Impacts of Pyrolytic Interactions during the Co-pyrolysis of Biomass/Plastic: Synergies in Lignocellulose-Polyethylene System

Shogo KUMAGAI†, Kohei FUJITA, Yusuke TAKAHASHI, Tomohito KAMEDA, Yuko SAITO, and Toshiaki YOSHIOKA
(Received April 26, 2019)

Multiple pyrolytic interactions in the cellulose-hemicellulose-lignin-polyethylene system were thoroughly investigated using a novel approach, which evaluates the pyrolytic interaction impacts through product recovery tests and the in-situ pyrolysate monitoring by evolved gas analysis-mass spectrometry. Fast pyrolysis of neat cellulose, xylan, milled wood lignin, beech wood, polyethylene, and their mixtures was conducted at 650°C using the combined approach. Interactions in the cellulose/polyethylene, xylan/polyethylene, and milled wood lignin/polyethylene systems enhanced the production of CO and C2-C3 hydrocarbons, and simultaneously inhibited that of solids such as heavy tar, wax, and coke. Polyethylene worked as a dispersant of biomass upon injection, and the improved gasification was mainly due to the enhanced hydrogen-exchange between hydrogen-rich polyethylene pyrolysates and carbon-centered radicals in vapor phase. The results suggested that pyrolytic interactions in the biomass components (cellulose-hemicellulose-lignin) occur preferentially before contact with polyethylene, and then the beech wood pyrolysates further interact with the polyethylene pyrolysates. Thus, this novel approach allowed advanced evaluation of pyrolytic interactions and can be applied to different combinations and compositions in the cellulose-hemicellulose-lignin-plastic system. It will help understand the nature of co-pyrolysis systems and predict the significance of co-pyrolysis in practical energy and chemical feedstock production.

Key Words
Co-pyrolysis, Synergies, Cellulose, Hemicellulose, Lignin, Polyethylene

Graduate School of Environmental Studies, Tohoku University
6-6-07 Aoba, Aramaki-aza, Aoba-ku, Sendai-shi, Miyagi 980-8579, Japan
† Corresponding author: kumagai@tohoku.ac.jp
1. Introduction

Lignocellulosic-based biomasses, such as wood and cellulose-rich plant fiber can be combined with plastic as composites. These composites have recently attracted growing attention for automotive, aerospace, and construction applications. However, at the recycling stage, their complete separation into biomass and plastic by physical means is both technologically difficult and uneconomical. Most of these mixtures are disposed in landfills or by incineration. However, they may be converted to feedstocks for the petrochemical industry and/or hydrocarbons for energy to meet the growing energy demand while reducing the carbon footprint.

Thermochemical and biochemical conversions have been suggested for such conversions of lignocellulosic biomass and waste plastic. Selective solvolysis-induced depolymerization is another promising way to recover high-purity chemical feedstock from single polymers at comparatively moderate conditions. Biochemical and sub- and super-critical solvent-induced degradation are also beneficial for recovering chemicals and fuels from wet polymeric wastes. In comparison, pyrolysis is a promising method to simultaneously cleave several chemical bonds in biomass and plastic by heat alone and produce gases, liquids, and solids. It has a distinct advantage in treating mixtures that cannot be physically separated.

To control the reactions, it is important to elucidate the pyrolytic interactions between wood and plastic in their co-pyrolysis. Such control can impart significant advantages on the subsequent catalytic upgrading processes, thereby improving the yield and selectivity of the desired products or reducing undesirable products such as coke precursors and catalyst poisons.

The interactions during the co-pyrolysis of various wood/plastic combinations have been researched. Previous works suggested that hydrogen exchange between biomass and plastic pyrolysates is common during co-pyrolysis. The present authors have observed enhanced production of levoglucosan (LG) and methoxyphenols by hydrogen donation from polyethylene (PE) pyrolysates to beech wood (BW) pyrolysates at comparatively mild pyrolysis conditions. The presence of radical species at 400 °C was monitored by employing an electron spin resonance spectrometer featuring a novel heating unit for the first time.

Lignocellulosic biomass typically contains 40–50 wt.% cellulose, 20–40 wt.% hemicellulose, and 20–35 wt.% lignin. Therefore, studying the interactions of each component with plastic is vital to understand the nature of the whole wood/plastic co-pyrolysis system. While there is no report on the co-pyrolysis of hemicellulose and plastic without catalysts. Although the co-pyrolysis of alkaline lignin with plastics has been studied, alkaline lignin is completely different in molecular structure from the natural lignin. Thus, it can be said that, despite studies of the interactions in various wood/plastic combinations, a better understanding of the co-pyrolysis of each biomass component/plastic combination is urgently required. Also, elucidation of the pyrolytic interaction mechanism and the subsequent reaction control are far from complete.

The interactions during co-pyrolysis are often studied by either product recovery tests and subsequent quantification of the pyrolysates, or by thermogravimetric analysis-mass spectrometry (TG-MS) for monitoring weight loss and online product monitoring. The former method is available for a wide variety of pyrolysis conditions (e.g., slow, fast, and flash pyrolysis). In contrast, in-situ product monitoring itself has a high technical hurdle, as it cannot be applied to fast pyrolysis or products quantification. Thus, an approach that combines these two (quantification of pyrolysis products and subsequent evaluation of pyrolytic interactions, and in-situ product monitoring at fast pyrolysis condition) has not been reported.

The present work employed such a combined approach, namely product recovery tests using a tube reactor and in-situ product monitoring by evolved gas analysis-mass spectrometry (EGA-MS). Multiple pyrolytic interactions in the cellulose-hemicellulose-lignin-PE system during fast pyrolysis were comprehensively studied by the co-pyrolysis of many combinations of cellulose/PE, xylan/PE, MWL/PE, and BW/PE using this approach for the first time. BW is a common hard wood, and PE has the largest production among all resins and is the most demanded one for wood/plastic composites. Therefore, the findings in this work will have broad utility and high impacts on the related fields.

