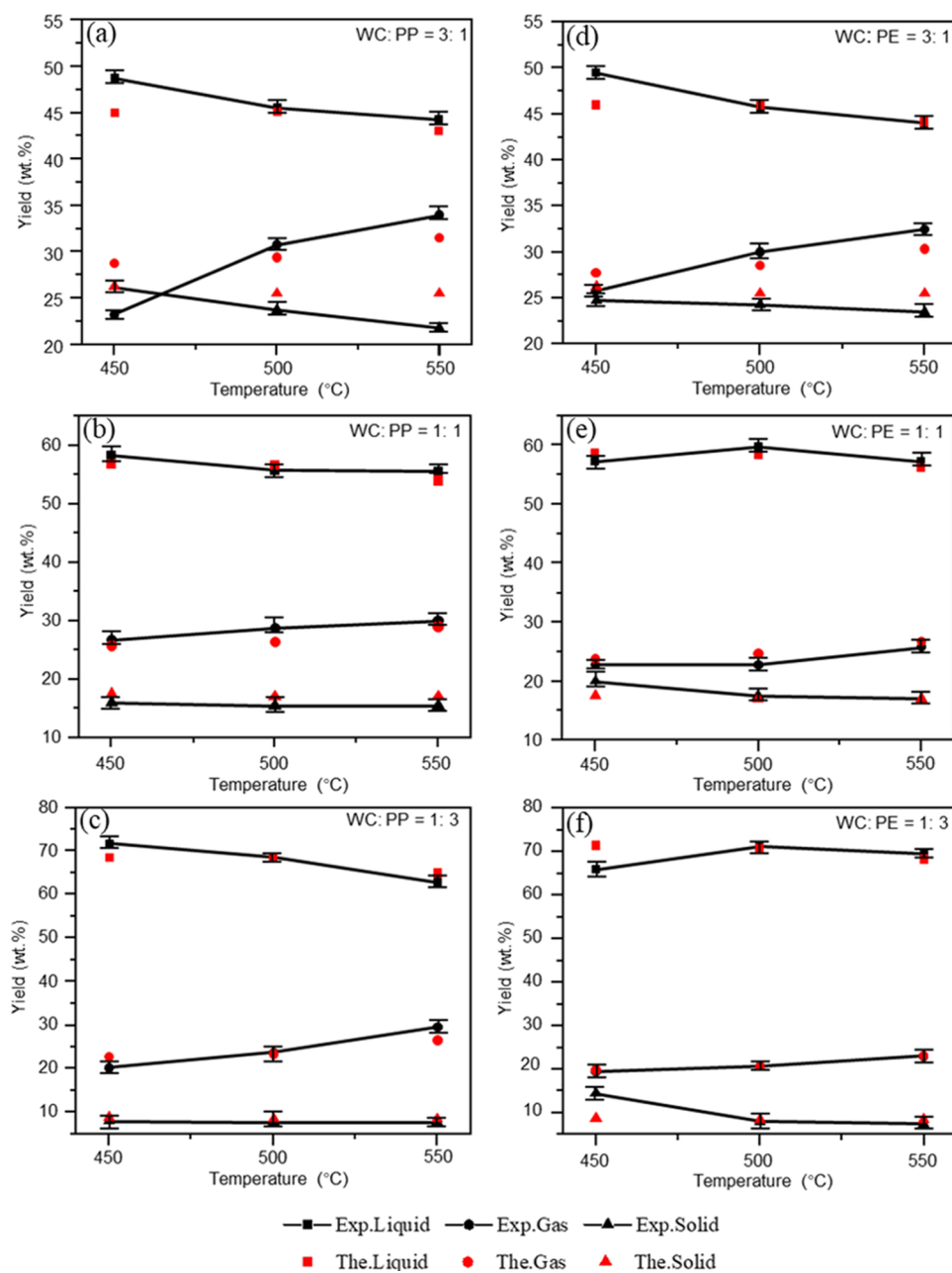


Figure 3. Product yields of waste cartons and plastics at different ratios: (a) WC/PP = 3:1, (b) WC/PP = 1:1, (c) WC/PP = 1:3, (d) WC/PE = 3:1, (e) WC/PE = 1:1, and (f) WC/PE = 1:3.

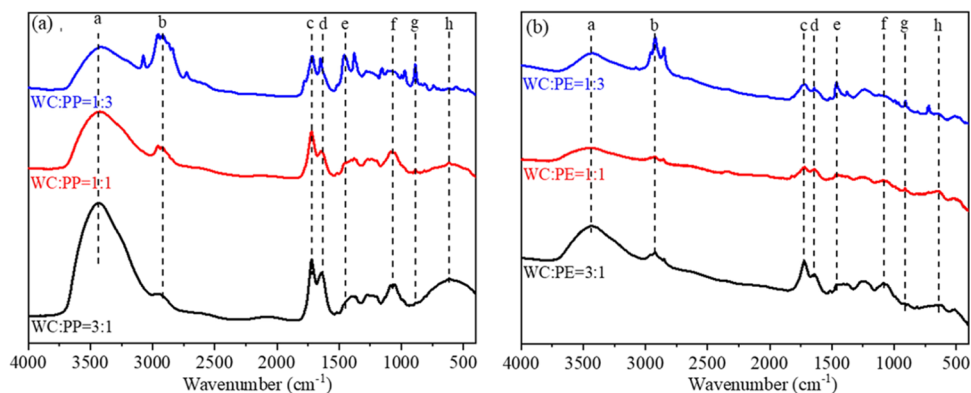


Figure 4. FT-IR spectra of pyrolysis liquids under different raw materials: (a) waste cartons and PP and (b) waste cartons and PE.

