

Copyrolysis of block polypropylene with waste wood chip

Mi-Jin Jeon*, Suek Joo Choi*, Kyung-Seun Yoo**, Changkook Ryu***, Sung Hoon Park****,
Jong Min Lee*****, Jong-Ki Jeon*****, Young-Kwon Park*****†, and Seungdo Kim*****

*Graduate School of Energy and Environmental System Engineering, University of Seoul, Seoul 130-743, Korea

**Department of Environmental Engineering, Kwangwoon University, Seoul 139-701, Korea

***School of Mechanical Engineering, Sungkyunkwan University, Suwon 440-746, Korea

****Department of Environmental Engineering, Suncheon National University, Suncheon 540-742, Korea

*****Power Generation Lab., Korea Electric Power Research Institute, Daejeon 305-380, Korea

*****Department of Chemical Engineering, Kongju National University, Cheonan 331-717, Korea

*****School of Environmental Engineering, University of Seoul, Seoul 130-743, Korea

*****Department of Environmental Sciences and Biotechnology, Hallym University, Chuncheon 200-702, Korea

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Abstract—In this study, the copyrolysis of waste wood chip (WC) and block polypropylene (PP) was studied to investigate how the characteristics of bio-oils are affected by copyrolysis. The thermogravimetric analysis performed with a temperature rise of 20 °C/min, from room temperature to 600 °C, showed that the decomposition temperature of PP was a little higher via copyrolysis than the single-component pyrolysis. This result suggests that the characteristics of the pyrolysis of PP were affected by the pyrolysis products of WC. The Py-GC/MS analysis of the copyrolysis products detected some new compounds that had not been detected in the single-component pyrolysis products, indicating interactions between the products of WC and PP pyrolyses. The results of the experiments using a fixed bed reactor showed improved properties of the bio-oil obtained from the copyrolysis compared to those of the bio-oil obtained from the single-component pyrolysis: increased carbon and hydrogen contents, decreased water content and a significantly increased heating value.

Key words: Copyrolysis, Waste Wood Chip, Block Polypropylene, Interaction, Bio-oil

INTRODUCTION

Global air pollution, resulting from increasing fossil energy consumption, and the energy supply crisis, due to imminent exhaustion of fossil fuel, call for the development of alternative renewable energy sources. Biomass, which uses solar energy, is an energy storage material that is inherently similar to fossil fuels, in that it is a mixture of carbon compounds produced by fixation of carbon dioxide, the most important global warming component. Biomass is an abundant resource widely distributed all over the world. It has two important merits over fossil fuels: its security of supply and the reduction of global warming. Biomass is also advantageous over other renewable energy sources in that it can play a role not only as an energy source, but also as a raw material source for the chemical industry.

There are a number of ways of converting biomass to energy, of which thermochemical methods have received much attention of many researchers. Pyrolysis, a representative thermochemical method for the conversion of biomass, which aims to maximize the yield of liquid products, such as bio-oil, can be applied to a variety of biomasses, including wood, miscanthus purpurascens, herbs, wastewater sludge, and agricultural, forest and municipal wood wastes [1-14]. In particular, municipal wood waste is composed of various components, such as wood chip, particle board and MDF.

The stability as a fuel of bio-oil produced from pyrolysis of biomass is often too low due to the high fractions of water and oxygen; therefore, methods of increasing the energy value of pyrolysis-produced bio-oil are required. Plastics have a higher hydrogen fraction than biomass, and its pyrolysis produces bio-oil with lower water content. In this regard, the copyrolysis of biomass and plastic can enhance the stability of bio-oil as a fuel, as plastic can provide the hydrogen that the biomass lacks. Despite their high potential as renewable energy sources, waste plastics have been discarded, which has caused many social problems. Therefore, the copyrolysis of waste plastics and biomass has important implications.

Several studies on the copyrolysis of biomass and plastics have been conducted [15-21]. The use of municipal wood waste, including wood chip, particle board and MDF, however, has never been considered in previous copyrolysis studies. In particular, research using waste wood chip is important because it is a standardized fuel. In this study, the copyrolysis of wood chip (WC), a representative municipal wood waste, and block polypropylene (PP), a representative plastic material, was studied to investigate the characteristics of the bio-oils produced.