2. Materials and Methods

2.1 Materials

Commercial cellulose, xylan extracted from BW, and PE resin were delivered from Sigma-Aldrich. The inorganic contents in the purchased xylan were determined as Na 2.8 wt.%, K 0.1 wt.%, Ca 1.8 wt.%, Mg 0.2 wt.%, and Al 0.2 wt.% by inductivity coupled plasma-mass spectrometry (ICP-MS, Agilent 8800, Agilent Technologies, Tokyo, Japan). MWL was isolated from purchased BW by Bjorkman’s method. Moisture-, extractive-, and ash-free BW (free-BW) was used for all experiments to reduce interfering components during pyrolysis. The detailed characteristics of the purchased BW and the free-BW have been summarized in Table A1.
the appendix. All materials were ground, mixed, and sieved to yield particles less than 250 μm in size. Other chemicals and standard gases used in this work were purchased from Kanto Chemical (Tokyo, Japan), Tokyo Chemical Industry (Tokyo, Japan), or Tanuma Sanso Shoukai KK (Sendai, Japan).

BW/PE mixtures with weight ratios of 100:0, 60:40, 40:60, and 0:100 were investigated in the present work. According to the BW mixing ratios (RBW [wt.%]), PE mixing ratios (RPE [wt.%]), and the cellulose, hemicellulose, and MWL contents in the free BW (CCel = 0.456 [-], CXyl = 0.290 [-], and CMWL = 0.254 [-] as reported in the previous work22), the corresponding mixing ratios of cellulose, xylan, or MWL (RCell or Xyl or MWL [wt.%]) and PE (RPE [wt.%]) were determined by the following equations:

\[ R_{\text{Cell or Xyl or MWL}} = \frac{C_{\text{Cell or Xyl or MWL}} \times R_{\text{BW}}}{C_{\text{Cell or Xyl or MWL}} \times R_{\text{BW}} + R_{\text{PE}}} \times 100\% \]  

(1)

\[ R_{\text{PE}} = 100 - R_{\text{Cell or Xyl or MWL}} \]  

(2)

The ratios of each biomass component to PE are summarized in the upper part in Table 1. For instance, cellulose/PE mixtures with the weight ratios of 100:0, 41:59, 23:77, and 0:100 are abbreviated as Cel100, Cel41, Cel23, and PE, respectively.

2.2 Product recovery tests using a tube reactor and product analysis

Pyrolysis experiments were carried out using a horizontal quartz tube reactor connected to liquid N\(_2\)-cooled-trap and gas bag (Fig. A1 (a)). Samples (0.2 g) were loaded into the ceramic sample holder, which was pushed to the center of the heating zone that was heated at 650 °C under helium flow of 100 mL min\(^{-1}\). An actual sample heating rate of ~ 550 °C/min was observed directly using a thermocouple. The furnace temperature was kept for 15 min after the sample injection. The set temperature and time were enough to complete the pyrolysis of all biomass components and PE. Each experiment was repeated at least two times to ensure the reliability of the results. The walls of the reactor and connector and the inside of the trap were washed afterwards with super dehydrated tetrahydrofuran (THF, 20 mL). The gaseous products were gathered in an aluminum bag.

The pyrolysis products include (1) gas collected in the aluminum bag; (2) tar and (3) oil derived from biomass and PE that were THF-soluble and collected from the reactor, connector, and liquid N\(_2\)-cooled trap; (4) water; (5) char that remained in the sample holder; and (6) solid derived from PE and biomass, which were THF-insoluble wax and coke, respectively, and heavy oil and tar that cannot be detected by GC.

Table 1 Weight fraction of pyrolysis products obtained from cellulose, xylan, MWL, BW, PE, and their mixtures

| Gas [wt%]          | 1000 | 41.59 | 23.77 | 1000 | 30.7 | 16.84 | 1000 | 27.73 | 14.86 | 1000 | 60.40 | 40.60 | 1000 |
|-------------------|------|-------|-------|------|------|-------|------|-------|-------|------|-------|-------|------|
| H\(_2\)           | 0.5  | 0.3   | 0.2   | 0.9  | 0.7  | 0.3   | 0.4  | 0.2   | 0.2   | 0.4  | 0.3   | 0.3   | 0.2  |
| CO                | 23.5 | 10.1  | 6.5   | 101  | 39   | 2.3   | 124  | 3.9   | 2.4   | 161 | 12.0  | 8.5   | -    |
| CO\(_2\)          | 5.3  | 2.2   | 1.1   | 16.4 | 50   | 2.9   | 46   | 1.4   | 0.8   | 61  | 3.9   | 2.8   | -    |
| CH\(_4\)          | 1.0  | 3.0   | 3.5   | 1.0  | 27   | 3.0   | 3.3  | 3.7   | 3.7   | 17  | 2.9   | 3.1   | 3.3  |
| C\(_2\)           | 18.3 | 10.3  | 12.4  | 1.2  | 12   | 1.5   | 0.7  | 11.7  | 13.4  | 1.3  | 7.5   | 10.5  | 13.6 |
| C\(_3\)           | 11.7 | 7.1   | 8.5   | 0.4  | 67   | 8.1   | 0.3  | 7.9   | 9.0   | 0.7  | 5.0   | 7.4   | 9.1  |
| C\(_4\)           | 0.5  | 0.3   | 0.3   | 0.1  | 1.3  | 1.5   | 0.1  | 1.5   | 1.7   | 0.2  | 0.9   | 1.6   | 1.8  |
| Others            | 0.1  | 0.7   | 1.0   | +    | 1.0  | 1.0   | 0.2  | 0.9   | 1.2   | 0.2  | 0.5   | 1.1   | 1.3  |
| Water [wt%]       | 15.0 | 7.4   | 3.0   | 0.6  | 0.2  | 0.2   | 2.8  | 0.8   | 0.5   | 10.4 | 5.7   | 27.   | -    |
| Tar [wt%]         | 106  | 5.5   | 2.2   | -    | -    | -    | -    | -    | -    | -    | -    | -    | 72   |
| Oil [wt%]         | 0.2  | 0.1   | +\(^a\) | -    | -    | -    | -    | -    | -    | -    | -    | -    | 0.1  |
| Wax and heavy molecular weight tar and oil which cannot be detected by GC analysis |
| Solid b [wt%]     | -    | -    | -    | 0.1  | +    | -    | -    | -    | -    | -    | -    | -    | -    |

\(^a\) hydrocarbons, \(^b\) wax and heavy molecular weight tars and oils which cannot be detected by GC analysis

\(^c\) not detected, \(^d\) less than 0.05 wt.\%
The detailed product analysis procedure and conditions were summarized in the previous work 22. Briefly, identification and quantification of gas, tar, and oil were carried out by GC/MS (GC: 6890; MS: 5975C, Agilent Technology, Tokyo, Japan), GC/ flame ionization detection (GC/FID) (GC4000 and GC390, GL Science, Tokyo, Japan), and GC/ thermal conductivity detection (GC/TCD) (GC323, GL Science, Tokyo, Japan). The yield of water was determined by the Karl Fischer titration method using an 870 KF Titrino plus system (Metrohm Japan, Tokyo, Japan). The char yield was determined by the weight difference of the sample holder before and after the reaction. The char morphology was investigated by optical microscopy (VHX-2000, Keyence, Tokyo, Japan) and scanning electron microscopy (SEM; TM3000, accelerating voltage: 15 kV, chamber pressure: 30 Pa, Hitachi High-Technologies, Tokyo, Japan). Yield of solids was balanced.