Table 3. Content of Components in Liquid Products under Different Materials at 450 °C^a

compound		content (%)				
name	molecular formula	WC	PP	PE	WC/PP = 1:1	WC/PE = 1:1
acetic acid	C ₂ H ₄ O ₂	7.5			3.2	2.6
propionic acid	C ₃ H ₆ O ₂	1.6			1.1	1.5
methyl formate	C ₂ H ₄ O ₂	1.1				0.6
hydroxyacetone	C ₃ H ₆ O ₂	7.4			5.4	3.6
hydroxyacetaldehyde	C ₂ H ₄ O ₂	4.4			2.4	4.2
1-hydroxy-2-butanone	C ₄ H ₈ O ₂	1.4				1.3
1-acetoxy-2-butanone	C ₆ H ₁₀ O ₃	4.5			3.4	3.6
2-cyclopentenone	C ₅ H ₆ O	0.7			0.3	
2-hydroxy-2-cyclopenten-1-one	C ₅ H ₆ O ₂	2.7			1.2	
methylcyclopentenolone	C ₆ H ₈ O ₂	3.2			2.2	2.6
ethylcyclopentenolone	C ₇ H ₁₀ O ₂	1.4			1.5	2
2,5-dimethoxytetrahydrofuran	C ₆ H ₁₂ O ₃	1.1				
5-methylfuranal	C ₆ H ₆ O ₂	1.9			1.8	1.3
5-hydroxymethyl-2-furaldehyde	C ₆ H ₆ O ₃	1.4			0.7	1.2
furfural	C ₅ H ₄ O ₂	0.6			0.6	
furfuryl alcohol	C ₅ H ₆ O ₂	1.0				0.5
phenol	C ₆ H ₆ O	0.3			0.2	
catechol	C ₆ H ₆ O ₂				0.8	
maltol	C ₆ H ₆ O ₃	1.6			0.6	1.4
1,4:3,6-dianhydro- α -D-glucopyranose	C ₆ H ₈ O ₄	2.0			1.0	0.8
L-glucose	C ₆ H ₈ O ₅	14.0			3.3	5.7
4-methyl-heptane	C ₈ H ₁₈		1.3			
2,4-dimethyl-1-heptene	C ₉ H ₁₈		19.6		4.8	
1,3,5-trimethylcyclohexane	C ₉ H ₁₈		2.1		0.4	
2-isopropyl-1-octene	C ₁₁ H ₂₂		2.2		0.6	
5-ethyl-1-nonene	C ₁₁ H ₂₂		7.3		3.3	
4,6,8-trimethyl-1-nonene	C ₁₂ H ₂₄		18.1		10.0	
nineteenth alkene	C ₁₉ H ₃₆		10.0		2.0	
1-pentadecene	C ₁₅ H ₃₀			4		
1-hexadecene	C ₁₆ H ₃₂			3.7		2.5
1-heptadecene	C ₁₇ H ₃₄			4.2		3.6
1-octadecene	C ₁₈ H ₃₆			4.2		4.5
1-nonadecene	C ₁₉ H ₃₈			4.8		2.4
1-eicosenal	C ₂₀ H ₄₀			4.6		2.8
1-heneicosene	C ₂₁ H ₄₂			5.0		3.8
1-docosene	C ₂₂ H ₄₄			4.6		3.7

^aThe content is the ratio of the peak area of each compound to the total area.

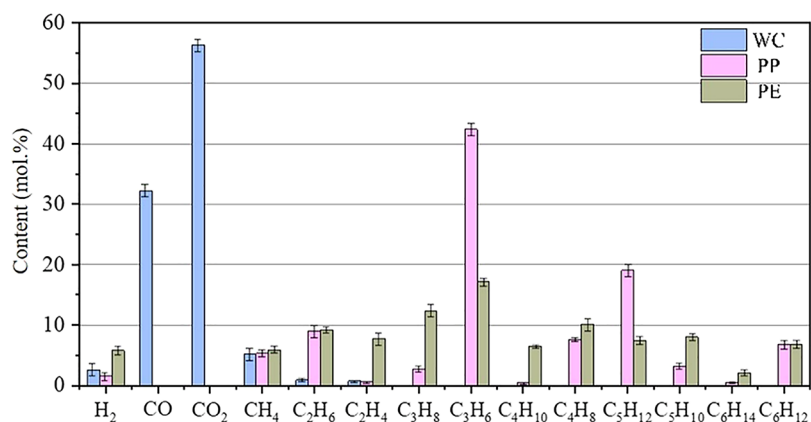


Figure 5. Content of each component in the gases of WC, PP, and PE pyrolyzed.