EXPERIMENTAL

1. Materials

The raw materials used in this study were waste WC and block PP. Before the experiments, the WC was dried for 24 hours at 110 °C and then sieved, with only chips 0.6-1.0 mm in size used. The size

†To whom correspondence should be addressed.
E-mail: catalica@uos.ac.kr

of the PP used in the experiments was less than 500 μm . The WC : PP ratio of the mixture was 1 : 1.

Proximate analyses of the samples were performed based on ASTM methods E871, E872-82 and D1102-84. The moisture was evaporated in an oven at 110 $^{\circ}\text{C}$ for 4 hours. The volatile matter was removed in a furnace, using an inert atmosphere, at 950 $^{\circ}\text{C}$ for 7 minutes. The ash content was then measured by burning the combustible matter in air at 600 $^{\circ}\text{C}$.

The C, H, N and S contents of the samples were determined using

Table 1. Proximate analysis of waste biomass

	WC (wt%)	PP (wt%)
Water	9.5	
Volatile matter	74.8	100.0
Fixed carbon	14.6	
Ash	1.1	

Table 2. Ultimate analysis and higher heating value of waste biomass

		WC	PP
Ultimate analysis (wt%)	C	50.1	85.4
	H	5.7	14.6
	O ^a	44.0	-
	N	0.1	-
	S	-	-
HHV ^b (MJ/kg)		18.2	49.4

^aBy difference

^bCalculated

a Vario-EL III analyzer (Elementar Analysensysteme GmbH), which can burn up to 2 mg of sample at 1,150 $^{\circ}\text{C}$, using a sulfanilic acid standard, with the oxygen content calculated by difference. The higher heating value (HHV) of the samples was then estimated from the elemental composition, using the Dulong equation.

The results of the proximate and ultimate analyses for the WC and PP are shown in Tables 1 and 2.

2. TGA

A thermogravimetric analyzer (Perkin Elmer Pyris 1 TGA, USA) was used to characterize the coprolysis. About 10 mg of sample was pyrolyzed, under 30 ml/min of N₂ flow conditions, by increasing the temperature, at a rate of 20 $^{\circ}\text{C}/\text{min}$, from room temperature to 600 $^{\circ}\text{C}$. The precision of the weight and temperature measurements was $\pm 0.001\%$ and $\pm 2^{\circ}\text{C}$, respectively. The temperature was maintained at a constant value for five minutes before each analysis. Each analysis was repeated at least three times to obtain an average result. In this paper, the reduction in weight due to the temperature rise is represented by TG, while the rate of weight reduction is represented by DTG.

3. Fixed Bed Reaction

Pyrolysis tests were carried out in a fixed bed reactor, as shown in Fig. 1. A quartz U-tube reactor, with an internal volume of 50 ml, height of 160 mm and diameter of 15 mm, was filled with 8 g of WC sample and purged with nitrogen at a flow rate of 50 ml/min, for 15 minutes. The reactor was then inserted into the furnace, at prescribed temperatures of 400, 500 and 600 $^{\circ}\text{C}$, and kept at the specified temperature for 1 hour in order for the pyrolysis reactions to be completed. The pyrolyses of the PP and WC/PP mixture were also carried out at 500 $^{\circ}\text{C}$. The vapor-phase products produced during the pyrolysis were passed through a condenser (RW 1025G, JEIO TECH) at -20°C , using ethanol as the coolant, for collection of the bio-oil.