### 2.3 Definition of pyrolytic interaction impact, \( I_{\text{Py}} \)

The weight fraction of the decomposition products \( (F_\text{i}; \text{wt.\%}) \) was normalized by the initial sample weight \( (W_{\text{sample}}; \text{g}) \) as follows:

\[
F_\text{i}[\text{wt.\%}] = \frac{W_\text{i}}{W_{\text{sample}}} \times 100\%
\]

where \( W_\text{i}[\text{g}] \) is the product weight.

The interactions between biomass components (cellulose, xylan, and MWL) and PE and those between BW and PE were distinguished by the yield difference \( (YD\text{, \text{[-]} }) \) as defined by equation (4):

\[
YD\text{, \text{[-]}} = \frac{F_\text{i}}{F_{\text{B,\text{all}} \times R_{\text{BW}}} / 100 + F_{\text{PE,\text{all}}} \times R_{\text{PE}} / 100}
\]

where \( F_{\text{B,\text{all}}} \text{PE} [\text{wt.\%}] \) is the weight fraction of product \( \text{i} \) obtained from pyrolysis of neat biomass components (cellulose, xylan, and MWL), BW, or PE, while RB or PE [wt.%] is the mixing ratio of biomass component, BW, or PE, respectively. Interactions in the cellulose-hemicellulose-lignin-PE system were also evaluated by equation (5):

\[
YD_{\text{BW,PE}}[\text{wt.\%}] = \frac{F_\text{i}}{(0.456 \times F_{\text{i,\text{PE}}} + 0.290 \times F_{\text{i,\text{MWL}}} + 0.234 \times F_{\text{i,\text{xylan}}}) \times R_{\text{BW}} / 100 + F_{\text{i,\text{cellulose}}} \times R_{\text{PE}} / 100}
\]

The weight fractions of cellulose, xylan, and MWL in free-BW were determined to be 0.456, 0.290, and 0.254, respectively in Section 2.1 Materials. Therefore, \( YD \geq 1 \) suggests that the yield of product \( \text{i} \) is enhanced by mixing, whereas \( YD < 1 \) means that it is inhibited by mixing. Note that \( YD \) is only applicable to compounds produced from both biomass components and PE, which is the case for all compounds observed in the present work.

As a drawback, \( YD \) does not include the impact of each product yield, even though these yields are variable. Therefore, in this work we evaluated the pyrolytic interaction impact \( (I_{\text{Py}}) \) that takes into account \( F_\text{i} \), to represent the synergistic effects on each product:

\[
I_{\text{Py}}[\%] = \frac{(YD\text{, \text{[-]}} - 1) \times F_\text{i}}{100}
\]

To better distinguish the enhancement or inhibition by mixing the term \( (YD\text{, \text{[-]}} - 1) \) is multiplied by \( F_\text{i}/100 \). Therefore, when \( YD \) is above or below 1, \( I_{\text{Py}} \) becomes positive or negative, respectively.

### 2.4 In-situ monitoring of BW/PE pyrolysates by EGA-MS method

In-situ monitoring of BW/PE pyrolysates was carried out by the EGA-MS technique using a multi-shot pyrolyzer (EGA/Py-3030D, Frontier Laboratories Ltd., Koriyama, Japan) installed in a GC/MS using an Agilent system (GC: 6890; MS: 5975C; column: Ultra ALLOY® deactivated metal capillary tube (UADTM, Frontier Laboratories), Fig. A1 (b)). The furnace temperature in the pyrolyzer was set to 650 °C. The sample holder filled with 1 mg sample was dropped into the heated furnace in the pyrolyzer. The pyrolysates were directly carried into the MS chamber through the UADTM column heated at 300 °C. Thus, the product emission behavior was monitored in-situ from the sample injection to the end of reaction.

The plots of ion counts \( (Y_i; \text{[ion]} / \text{[mg]} \) vs. time \( t \) \) were compared with estimated plots \( (Y_i; \text{[ion]} / \text{[mg]} \) vs. \( t \) \) determined by equation (7):

\[
Y_i(t) = Y_{i,\text{cal}}(t) + Y_{i,\text{exp}}(t) \times R_{\text{BW}} / 100 + Y_{i,\text{PE}}(t) \times R_{\text{PE}} / 100
\]

where \( Y_{i,\text{cal}}(t) \) and \( Y_{i,\text{exp}}(t) \) are the counts of ion \( i \) obtained from neat BW or PE at \( t \), and \( R_{\text{BW}} \text{PE} \text{ wt.\%} \) are their mixing ratios, respectively.

### 3. Results and discussion

#### 3.1 Evaluation of pyrolytic interaction impact by pyrolysate recovery tests

The weight composition of pyrolysis products obtained at 650 °C is summarized in Table 1. Tar compounds are categorized into 7 groups: 1: levoglucosan; 2: 1,4,3,6-dianhydro-a-D-glucopyranose; 3: C_{2}-C_{4} carbonyl compounds; 4: five-membered ring compounds; 5: phenols; 6: catechols; and 7: methoxyphenols. CO (23.5 wt.%) and CO_{2} (5.3 wt.%) were the major gaseous products during pyrolysis of neat cellulose. LG (10.6 wt.%) was the main compound in tar: C_{2}-C_{4} carbonyl compounds (3.7 wt.%) such as glycolaldehyde, acetaldelyde, acrolein, and hydroxyacetone were also observed in tar, as well as traces of anhydrosugars, five-membered-ring compounds, and phenols.
Pyrolysis of neat PE produced 29.3 wt.% gas, 9.2 wt.% oil, and 61.5 wt.% wax without char or coke formation. Notably, slow pyrolysis of this sample (from ambient temperature to 650 °C at 10 °C/min) in the same reactor produced only 21 wt.% gas, 3.2 wt.% oil, and 79.9 wt.% wax. Thus, the present condition (fast pyrolysis at 650 °C) enhanced the gasification compared to the slow pyrolysis condition. Ethylene (10.8 wt.%), propylene (8.3 wt.%), and methane (3.3 wt.%) were the three most abundant products.