Table 3, the liquids of waste cartons were mainly dehydrated sugars, acids, aldehydes, ketones, and furans.³² The substances with higher content are L-glucose, acetic acid, hydroxyacetone, 1-acetoxy-2-butanone, and hydroxyacetaldehyde. The liquid

products of PP pyrolysis are unsaturated hydrocarbon homologues formed by random fracture of the polymer, and the main substances are olefins with carbon numbers between 10 and 20 such as 2,4-dimethyl-1-heptene, 4,6,8-trimethyl-1-

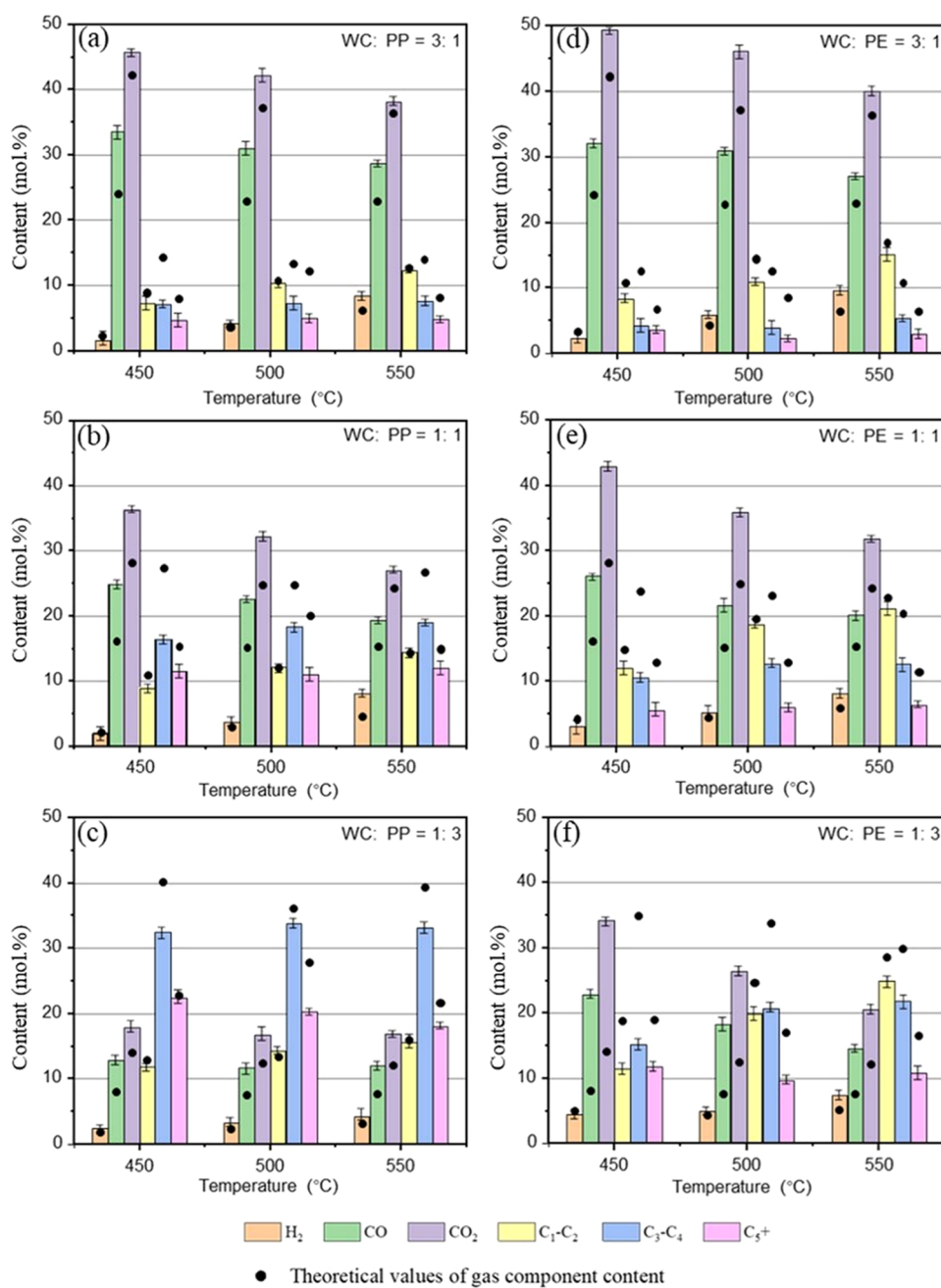


Figure 6. Pyrolysis gas of waste cartons and plastics at different ratios: (a) WC/PP = 3:1, (b) WC/PP = 1:1, (c) WC/PP = 1:3, (d) WC/PE = 3:1, (e) WC/PE = 1:1, and (f) WC/PE = 1:3.