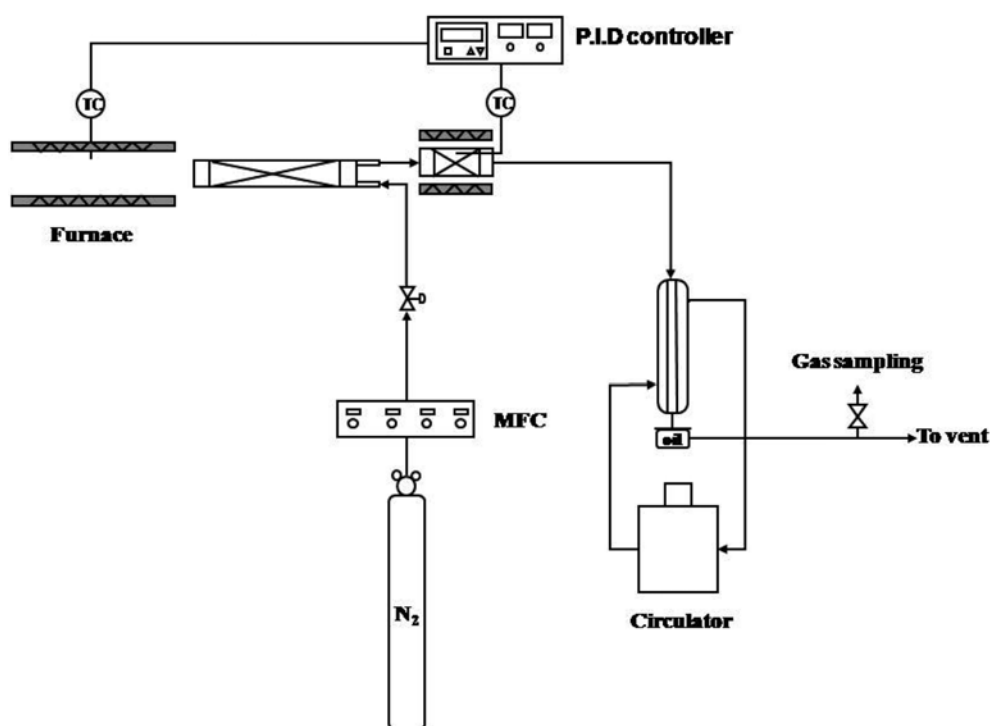


Fig. 1. Schematic of pyrolysis reactor.

4. Py-GC/MS Analysis

A double-shot pyrolyzer (Frontier-Lab Co., Py-2020iD), coupled directly to GC/MS, was used to identify the pyrolysis products of the WC, PP and mixture of WC and PP. The detailed experimental procedures have been described in our previous study [22].

RESULTS AND DISCUSSION

1. TGA

The TGA/DTG curves of the WC and PP are shown in Fig. 2. The reduction in the sample weight as a result of the rising temperature is clearly shown, in that WC begins to be decomposed at about 210 °C; whereas, decomposition of the block PP begins at a higher temperature of 350 °C.

The reduction in the weight of WC took place mainly at the temperature range 230 to 400 °C via rapid devolatilization. Above 400 °C, the pyrolysis was almost complete, and rate of weight reduction remained slow. For the pyrolysis of wood, which has a high fraction of fixed carbon of about 15% (Table 1), the fraction of the carbon residue in the product was generally high compared to that of the PP. The chemical bonds in plastic materials, such as PP, are broken at a higher temperature. Therefore, the pyrolysis of PP would begin, to a large extent, after that of WC has finished. The fraction of carbon residue of with the pyrolysis of PP was much lower than that of

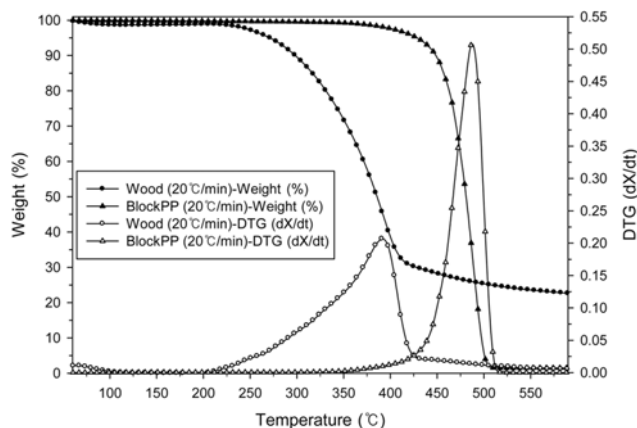


Fig. 2. TGA/DTG curves of WC and PP.