The net yield of gas did not change significantly with the mixing ratio (Cel41: 33.9 wt.%, Cel23: 33.6 wt.%), while the yields of hydrocarbons increased and those of CO and CO2 decreased with increasing PE content as expected. The values of \( I_{Py} \) are summarized in Fig. 1. Mixing cellulose and PE enhanced gas production, while the productions of solid and char were apparently inhibited (Fig. 1 (a1)). Tar, oil, and water were enhanced in Cel41, while Cel23 showed reduced tar and oil fractions. The main contributors to the enhanced gas production in Cel41 were C2-C3 hydrocarbons (Fig. 1 (a2)). Increasing the PE ratio enhanced the CO and water production. Since LG was the main component of tar, the changing behaviors of both tar and LG were well synchronized (Fig. 1 (a3)). The LG production was enhanced in Cel41 and inhibited in Cel23. Thus, it is clear that the mixing ratio of cellulose and PE had a strong effect on their pyrolytic interaction.

The carbon number distribution of hydrocarbons standardized by PE input is summarized in Fig. 2 (a). The production of gaseous C1-C3 hydrocarbons was apparently enhanced by mixing cellulose and PE (left Y axis), while the change in oil production by sample mixing was not significant (right Y axis). The total production of hydrocarbons (sum of C1-C3 hydrocarbons) increased from 383 mg/g-PE at PE to 461 mg/g-PE at Cel41.

THF-insoluble heavy tar was observed at the edge of heating zone during pyrolysis of cellulose (Fig. 3 (a1)), which is due to LG re-polymerization on the warm wall there. Wispy black carbon was also observed within a wide area on the reactor wall. PE did not form coke on the reactor wall (Fig. 3 (a9)). Therefore, the deposition from Cel23 was inhibited in the presence of PE as expected (Fig. 3 (a2)). Even though the quantitative evaluation of solid inhibition by photographic images was difficult, the solid yield was apparently inhibited by mixing cellulose and PE (Fig. 1 (a1)). Images of char recorded by digital microscope and SEM are summarized in Figs. 3 (b) and (c), respectively. Char from Cel100 is densely aggregated (Fig. 3 (b1)) but appears to be dispersed with increasing PE content (Fig. 3 (b2)). The SEM image obtained from Cel100 shows a smooth char surface (Fig. 3 (c1)), which becomes rugged with numerous small pores in the presence of PE (Fig. 3 (c2)). These morphological changes might be due to the inhibited char production by mixing cellulose and PE as observed in Fig. 1 (a1).

### 3.1.2 Xylan/PE

The product distribution from xylan (30.1 wt.% gas, 0.6 wt.% tar, 6.7 wt.% water, 41.0 wt.% solid, and 21.6 wt.% char) is totally different from that obtained from cellulose. Since the xylose unit does not have a sixth carbon or substituted oxygen on the fourth carbon like cellulose, it does not form stable 1,6-anhydride structures like LG. Instead, the unstable molecules are easily coupled together to form longer polymers, which are further converted into char via dehydration. Therefore, higher yield of char might be observed for xylan compared to cellulose. The yield of gas is comparable with that derived from cellulose, while the production of CO (16.4 wt.%) is more significant than that of CO2 (10.1 wt.%). Decarboxylation or decarbonylation from xylan pyrolysates is the origin of CO2, while CO is the result of ring-opening depolymerization and rearrangement of xylose unit.

During the co-pyrolysis, the yields of hydrocarbons increased and those of CO and CO2 decreased with increasing PE content, while the net yield of gas did not change significantly with the mixing ratio, the same as in the cellulose/PE mixes. The \( I_{Py} \) values are summarized in Figs. 1 (b1)-(b3). The pyrolytic interactions between xylan and PE enhance the production of gas, water, and char in Xyl30 and that of oil in Xyl16, while solid production is inhibited in both cases (Fig. 1 (b1)). This trend is similar to the cellulose/PE mixtures. Among gaseous compounds, CO, CO2, and C2-C3 hydrocarbons are mainly enhanced in Xyl16 (Fig. 1 (b2)). In Xyl30, H2, CO, and CO2 are the main contributors of the enhanced gas, and the impacts on C2-C3 hydrocarbons are not significant compared to the case of Xyl16. While the \( I_{Py} \) on increased tar production is negligible compared to those on gas, water, and solid; all tar compounds are enhanced in Xyl16, and five-membered-ring compounds and catechols are enhanced in Xyl30 (Fig. 1 (b3)). Char production is enhanced by PE addition, which is the opposite of that observed in cellulose/PE.

The production of gaseous C2-C3 hydrocarbons is enhanced by mixing xylan and PE (Fig. 2 (b)), although this trend is not significant compared with that from cellulose/PE. A slightly increased oil production with carbon number C12- in Xyl16 was observed, which is consistent with the enhanced oil production.

Traces of tar deposited on the reactor wall were washed off by THF, and so they are invisible in the
Fig. 1 Pyrolytic interaction impacts in (a) cellulose/PE, (b) xylan/PE, and (c) MWL/PE on (1) gas, tar, oil, water, char, and solid; (2) gaseous compounds; and (3) tar compounds.
photographs in Fig. 3 (a3). Wispy black carbon is visible on a wide section of the reactor wall for Xyl100 (Fig. 3 (a3)), but is invisible for Xyl16 (Fig. 3 (a4)). As shown in Fig. 1 (b1), solid production was inhibited during co-pyrolysis of xylan/PE. In the presence of PE, the surface morphology of char is dispersed (Fig. 3 (b4)) and very different from that from Xyl100. The SEM image of char obtained from Xyl100 shows numerous small pores (Fig. 3 (c4)), and needle-shaped particles (Na2O derived from ash, see Fig. A2 in the appendix) are covered by the carbon matrix. After adding PE, the porous surface seems to be destroyed (exposed needle-shaped ash) and a rugged surface is formed (Fig. 3 (c4)).