Table 4. Elemental Content of Liquid Products

raw material	element composition (wt %)				
	C	H	O ^a	N	S
waste carton alone	25.5	9.2	65.3	<0.1	<0.1
	WC/PP				
3:1	80.0	12.8	6.8	<0.1	0.3
1:1	85.4	13.9	0.5	<0.1	0.1
1:3	85.6	14.0	0.3	<0.1	<0.1
	WC/PE				
3:1	68.2	11.8	19.8	0.1	<0.1
1:1	82.8	13.5	3.4	0.3	<0.1
1:3	84.8	14.0	0.9	0.2	<0.1

^aCalculated by difference.

Table 5. Elemental Analysis of Solid Products at 450 °C

raw material	element composition (wt %)					H/C (mole ratio)
	C	H	O	N	S	
waste carton alone	57.3	3.7	38.5	0.3	0.2	0.8
	WC/PP					
3:1	56.4	2.8	40.1	0.2	0.5	0.6
1:1	51.8	2.6	44.8	0.3	0.5	0.6
1:3	50.7	2.6	45.9	0.4	0.5	0.6
	WC/PE					
3:1	51.8	2.8	44.6	0.3	0.5	0.7
1:1	52.7	4.1	42.7	0.3	0.2	0.9
1:3	65.0	7.2	27.3	0.2	0.3	1.3

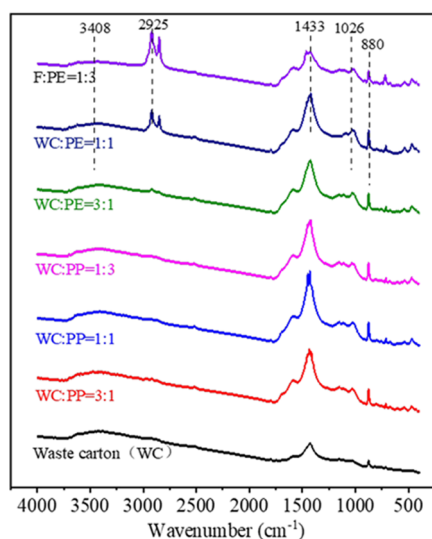


Figure 7. FT-IR spectra of the solid product at 450 °C.

nonene, and 1-nonadecene. The cleavage process of PE involves a series of random molecular chain breaks, consisting intramolecular and intermolecular hydrogen transfer and β -break. The main products are C_8 – C_{24} hydrocarbons, such as 1-nonadecene, 1-eicosenal, and 1-heneicosene.³³ However, the liquid product of PP with branched methyl groups contains a large number of branched chains with variable double bond positions, while the liquid product of PE is mainly straight chains with double bonds mainly at the end points of the chains. The copyrolysis liquid products are oxygenated compounds ($C \leq 6$) and olefins ($9 \leq C \leq 20$), most of which are consistent with the single pyrolysis of the two feedstocks. Several new phenolic substances (such as catechol) appeared in the copyrolysis liquid due to the fact that small olefinic molecules from plastics can form alkylbenzenes in the environment of the hydrocarbon pool.³⁴ However, the amount of benzene formed in this way is very small. So, there is few new products in the copyrolysis liquid, and the content is very small, which indicates that the main reaction pathway of feedstock degradation did not change.

FT-IR spectra of the copyrolysis liquid are shown in Figure 4. The liquid products of WC/PP and WC/PE possess similar infrared spectra. The absorption peak at 3440 cm^{-1} (peak a) is an O–H stretching vibration, indicating the presence of phenols and alcohols. The absorption peak at 2952 cm^{-1} (peak b) is the C–H stretching vibration in alkanes. The C=O stretching vibration in ketones is at 1720 cm^{-1} (peak c), and C=C in olefins is recorded from 1637 cm^{-1} (peak d). The bending vibration of the methylene group is at 1450 cm^{-1} (peak e) and comes from aliphatic hydrocarbons of plastics. The C–H bending vibrations in sugars are concentrated between 1450 cm^{-1} (peak e) and 1058 cm^{-1} (peak f).²⁸ The C–O extension bending in alcohols is at 1058 cm^{-1} (peak f) and the C–H bond in olefins is at 895 cm^{-1} (peak g). The presence of the peak at 605 cm^{-1} (peak h) indicates the presence of aromatic compounds. It can be seen that the liquid products at different ratios possess the same functional groups, with the main groups being O–H, C=O, and C–H. The oxygen-containing functional groups (peaks a, c, f, h) come from waste cartons, and the chemical bonds of alkanes and olefins (peaks b, e, d, g) mainly come from plastics.