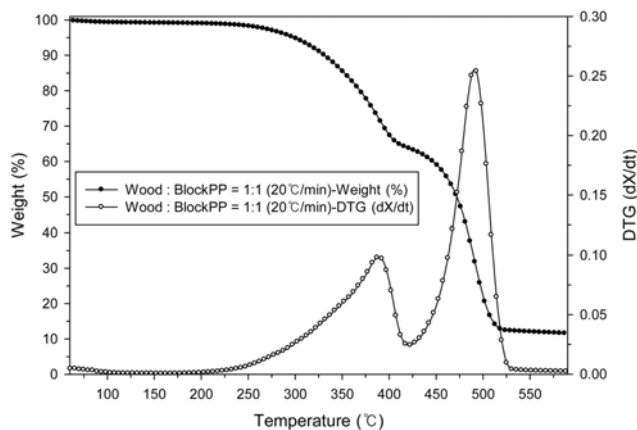


Fig. 3. TGA/DTG curves of mixture of WC and PP.

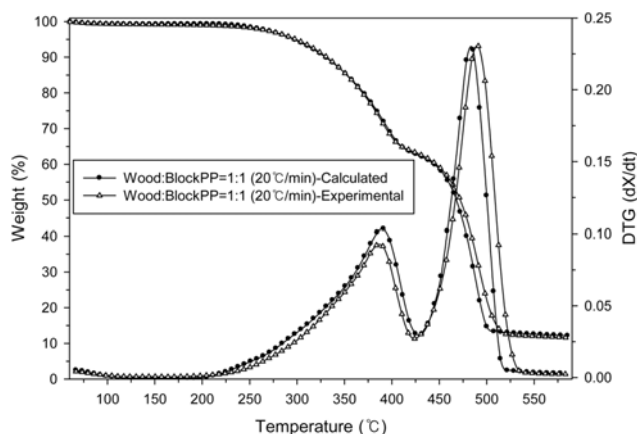


Fig. 4. Calculated and experimental TGA/DTG curves of mixture of WC and PP.

WC. As shown in Fig. 2, the WC and PP have distinct DTG evolution profiles. The DTG curve of the WC has a peak at a relatively low temperature of about 380 °C; whereas, that of the PP has a peak at a much higher temperature of about 490 °C, as a result of its high activation energy.

Fig. 3 shows the TGA/DTG curves of the mixture of WC and PP. As shown in Fig. 2, the rapid weight reduction at low temperature (<400 °C) was the result of the decomposition of WC, while the rapid weight reduction at high temperature (>400 °C) was due to the decomposition of the PP. The DTG curve of the copyrolysis of WC/PP shows two distinct peaks: one due to the decomposition of biomass, which appeared at the lower temperature, and the other due to the decomposition of plastic, with devolatilization appearing at the higher temperature.

To find if there was any interaction between WC and PP during their pyrolysis, the theoretical and experimental TGA/DTG curves for the copyrolysis of WC/PP were compared (Fig. 4). In this figure, “theoretical” refers to an ideal combination of pyrolyses of two components, where the pyrolysis of each component is assumed not to interfere with another. The theoretical TGA curve for the copyrolysis was obtained by applying the following equation to the reduction in weight of the mixture:

$$W_{SUM} = X_1 W_{WC} + X_2 W_{PP}$$

where W_{WC} and W_{PP} are the reductions in the weights of the single-component pyrolyses of WC and PP, respectively, and X_1 and X_2 the mass fractions of WC and PP in the copyrolyzed mixture.

Also, the theoretical DTG curve for the copyrolysis was obtained by using the following equation:

$$dX/dt_{SUM} = X_1 dX/dt_{WC} + X_2 dX/dt_{PP}$$

where dX/dt_{WC} and dX/dt_{PP} are the differential rate of conversion of the single-component pyrolyses of WC and PP, respectively.

Compared to the theoretical curve, a shift to the right was observed in the experimental weight reduction curve within the PP decomposition temperature range shown in Fig. 4. This suggests that the presence of WC might have influenced the pyrolysis of the PP. A similar result was shown in the DTG curve: the temperature at which the WC decomposition peak appeared was little changed, while that

for the PP was shifted noticeably to the right.