3.1.3 MWL/PE

The pyrolysis of neat MWL produces 22.0 wt.% gas, 2.8 wt.% tar, 6.7 wt.% water, 34.8 wt.% solid, and 33.7 wt.% char. The gas yield is lower than those from cellulose and xylan, while the char yield is significantly higher. CO (12.4 wt.%) is a major gaseous product here, and the yield of methane (3.3 wt.%) is slightly higher than those from cellulose and xylan. The main products in tar are phenol, alkylphenols, catechol, and alkylcatechols. Traces of methoxyphenols (0.1 wt.%) such as guaiacol, eugenols, and vanillin are observed in the present condition. Therefore, it is clear that the pyrolysis of side chains and methoxy group in methoxyphenols is significant in MWL/PE.

The total gas yield of MWL is enhanced by PE addition due to the hydrocarbons from PE, as expected. Mixing MWL and PE significantly enhances gas and water production, while solid production is inhibited (Fig. 1 (c1)). All gases are enhanced, especially CO and C2-C3 hydrocarbons are the main contributors to the net gas enhancement in the mixtures (Fig. 1 (c2)), a trend similar to those for cellulose/PE and xylan/PE. The mixing ratio does not significantly influence the Ic on each gaseous compound. While the synergistic impact on tar compounds is not significant, enhancement of methoxyphenols (Fig. 1 (c3)) is the main cause of the enhanced tar production.

Fig. 2 Carbon number distribution of gas and oil standardized by PE input in the sample obtained from (a) cellulose/PE, (b) xylan/PE, (c) MWL/PE, and (d) BW/PE. The left Y-axis represents gas (C1-C8) production and the right Y-axis represents oil (C9-C33) production.
Fig. 3  (a) Photographs of the quartz tube reactor after pyrolysis, (b) optical microscopic images of char, and (c) SEM images of char obtained from (1) Cel100, (2) Cel23, (3) Xyl100, (4) Xyl16, (5) MWL100, (6) MWL14, (7) BW100, (8) BW40, and (9) PE.
The production of gaseous C_{1}-C_{3} hydrocarbons was clearly enhanced by mixing MWL and PE, but the carbon number distribution of the oil fraction was hardly affected (Fig. 2 (c)). The total production of hydrocarbons increased to 443 mg/g-PE at MWL14.

There were significant yields of char and carbonaceous coke deposited on a large section of the reactor wall (Fig. 3 (a5)). Coke deposition on a wide range of the reactor wall decreased with increasing PE content in the sample (Fig. 3 (a6)). Even though it is difficult to quantitatively discuss solid inhibition by photographic images, Fig. 1 (c1) supported the inhibited solid production by mixing MWL and PE. Strongly aggregated char was obtained from MWL100 (Fig. 3 (b5)), which was apparently dispersed by PE addition (Fig. 3 (b6)). SEM image of char from MWL100 shows a smooth surface (Fig. 3 (c5)), which changes to a porous and spongy structure in the presence of PE (Fig. 3 (c6)).

3.1.4 BW/PE

Pyrolysis of BW produced 26.6 wt.% gas, 10.4 wt.% tar, 6.6 wt.% water, and 14.0 wt.% char. CO (16.1 wt.%), CO_{2} (6.1 wt.%), and CH_{4} (17.7 wt.%) are the three most abundant gaseous products. The previous sections 3.1.1–3.1.3 revealed significant production of CO from cellulose, higher CO_{2} production than CO from xylan, and higher CH_{4} production from MWL. LG (7.2 wt.%) is the primary and major intermediate of cellulose pyrolysis. C_{2}-C_{1} carbonyl compounds (2.3 wt.%) such as glycolaldehyde and hydroxyacetone are the second major products in tar, which could be produced from cellulose and hemicellulose. Acetaldehyde, acrolein, acetone, 2-butenal, and 2-butanone are common pyrolysates from cellulose and xylan under the same pyrolytic conditions. The trace of five-membered-ring compounds (0.1 wt.%) is consistent with that observed from cellulose and xylan, because the transformation from pyran ring to furan ring is necessary for their formation. Phenols and catechols (0.3 wt.% each) but not methoxyphenols were observed in the present condition. A significant amount of coke was deposited on a wide range of the reactor wall (Fig. 3 (a7)), mainly produced by polymerization of lignin pyrolysates (Fig. 3 (a5)) and polymerization of LG (Fig. 3 (a1)).

The above results are compared to the fractions estimated using the yield obtained from neat cellulose, xylan, and MWL. The \( I_{n} \) on each pyrolysate is summarized in category "BW100" in Fig. 4. The yields of gas and char from BW are lower than the estimated yields, while those of tar and solid are higher (Fig. 4 (a1)). The main decrease in gas yield is due to the reduction of CO_{2} and CO yields (Fig. 4 (b1)), and LG and C_{2}-C_{1} carbonyl compounds are the main contributors of increased tar (Fig. 4 (c1)).

Gas production is significantly enhanced by mixing BW and PE (Fig. 4 (a2)), which is mainly due to the enhanced CO and C_{2}-C_{3} hydrocarbons (Fig. 4 (b2)). This trend is consistent with that obtained from cellulose/PE, xylan/PE, and MWL/PE mixtures. The amount of PE influences the C_{2}-C_{3} hydrocarbons for BW/PE, while it does not significantly influence these hydrocarbons during each biomass component/PE pyrolysis. Significant decrease of solid and slight decrease of oil and char were observed.

The production of gaseous C_{2}-C_{3} hydrocarbons is significantly enhanced in the presence of BW, while that of light hydrocarbons in the oil (C_{9}-C_{14}) is slightly decreased (Fig. 2 (d)). The enhanced production of gaseous C_{2}-C_{3} hydrocarbons is in the same trend as shown in cellulose/PE, xylan/PE, and MWL/PE mixtures. The production of hydrocarbons increases with increasing BW ratio in the mix (497 mg/g-PE at BW40, Fig. 2 (d)). Coke formation on the reactor wall is decreased with increasing PE content in the mixed sample (Fig. 3 (a8)). Char obtained from BW/PE mixtures is dispersed by PE addition (Fig. 3 (b8)), the same trend as in the cellulose/PE, xylan/PE, and MWL/PE systems. In fact, solid production is inhibited by mixing BW and PE (Fig. 4 (a2)). The SEM images in Figs. 3 (c7) and (c8) suggest that the char surface changes from smooth to slightly more rugged by PE addition. Note that the pores in the image are pits from the wood structure.