Table 4 shows the elemental content of the liquid products. When the waste carton is pyrolyzed alone, the oxygen content is

65.3% and mainly from the moisture. The addition of PP provides enough C–H groups to reduce the oxygen content to less than 10%.¹² Since PE is not branched, pyrolysis is difficult to get more C–H into the liquid, so the O content of the liquid of the waste carton and PE is higher than that of WC/PP at the same mixing ratio. Under the condition of copyrolysis, the oxygen in the raw material mainly stays in the solid product or is released in the form of gas, so that the oxygen content in the liquid is reduced.

3.4. Analysis of Gas. Figure 5 shows the gas products of single pyrolysis of different raw materials at 450 °C. It can be seen that the gas products of the waste carton are CO_2 and CO, which mainly come from the carbonyl (–CO) and carboxyl (–COOH) groups that are removed in the process of generating small molecules.³⁵ The gas products of PP and PE are low-carbon alkanes and olefins, which mainly come from the random breakage and transfer of molecular chain radicals. In the gaseous products of PP, C_3H_6 , and C_5H_{12} content is higher than other components. PE generates a large number of end-group radicals by random fracture, and then, the probability of forming alkane or olefin radicals by β -fracture is equal, so a similar number of stable alkane and olefin compounds will be formed after combining with H radicals, resulting in a small difference in the content of various components of gas.³⁶

Figure 6 shows the content of gas components under copyrolysis. It can be seen that, when the ratio of the waste carton to plastic is 3:1, the sum of CO_2 and CO contents is in the range of 70–80%. When the ratio is 1:1, the sum of CO_2 and CO contents is in the range of 45–55%. The ratio of the waste carton to plastic pyrolysis gas content corresponds to the raw material ratio. We further analyzed the synergistic effect on the gas. Compared to the theoretical value, the CO_2 and CO content under copyrolysis increases by 5–15% and the hydrocarbon content decreases by 5–10%. This is because the hydrogen atom in the plastic are transferred to the biomass through free radical interactions, which promote biomass degradation and release CO_2 and CO but inhibit hydrocarbon gases.³⁷ When the temperature was increased from 450 to 550 °C, the difference between the experimental and theoretical values of the CO content decreased from 9 to 5% and that of CO_2 decreased from 5 to 2%, while the H_2 content increased 3% above the theoretical value. This is due to the fact that decarboxylation and decarbonization reactions are more likely to occur at low temperatures, while dehydrogenation reactions are more likely to occur at high temperatures.³⁸ Synergistic effects exist in both WC/PP and WC/PE copyrolysis, but the impact of PP and PE on waste cartons is quite different. At the same temperature and mixing ratio, the CO_2 and CO contents of WC/PP copyrolysis are about 5% lower than those of WC/PE, which is because PP with lower cracking activation energy is more likely to generate hydrocarbon gases, resulting in smaller CO_2 and CO contents.³³

3.5. Analysis of the Solid. Table 5 shows the elemental analysis of the solid at 450 °C. It can be seen that the elemental oxygen content of the waste carton at single pyrolysis is 38.5%, while the oxygen content under copyrolysis is higher than 40%. It indicates that copyrolysis increases the oxygen content in the solid and decreases the calorific value. H/C also decreased from 0.8 to 0.6, indicating that the hydrogen atoms in the solid product decreased, representing a decrease in volatile fraction in the solid.³⁹ Unlike waste cartons and PP, incomplete cracking of PE at 450 °C leaves some hydrocarbon molecules in the solids, so the oxygen content in the solids decreases and the hydrogen-to-carbon ratio increases.