From the DTG curves in Figs. 2 and 3, the WC and PP decomposition peaks were observed to overlap at around 420 °C. Therefore, it is possible that the WC decomposed at a low temperature to produce char and gases, which then react with PP. In their paper on the copyrolysis of olive residue and PP, Aboulkas et al. [15] suggested that the char and gases produced by the decomposition of biomass could cause solid-solid or solid-gas interactions with the PP decomposition products. They argued that the char acted as a thermal stabilizer for PP, increasing its decomposition temperature. Based on their argument, the char and gases produced by the decomposition of biomass could cause solid (PP)-solid (WCs char) or solid (PP)-gas (gases from WC) interactions with the PP decomposition products. Especially, the char from WC acts as a thermal stabilizer for PP, increasing its decomposition temperature compared to the single-component pyrolysis of PP. Jakab et al. [16] reported that the char produced from biomass increased the thermal decomposition temperature of polyethylene, which they attributed to the effect of the char on the radical decomposition of polyethylene. Fraga et al. [17] also reported an increase in the thermal stability due to solid-solid and gas-solid interactions in the copyrolysis of poly(3-hydroxybutyrate-8%-3-hydroxyvalerate) and cellulose derivatives.

2. Py-GC/MS

In the characterization of copyrolysis using TGA, the successive pyrolysis of each component makes it difficult to observe the characteristics of copyrolysis. To investigate the effect of copyrolysis, an analysis of the product species resulting from the interaction be-

tween the biomass and plastic has to be performed. The existence of any species not detected in the products from single-component pyrolyses, but detected in the copyrolysis product, indicates the existence of a cross reaction due to the interaction between the biomass and plastic. Dong et al. [18] discovered interactions between the volatile components in the copyrolysis process. Sharypov et al. [19,20] proposed that the interactions between fragments of the biomass and polymers were responsible for changing the composition of the liquid products.

To see if new compounds were produced via the copyrolysis in this study, Py-GC/MS was used for a compositional analysis, the results of which are summarized in Table 3. It was observed that some new compounds not detected in the single-component pyrolysis, such as 1-decene, 4-hydroxy-3-methoxy benzoic acid, and 4-methoxy-4', 5'-methylenedioxybiphenyl-2-carboxylic acid, were detected in the copyrolysis products. Conversely, some of the species detected in the single-component pyrolyses products of WC and PP were not detected in the copyrolysis products, confirming that there was interaction between the WC and PP.

3. Pyrolysis Experiments Using a Fixed Bed Reactor

Fig. 5 shows the results of the pyrolyses of the WC, using a fixed bed reactor, at 450, 500 and 550 °C. From the TGA results, the pyrolysis of the WC began at about 210 °C and was almost complete at about 400 °C. In the fixed bed reactor experiments, however, the bio-oil yield was highest at 500 °C, as is shown in Fig. 5. Therefore, the copyrolysis experiments using the WC and PP were conducted at 500 °C. Each experiment was conducted for one hour to ensure the reaction was complete.

The characteristics of bio-oils obtained through the pyrolysis experiments are summarized in Table 4. Generally, a high oxygen fraction and high water content are regarded as shortcomings of bio-oils. In the copyrolysis of the WC and PP, however, the oxygen fraction and water content in the oil were significantly reduced, which can be attributed to the influence of the PP. In particular, the heating value was shown to be much higher, 45 MJ/kg, which is close to that of pure PP, 49 MJ/kg. This result demonstrated the importance of the role of PP as a hydrogen provider. The yields of oil from PP and WC were 82.6 wt% and 56.6 wt%, respectively. Compared to

Table 3. Selected compounds after pyrolysis of WC, PP and mixture of WC and PP

Compound	WC	PP	WC+PP
Pentane		○	○
1-Pentene, 2-methyl-		○	○
Acetic acid	○		
2,4-Dimethyl 1,4-pentadiene		○	
2-Propanone, 1-hydroxy-	○		
1-Heptene, 2-methyl-		○	
2(5H)-Furanone	○		
2-Cyclopenten-1-one, 2-hydroxy-	○		○
Phenol	○		
1-Decene			○
Nonane, 2,6-dimethyl-		○	
Phenol, 4-methyl-	○		
1-Undecene	○	○	
2-Furancarboxaldehyde, 5-(hydroxymethyl)-	○		
Homovanillyl alcohol	○		
Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	○		○
Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	○		
Benzoic acid, 4-hydroxy-3-methoxy-			○
4-Hydroxy-2-methoxycinnamaldehyde	○		
3-Ethyl-4-octan		○	
4-Methoxy-4',5'-methylenedioxybiphenyl-			○
2-Carboxylic acid			○