3.2 Evaluation of pyrolytic interaction by in-situ pyrolysates monitoring by EGA-MS

The time-dependent behavior of selected ions generated from BW/PE is summarized in Fig. 5 for the experimental data (solid line) and estimated values (dotted lines). The difference between the solid and dotted lines indicates synergistic effects of co-pyrolysis. The time-dependent behaviors of the total ion chromatogram (TIC) and selected ions generated from cellulose/PE, xylan/PE, and MWL/PE are summarized in Fig. A3 in the appendix.

TIC obtained from BW100 suggests that the main degradation is finished within 20 s (from sample injection at 15 s to the end of the first peak at 35 s), as demonstrated by the peaks of cellulose, hemicellulose, and MWL degradation (Fig. A3). PE is also pyrolyzed at the same time as the BW degradation, while it shows a broader peak since PE pyrolysates with high boiling points are gradually pyrolyzed and evaporated. The experimental plots of BW60 seem to show the combined behavior of neat cellulose and PE, which are not significantly different from the estimated plots. This trend is the same as that for BW40. PE addition slightly accelerates the initial rise of the first peak (Fig. 5 (a1)).
m/z 18 (molecular ion of H₂O derived from BW, Fig. 5 (b)) in BW100 shows a first strong peak derived from all components, and a subsequent shoulder peak mainly derived from lignin unit (Fig. A3). In the presence of PE, the intensity of experimental plots and estimated plots are comparable, which is consistent with the change in H₂O production during the tube reactor test (Fig. 4 (a2)).

m/z 28 (molecular ion of CO derived from BW and C₃H₇⁺ produced from both BW and PE, Fig. 5 (c)) in BW100 shows a sharp peak while PE shows a broad peak top. Therefore, BW60 and BW40 show combined two-step emissions. The difference between experimental and estimated plots is not significant despite the enhanced CO and C₃H₇⁺ production during tube reactor tests (Fig. 4 (b2)). Also, the behavior of m/z 43 (main fragment ion of hydroxyacetone and acetic acid derived from BW, and C₃H₇⁺ produced from BW and PE, Fig. 5 (d)) in BW60 and BW40 is not significantly changed in the presence of PE, which is inconsistent with the enhanced C₃ hydrocarbons during tube reactor tests (Fig. 4 (b2)). Recall that the residence time of gas in the pyrolyzer is set to less than 0.1 s, which is a much shorter time than in the tube reactor (16 s), pyrolytic
interactions in the vapor phase could be diminished under the present conditions. Therefore, it is implied that the synergistic production of CO and gaseous hydrocarbons corresponds to interactions in the vapor phase.

\( m/z \) 44 (molecular ion of CO\(_2\)) derived from BW, Fig. 5 (e) in BW100 shows a sharp first peak at the point of sample injection and a broad second peak. Comparable two-step behavior is observed from cellulose, xylan, and MWL; and the second peak is inhibited by PE addition, also the same as for cellulose/PE, xylan/PE, and MWL/PE systems (Fig. A3).

\( m/z \) 60 (main fragment ion of LG derived from cellulose, Fig. 5 (f)) in BW100 shows a broader peak than other pyrolysates, since the evaporation of LG with a comparatively high boiling point (385 °C) is slow. In BW100, the first trace of peak and a following broad peak are observed. Interestingly, the production behavior of \( m/z \) 60 is significantly different from that observed in cellulose (Fig. A3), likely due to the cellulose-hemicellulose-lignin pyrolytic interactions in BW. In the case of BW60, the peak intensity is significantly suppressed and there is a second peak. The second peak is almost diminished in BW40. The inhibited LG production is consistent with the results observed in tube reactor tests (Fig. 4 (c2)).

The behavior of \( m/z \) 94, corresponding to the molecular ion of phenol mainly derived from the lignin unit, is summarized in Fig. 5 (g). A single peak is observed at BW100, while it is diminished in the presence of PE. However, it is inconsistent with the phenol production observed in the tube reactor in the presence of PE (Table 1). Possibly, phenol is produced in the tube reactor from vapor-phase reaction due to the much longer residence time of gas (16 s) than that in the pyrolyzer (0.1 s).

\( m/z \) 124 (Fig. 5 (h)) corresponds to the molecular ions...
of methylcatechols and methoxyphenol. Two separated peaks, the first sharp and the second broad, are observed in BW100. Aliphatic ions (C9H16+) derived from PE are also clearly observed. BW60 and BW40 each show a combined broad peak, while the second BW-derived peak is apparently decreased in the presence of PE.

3.3 Suggested interactions in the cellulose-hemicellulose-lignin-PE system

The suggested pyrolytic routes of cellulose, hemicellulose, and lignin, and their pyrolytic interactions are briefly summarized in Fig. 6 based on a review of previous works 32, 33, 36 – 40. The figure also includes new pyrolytic interactions in the cellulose-hemicellulose-lignin-PE system, based on the experimental results of this work. At the moment of mixed sample injection, PE is immediately melted, and BW is dispersed in the PE melt to form dispersed BW char (Fig. 3 (b8)). The slight shift of BW pyrolysate emission to an earlier time (Fig. 5 (a')) supports that BW dispersion assists the prompt evaporation of BW pyrolysates. Because of the microscopic cell wall structure in BW, the pyrolysates of cellulose, hemicellulose, and lignin could initially interact with each other before contacting the PE pyrolysates or PE melt. Cellulose mainly produces LG, and a part of cellulose is directly decomposed into C2–C4 carbonyl compounds and five-membered-ring compounds accompanied by CO, CO2, and H2O production. The xylan skeleton is depolymerized into unstable 1,4-anhydro-α-D-xylopyranose (xylosan) which immediately decomposes into smaller molecules, similar to the case of cellulose 33. Lignin initially releases methoxyphenol radicals via H-abstraction from alpha carbon on the side chain or from the phenolic...
The radicals derived from lignin could abstract H on C2, C3, and C4 or OH in LG 38), as shown in Fig. 6(a). In contrast, LG radicals are stabilized by H-abstraction from C2-C4 aldehydes produced from cellulose and hemicellulose 32) 38) (Fig. 6(b)). In this work, more C2-C4 aldehydes are produced than the lignin pyrolysates (Table 1), therefore LG stabilization by aldehydes is a more important interaction in the present conditions. Thus, the differences between the experimental and estimated results are attributed to the interactions suggested above.