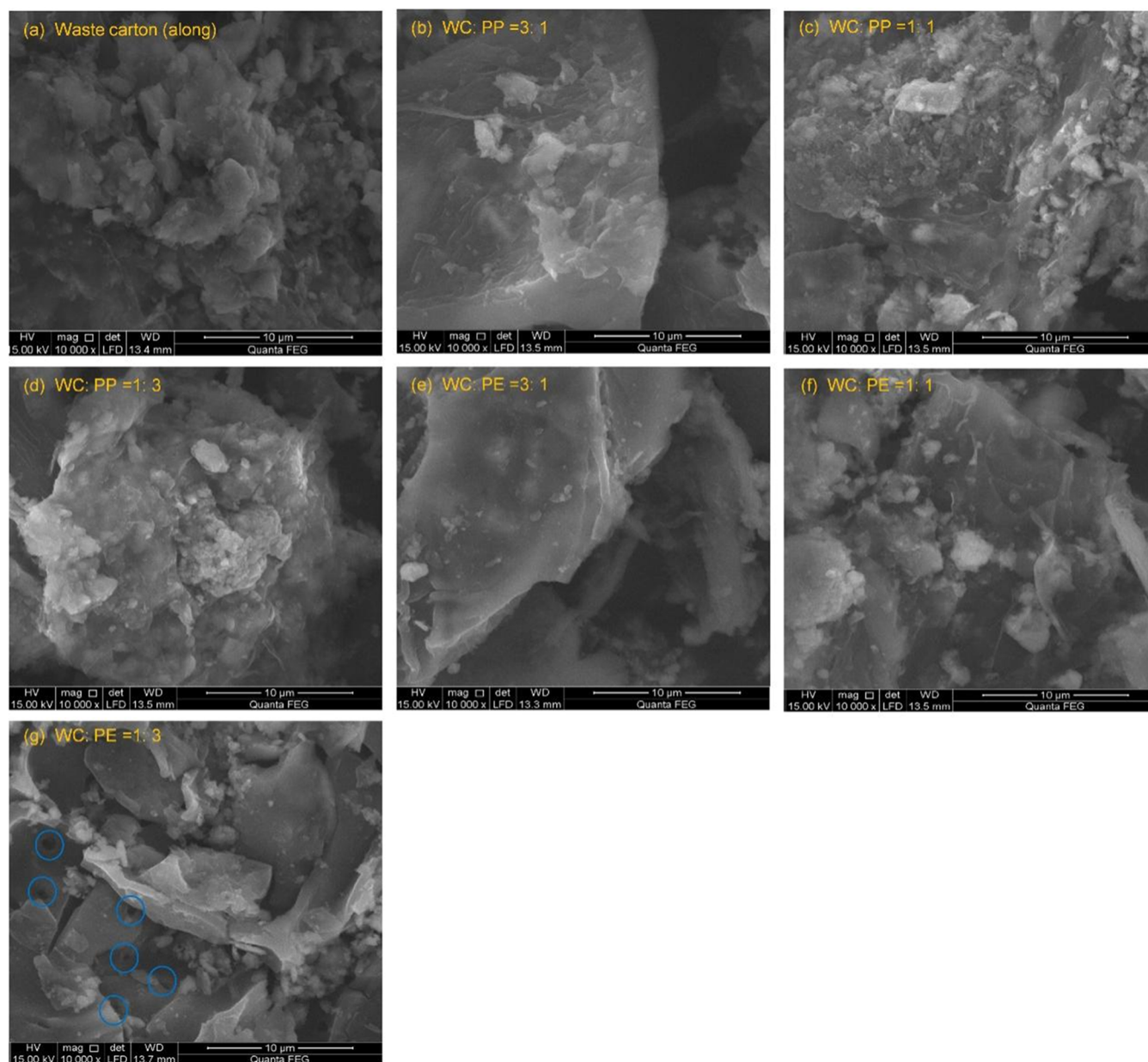


Figure 8. SEM analysis of pyrolysis solid products of different raw materials at 450 °C. (a) Separate pyrolysis of waste cartons. (b) WC/PP = 3:1. (c) WC/PP = 1:1. (d) WC/PP = 1:3. (e) WC/PE = 3:1. (f) WC/PE = 1:1. (g) WC/PE = 1:3.

FT-IR spectra of the solids are shown in Figure 7. All of the solid products possess the same peaks at 2000–500 cm^{-1} , such as C–H vibrations in aromatics at 880 cm^{-1} , C–O–C groups at 1026 cm^{-1} , and a C=C bond on the benzene ring at 1433 cm^{-1} , which indicates that the solid product has a highly aromatic structure with fewer alkyl groups of aliphatic compounds. In the range of 4000–2000 cm^{-1} , the presence of 3408 cm^{-1} peak indicates the presence of O–H groups, suggesting that oxygen is still mainly present in the form of hydroxyl groups. The 2925 cm^{-1} peak is the C–H group on saturated alkanes, which is caused by PE that is not completely reacted off. FT-IR analysis showed that the C=C bond on the benzene ring was the strongest, and the copyrolyzed solid had the same functional groups as the pyrolysis alone.

Figure 8 shows SEM analysis of copyrolysis solid products at 450 °C. When the waste carton is pyrolyzed alone, residual carbon particles and inorganic minerals that are difficult to

remove are left in the solid and collect during the interaction, which form a product with larger particles so that the surface is a number of unevenly distributed and aggregated masses (Figure 8a). The addition of PP and PE provides more H radicals, which promotes the decomposition of the carbon-containing substrates of the solid, resulting in a reduced number of particles and a flatter and smoother surface (Figure 8b,e).^{39,40} When the content of plastic increases, PP and PE in the molten state may cover the waste carton, resulting in uneven heating and some small particles on the solid surface (Figure 8c,f).¹⁴ It is noted that some micropores appear on the solid surface at the ratio of 1:3 of the waste carton to PE, while PP does not (Figure 8d,g), which may be related to the absence of straight chains in the liquid product of PE.^{39,41} At this time, the PE with a higher pyrolysis temperature still has some parts left in the solid product, which forms some small pores under the interaction and increases the specific surface area.