○: A compound present after pyrolysis

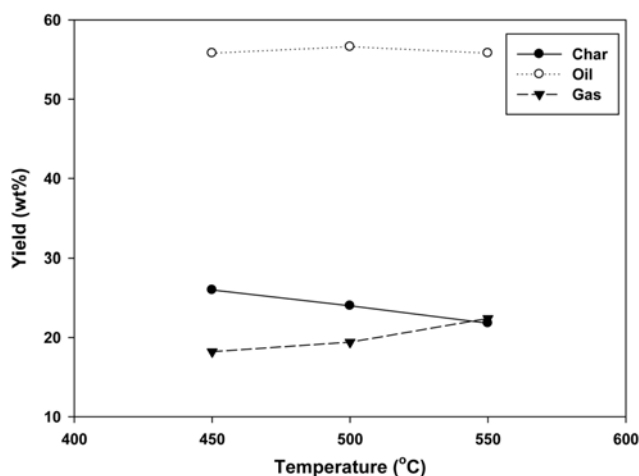


Fig. 5. Product distribution of pyrolysis of wood chip with temperature.

Table 4. Properties of bio-oils produced from pyrolysis of WC and copyrolysis of WC/PP at 500 °C^a

	Pyrolysis	Copyrolysis (1 : 1)
Yield of water-free bio-oil (wt%)	39.3	63.1
Elemental composition (wt%)		
C	48.9	76.6
H	7.2	12.6
O ^b	42.3	10.9
N	1.6	0.0
S	-	-
Water in bio-oil (wt%)	30.5	6.9
HHV ^c (MJ/kg)	19.9	45.0

^aDry basis

^bBy difference

^cBy calculated

the single-component pyrolyses, the copyrolysis resulted in increased oil content. The yield of water-free bio-oil obtained from the copyrolysis of the 1 : 1 mixture of WC/PP was 63.1 wt%; whereas, the theoretical water-free bio-oil yield, under the assumption that the WC and PP did not interact, was 61.0 wt%. When the weight ratio of WC/PP was increased to 1 : 3, the yield of water-free bio-oil was increased even further from the theoretical value of 71.8 wt% to 76.3 wt%. This result can be explained by a synergistic effect: the larger the fraction of PP in the mixture, the greater the amount of hydrogen will be provided, leading to a greater interaction. Cornelissen et al. [21] also reported that the flash copyrolysis of willow/PLA blends showed synergetic interactions. They obtained different bio-oil yields and water contents depending on the willow/PLA ratio. Among the blends tested; 10 : 1, 3 : 1, 1 : 1 and 1 : 2, the 1 : 2 willow/PLA blend ratio showed the most pronounced synergistic effect, i.e., the lowest water content and the highest water-free bio-oil fraction. The result from this study agreed very well with that of Cornelissen et al. [21].

CONCLUSIONS

During the copyrolysis of the waste WC and block PP mixture, an interaction was identified between the WC and PP. The TGA/DTG curves of the copyrolysis were different from those obtained theoretically under the assumption that there was no interaction between the WC and PP. The addition of PP to the WC resulted in an increased PP decomposition temperature, while the decomposition of WC was little affected, indicating an interaction between the WC and PP at a high temperature. In particular, the char produced by the pyrolysis of the WC appeared to contribute to the stabilization of PP. The Py-GC/MS analysis showed that new compounds not detected in the single-component pyrolysis products were produced by the copyrolysis, which was attributed to the reactions between the products of the pyrolyses of the WC and PP. The bio-oil obtained from the copyrolysis had improved properties compared to that obtained from the single-component pyrolysis. The carbon and hydrogen contents were increased, while the oxygen content was decreased. In particular, the heating value of the bio-oil obtained from the copyrolysis was very high, close to that of pure PP.

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