The pyrolysates from BW evaporate through the PE melt, and the PE melt physically prevents the condensation of lignin pyrolysates including conjugated C=C bonds (Fig. 6(c)), radical coupling (Fig. 6(d)), and repolymerization of LG (Fig. 6(e)). Therefore, the inhibited char production (Fig. 1) might be the result of the above interactions. As well, repolymerization of xylosyl radicals and cations (Fig. 6(f)) could be physically prevented in the PE melt, while char production is slightly enhanced in Xyl30 (Fig. 1(b1)). Recall that Xyl30 has significantly enhanced H2 and CO production (Fig. 1(b2)), steam reforming of hydrocarbons is promoted by Na2CO3 ash 49). Specifically, hydrocarbons derived from PE are converted into H2 and CO by two reactions (Na2CO3 + C2HmΔ3→ (m-1)H2O → Na2O + (m+1)CO + 2nH2; and Na2CO3 + C3HmΔ3→ (m-1)H2O → Na2O + (m+1)CO + (2m-1)H2). In fact, Na2O was found to remain in the xylan char (Fig. A2). Gibbs free energies of the suggested reactions for C2-C5 hydrocarbons were thermodynamically evaluated by FactSage 7.1 software (Thermofact and GTT-Technology) (Fig. A4). The results imply that hydrocarbons longer than C4 are thermodynamically favorable for reaction in the present condition. Therefore, the enhanced char production might be the result of coke deposition on Na2O during the catalytic steam reforming of PE pyrolysates 47) 48), and this effect is more significant than the physical prevention (Fig. 6(f)). In addition, PE is known as a low heat transfer material and its pyrolysis is endothermic. The previous works reported that a lower temperature favors the degradation of cellulose and hemicellulose pyrolysates via ionic mechanism in the liquid/solid phase 39) 49). Therefore, BW pyrolysis at lower temperatures could progress in PE melt, enhancing the ionic degradation of cellulose and xylan into H2O, dehydrated compounds, and C2-C4 carbonyl compounds (Fig. 1).

Pyrolysates from cellulose, hemicellulose, lignin, and PE more frequently interact with each other in the vapor phase than in the condensed phase. The evaporated PE pyrolysates are further decomposed into smaller hydrocarbons via homolysis of C-C in the polymer backbone, β-scission, and intramolecular H-abstraction 50). BW-derived radicals could abstract hydrogen from hydrogen-rich PE pyrolysates as suitable donors (Fig. 6(g)) 21), which might enhance the degradation of PE into light hydrocarbons such as C2-C5 (Fig. 5(h)). On the other hand, enhanced carbon-centered radicals derived from PE could abstract H from LG (Fig. 6(f)), methoxyphenols (Fig. 6(k)), and aldehydes (Fig. 6(o)). An excess amount of these radicals in the vapor phase could be a strong driving force for the above interactions in the present conditions. Therefore, the fragmentation of LG radical species (Fig. 6(i), the detailed mechanism has been reported in the previous works 36) 40) 49) enhances the production of H2, CO, CO2, and C2-C4 hydrocarbons. As well, H-abstraction from side chains on methoxyphenols induces side-chain rearrangement, and the H-radical donation promotes side-chain elimination (detailed mechanism has been reported in the previous work 42) 43) enhancing CO, CO2, and C2-C4 hydrocarbons in the vapor phase (Fig. 6(l)). Furthermore, an environment rich in H-donors favors the route of catechol production (Fig. 6(m)) over the competing rearrangement pathway (Fig. 6(n)), and so enhanced catechols and inhibited phenols might be observed in Figs. 1(c3) and 4(c2). Further, H-abstraction from aldehydes (Fig. 6(o)) enhances the production of CO and smaller compounds. Thus, the enhanced gasification and inhibited solids are mainly due to enhanced radical interactions in the vapor phase. In the BW/PE mixtures, the above-mentioned interactions between each biomass component and PE could compete with the cellulose-lignin interactions 37) (i.e. H-donation from cellulose- and xylan-derived volatiles to lignin pyrolysates), while pyrolytic interactions between cellulose and hemicellulose are not significant 51). Even though it is difficult to give a more specific discussion of the competing multiple interactions such as PE-cellulose-lignin based on the current results, the multiple interactions causes the different synergistic effects during BW/PE pyrolysis as compared to the pyrolysis of each biomass component/PE. There is no change in the emission behavior in the second broad peak of m/z 124, which corresponds to aliphatic ions (C3H7+′) derived from PE, under diminished vapor-phase interactions (Fig. 5(h)), suggesting that the enhanced production of short chain hydrocarbons (Fig. 1 and Fig. 4) occurs via vapor-phase interactions.

4. Conclusions

Multiple pyrolytic interactions in the cellulose-hemicellulose-lignin-polyethylene system during fast co-pyrolysis of beech wood/polyethylene at 650 °C were thoroughly evaluated by the combined approach of product recovery tests employing the pyrolytic interaction impacts and in-situ pyrolysate monitoring. This approach
revealed that, compared to neat cellulose, xylan, and milled wood lignin, beech wood showed enhanced tar and solid production in pyrolysis together with inhibited char and gas (mainly CO and CO\textsubscript{2}) production. On the other hand, adding polyethylene into beech wood changed the product distributions and emission behaviors in two aspects. (i) The production of CO and C\textsubscript{2}-C\textsubscript{5} hydrocarbons was enhanced, and that of solid was inhibited by mixing beech wood and polyethylene. (ii) Emission behaviors of levoglucosan, levoglucosan pyrolysates, phenols, and catechols were significantly changed by polyethylene addition.