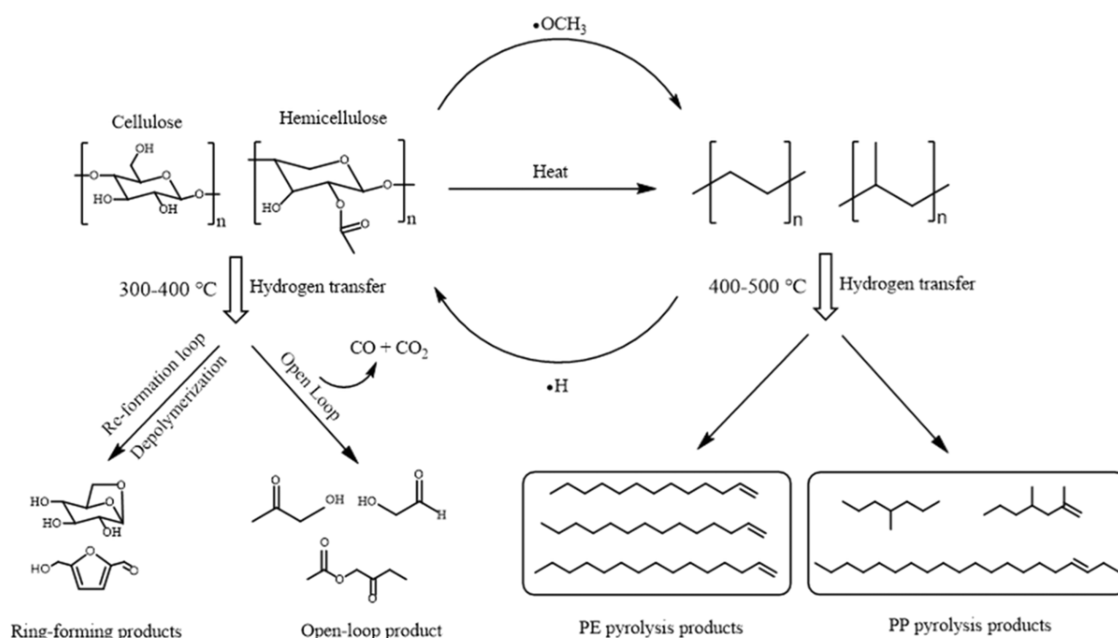


Figure 9. Interaction mechanism of the copyrolysis of waste cartons and polyolefin plastics.

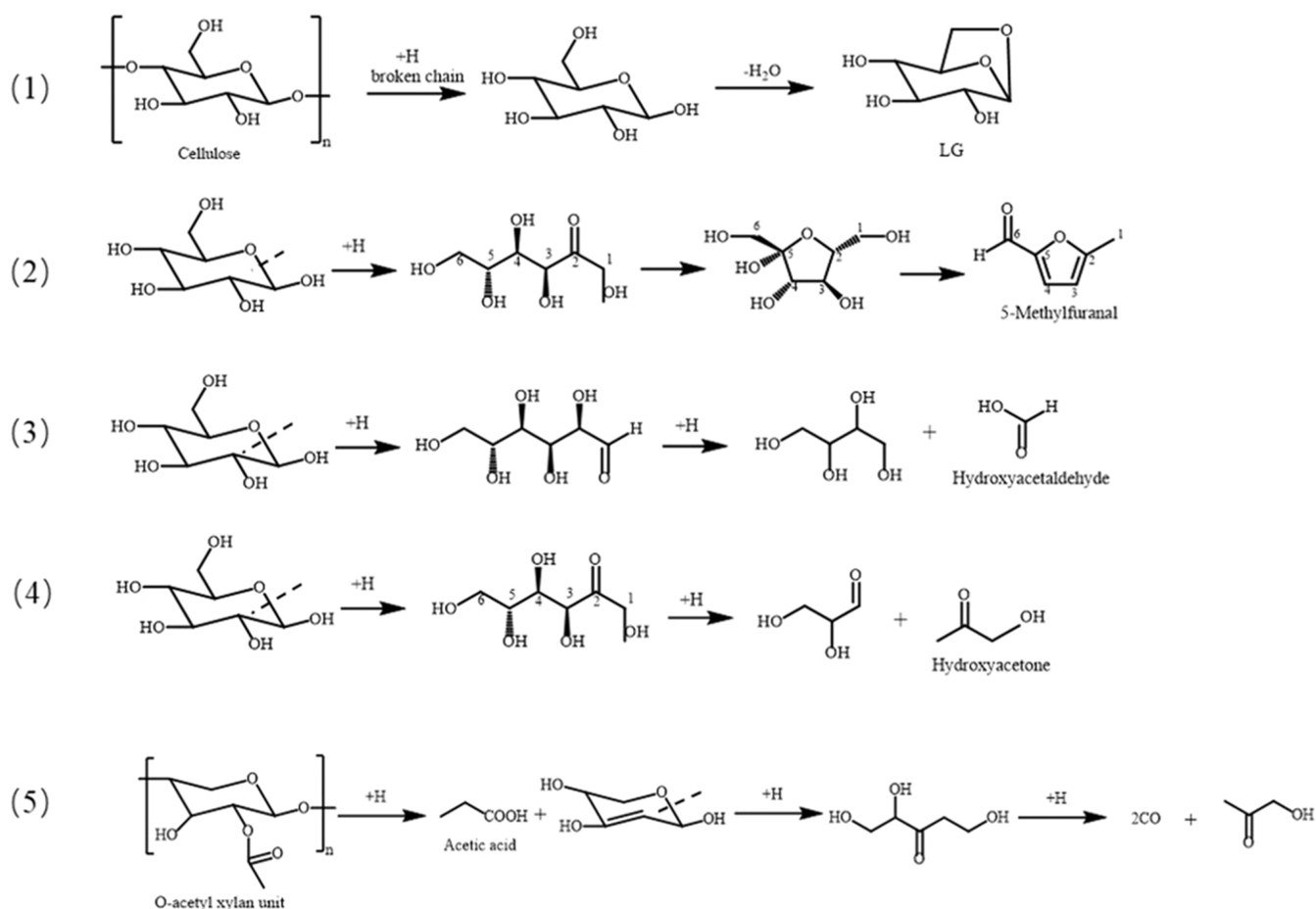


Figure 10. Main reaction formula of cellulose pyrolysis.

3.6. Mode of Action of Copyrolysis. The synergy of copyrolysis is the result of multifaceted interactions. In terms of heat transfer, waste cartons and plastics are two different substances, so their pyrolysis temperatures are not the same. The

waste carton is generally cracked at 300–400 °C, while PP and PE are between 400 and 500 °C, so there is heat transfer in the copyrolysis process. Under microwave heating, waste cartons are first heated rapidly and reach the pyrolysis temperature, and this

process is the heat absorption process. Lignin is an aromatic polymer compound, and its degradation process at a high temperature is exothermic. Therefore, the degradation of lignin may provide energy for the degradation of plastics.^{42,43}

In the exploration of the mechanism of copyrolysis, the mechanism of a free radical reaction is currently agreed upon, so the degradation of polymers also includes chain initiation, chain growth, and chain termination processes, and the mechanism of copyrolysis is shown in Figure 9.⁴⁴ First of all, cellulose and hemicellulose containing a large number of hydroxyl groups undergo H-transfer, rearrangement, and bond breaking processes during degradation. Some methoxy radicals are generated during these processes, which can be proved by the presence of a large number of small molecules of aldehydes and ketones in the liquid and the C–O bonds in the infrared spectrum. Moreover, both guaiacyl (G) and syringyl (S), which are the basic building blocks in lignin, contain methoxy.^{45–47} Methoxy without the push electron attached to the benzene ring attracts positively charged groups. The presence of methoxy attracts the hydrogen atoms on PP and PE, thus accelerating the degradation of plastics. Plastics randomly break C–C and C–H bonds, generating hydrocarbon and H radicals of different carbon numbers. H radicals can act as reactive groups for polymer degradation, while biomass, a strong hydrogen acceptor, can accept hydrogen radicals generated by plastics. It can be seen in Figure 10 that hydrogen-free radicals can promote the formation of L-glucose, furan, and molecular aldehydes and ketones and play an important role in the whole pyrolysis process of cellulose, so the H-free radicals provided by polyolefin plastics accelerate the degradation rate of waste cartons.^{48,49} On the other hand, the ring-opening reaction of oligosaccharides is an important process, which generates a large number of small molecules while removing carbonyl and carboxyl groups from the moiety in the form of CO₂ and CO. Hydrogen radicals accelerate the chain initiation and chain transfer processes in the ring-opening reaction, resulting in higher liquid yields and the release of more CO₂ and CO, as confirmed by gas analysis.^{50,51}

4. CONCLUSIONS

We explored the copyrolysis of waste cartons and plastic bottles (PP and PE) in a microwave reactor and analyzed the product composition and tried to explain the reaction mechanism of copyrolysis. The following research conclusions were obtained:

- (1) In copyrolysis, the addition of plastics increases the liquid yield and decreases the solid yield. The synergistic effect makes the experimental value of liquid yield higher than the theoretical value, thus producing more liquid. The synergistic effect at the copyrolysis temperature of 450 °C was best for the liquid yield, which was 48.75% at this time, 3.75% higher than the theoretical value.
- (2) Copyrolysis did not change the main composition of the liquid, with few new products, but reduced the oxygen content of the liquid from 65% to less than 8%, reducing acidity and increasing the calorific value. The synergistic effect increased the CO₂ and CO contents by 5–15% over the theoretical values. In the case of complete pyrolysis of plastic, the synergy reduced the carbon content of the solid by about 5% and increased the oxygen content by about 5%, and small shallow pores were formed on the surface of the solid from the waste carton/PE copyrolysis.
- (3) It is speculated that, in the early stage of pyrolysis, waste cartons and plastics in copyrolysis are interacting with

each other. First, the large amount of methoxy produced by cellulose and hemicellulose also promotes the C–H bond breaking of plastics, thus accelerating the degradation of polyolefin plastics. Biomass is a strong hydrogen acceptor, and the H radicals generated by plastic bond breaking in turn promote the chain initiation and chain transfer processes in the degradation pathway of waste cartons.

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Notes

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