Interactions during the co-pyrolysis of beech wood/polyethylene were discussed by combining the known pyrolysis mechanisms of cellulose, hemicellulose, and lignin and the experimental results obtained in this work. We started from the interactions within beech wood components (cellulose-hemicellulose-lignin), and then examined those between beech wood and polyethylene (cellulose/polyethylene, hemicellulose/polyethylene, and lignin/polyethylene). The experimental results suggested that the polyethylene melt contributed to beech wood dispersion in the sample holder, as well as the hydrogen-exchange between beech wood and polyethylene pyrolysates in the vapor phase. The results were enhanced gasification (H\textsubscript{2}, CO, CO\textsubscript{2}, and light hydrocarbons) and inhibited solid production under the present condition.

This work systematically examined a wide range of biomass/polyethylene mixing ratios. In practice, the typical wood/plastic composite materials used in construction are made out of 40–70% wood and 30–60% plastic. Therefore, the findings in this work will help to predict the co-pyrolysis behavior of biomass/plastic mixtures in a wide composition range and develop effective processes to produce energy and chemical feedstock.

Acknowledgement

This work was supported by JSPS KAKENHI grant numbers 16H05893 and 19H04306.

Nomenclature

BW: beech wood
EGA-MS: evolved gas analysis-mass spectrometry
FID: flame ionization detection
H\textsubscript{py}: pyrolytic interaction impact
LG: levoglucosan
MWL: milled wood lignin
PE: polyethylene
PP: polypropylene
PS: polystyrene
Py-GC/MS: pyrolyzer-gas chromatography mass spectrometry
SEM: scanning electron microscopy
TCD: thermal conductivity detection
TG-MS: thermogravimetry-mass spectrometry
THF: tetrahydrofuran
TIC: total ion chromatogram

References

1) Moon, R. J.; Martini, A.; Nairn, J.; Simonsen, J.; Youngblood, J., Chem. Soc. Rev., 40, 3941-3994 (2011)
2) Carus, M.; Eder, A.; Dammer, L.; Korte, H.; Scholz, L.; Essel, R.; Breitmayer, E.; Barth, M., Wood Plastic Composites (WPC) and Natural Fibre Composites (NFC): European and Global Markets 2012 and Future Trends in Automotive and Construction: WPC/NFC Market Study 2014-10, (2014)
3) Melero, J. A.; Iglesias, J.; Garcia, A., Energy Environ. Sci., 5, 7393-7420 (2012)
4) Goto, M., J. Jpn. Petrol. Inst., 59, 254-258 (2016)
5) Kumagai, S.; Yoshioka, T., J. Jpn. Petrol. Inst., 59, 243-253 (2016)
6) Lopez, G.; Artxetxe, M.; Amutio, M.; Bilbao, J.; Olazar, M., Renew. Sust. Energy Rev., 73, 346-368 (2017)
7) Bridgwater, A. V., Biomass Bioenergy, 38, 68-94 (2012)
8) Kumagai, S.; Grause, G.; Kameda, T.; Yoshioka, T., Environ. Sci. Technol., 48, 3430-3437 (2014)
9) Kumagai, S.; Grause, G.; Kameda, T.; Yoshioka, T., J. Mater. Cycles Waste Manag., 16, 282-290 (2014)
10) Yang, J.; Rizkiana, J.; Widyatno, W. B.; Karnjanakorn, S.; Kaewpanha, M.; Hao, X.; Abudula, A.; Guan, G., Energy Convers. Manage., 120, 422-429 (2016)
11) Xue, Y.; Zhou, S.; Brown, R. C.; Kelkar, A.; Bai, X., Fuel, 156, 40-46 (2015)
12) Sharypov, V. I.; Marin, N.; Beregovtsova, N. G.; Baryshnikov, S. V.; Kuznetsov, B. N.; Cebolla, V. L.; Weber, J. V., J. Anal. Appl. Pyrol., 64, 15-28 (2002)
13) Sharypov, V. I.; Beregovtsova, N. G.; Kuznetsov, B. N.; Memhrado, L.; Cebolla, V. L.; Marin, N.; Weber, J. V., J. Anal. Appl. Pyrol., 67, 325-340 (2003)
14) Sajdak, M., J. Anal. Appl. Pyrol., 124, 415-425 (2017)
15) Marin, N.; Collura, S.; Sharypov, V. I.; Beregovtsova, N. G.; Baryshnikov, S. V.; Kuznetsov, B. N.; Cebolla, V.; Weber, J. V., J. Anal. Appl. Pyrol., 65, 41-55 (2002)
16) Jakab, E.; Varhegyi, G.; Faix, O., J. Anal. Appl. Pyrol., 56, 273-285 (2000)
17) Han, B.; Chen, Y.; Wu, Y.; Hua, D.; Chen, Z.; Feng, W.; Yang, M.; Xie, Q., J. Therm. Anal. Calorim., 115, 227-235 (2013)
18) Dong, C.; Yang, Y.; Jin, B.; Horio, M., Waste Manage., 27, 1557-1561 (2007)
19) Brebu, M.; Ucar, S.; Vasile, C.; Yanik, J., Fuel, 89, 1911-
Appendix

Table A1 Characteristics of the purchased BW

| Components [wt.%] | Cellulose | Hemicellulose | Lignin | Water | Extractives | Ash |
|-------------------|-----------|---------------|--------|-------|-------------|-----|
|                   | 41.6      | 26.5          | 23.1   | 7.0   | 1.4         | 0.4 |

Proximate analysis* [wt.%]

| Water | Volatiles | Fixed carbon | Ash |
|-------|-----------|--------------|-----|
| 70    | 80.2      | 124          | 0.4 |

Ultimate analysis [wt.%]

| Carbon | Hydrogen | Nitrogen | Sulfur | Oxygen** |
|--------|----------|----------|--------|----------|
| 49.9   | 6.2      | -        | -      | 43.9     |

*Wet basis, **Calculated as mass difference (balance)

Fig. A1 Experimental setup of (a) horizontal tube reactor and (b) EGA-MS

Fig. A2 SEM-EDX images of char obtained from Xyl100. (a) SEM image, (b) Na mapping, (c) O mapping, and (d) Ca mapping
Fig. A3  Time-dependent product emission behavior during co-pyrolysis of (a) cellulose/PE, (b) xylan/PE, and (c) MWL/PE: (1) TIC, (2) m/z 18, (3) m/z 28, (4) m/z 43, (5) m/z 44, (6) m/z 60, (7) m/z 29, (8) m/z 94, and (9) m/z 124
Fig. A4  Estimated Gibbs free energy for reactions (a) and (b). The alkanes and alkenes are within the range of C₂–C₁₅