Investigation of Biochar Production from Copyrolysis of Rice Husk and Plastic

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ABSTRACT: Biomass renewable energy has become a major target of the Thailand Alternative Energy Development Plan (AEDP) since the country’s economy is largely based on agricultural production. Rice husk (RH) is one of the most common agricultural residues in Thailand. This research aims to investigate yields and properties of biochar produced from copyrolysis of RH and plastic (high-density polyethylene (HDPE)) at different ratios, temperatures, and holding times. For both individual and copyrolysis, the temperature variation generated more pronounced effects than the holding time variation on both biochar yields and properties. For individual pyrolysis of RH, the maximum biochar yield of ∼54 wt % was obtained at 400 °C. A shift in temperature from 400 to 600 °C resulted in RH biochars with higher fixed carbon (FC) and carbon (C) contents by ∼1.11−1.28 and 1.06−1.22 times, respectively, while undetectable changes in higher heating values (HHVs) were noticed. For copyrolysis, obvious negative synergistic effects were observed due to the radical interaction between the rich H content of HDPE and RH biochars, which resulted in lower biochar yields as compared to the theoretical estimation based on individual pyrolysis values. However, the addition of HDPE positively impacted the FC and C contents, especially when 10 and 20 wt % HDPE were added to the feedstock. Besides, higher HDPE blending ratios resulted in biochars with improved HHVs, and >1.5 times improvement in HHV was reported in the biochar with 50 wt % HDPE addition in comparison with RH biochar obtained under the same conditions. In summary, biochars generated in this study have the potential to be utilized as a solid fuel or soil amendment.

1. INTRODUCTION

The use of renewable energy from alternative resources including wind, solar, biomass, hydro, geothermal, tidal, and nuclear has grown significantly in the last few decades. The International Energy Agency1 reported a similar annual growth rate of renewable energy sources (2.0%) and world total energy supply (1.8%) since 1990. Asia had the highest consumption of renewable energy, accounting for ∼41% of the world total in 2018, of which 62% was derived from bioenergy.2 In developing countries, biomass is more attractive than other renewable energy resources, as it is seasonally abundant from a wide variety of agriculture residues and is simple to utilize in all forms.1 Global biofuel consumption has increased by ∼31% from 50.5 EJ in 2005 to 66.2 EJ in 2018.2

The Thai government promoted the usage of renewable energy for electricity, heat, and biofuel production through the 2015 Thailand Alternative Energy Development Plan (AEDP). The AEDP has set a target that renewable energy would account for 30% of total energy consumption by 2036,3 of which biomass shares the highest fraction in comparison with other renewable energy sources (52.08 and 88.09% for electricity and heat production, respectively).4 According to the Thailand Department of Agriculture Extension (DOAE) report, the amount of agricultural residues generated is ∼43 million Mg per year.5 A large amount of crop residues is also estimated to be generated in other Asian countries, e.g., Vietnam,6 Indonesia,7 and India8 with ∼15, 55, and 500 million Mg per year, respectively. Thus, the utilization of agricultural residues as alternative energy has great potential in Asia.

Rice husk (RH), a byproduct from the rice milling process, is an agricultural residue generated abundantly in Thailand, ∼7.5 million Mg per year.9 According to Pode,9 1 Mg of RH can generate up to 800 kW-h of electricity, which can substitute at least 0.098 Mg of coal. When RH is used to replace conventional fossil fuels, the SOx emission would be significantly reduced due to the lower sulfur content of RH.5 Pyrolysis is a promising biomass thermochemical conversion process, and the final products include liquid as bio-oil, solid as biochar, and gas with the presence of light hydrocarbons.
Pyrolysis is generally performed at mid-to-high temperatures under an inert atmosphere (usually nitrogen gas) and has attracted considerable attention due to its easy-to-operate characteristics, especially in optimizing the yields of targeted products. The products from biomass pyrolysis, however, have lower fuel quality in comparison with conventional fuels. Other types of processing, such as catalytic cracking, hydrotreating, and deoxygenation, can improve or upgrade the pyrolysis products but result in increased operating costs.

A huge amount of plastic waste, ~2.42 million tons, was generated in 2016 globally, which primarily came from three regions including East Asia and the Pacific, Europe and Central Asia, and North America. In Asia, an estimation of 1.21 million tons of plastic waste was reported in 2016, which accounted for 50% of the global generation. According to the United Nations Centre for Regional Development (UNCRD), Thailand is considered one of the top 11 major polluting countries in the Asia-Pacific region, indicated by the highest mismanagement of plastic waste. Thailand generated ~1.91 million tons of plastic waste in 2019. It was ranked in the top five countries with the highest plastic waste generation in 2016, based on the amount of plastic waste generation per capita (69.54 kg/year).

Energy recovery can be an option for plastic waste management. Copyrolysis of biomass and plastic is regarded as a promising pathway to obtain products with improved fuel qualities that require no additional processing. Plastics have high carbon (C) and hydrogen (H) content and can serve as a H donor during copyrolysis. The reaction mechanism of copyrolysis, however, is more complicated in comparison with biomass pyrolysis due to the diversity and heterogeneity of the feedstock. Although most of the reaction mechanisms in copyrolysis are similar to those in biomass pyrolysis, synergistic effects occur due to the interactions between the different types of species in the feedstocks. These effects may be positive or negative depending on the type of feedstocks and pyrolysis duration and temperature. Most of the previous copyrolysis studies focus on improving bio-oil production. Tang et al. reported increased yield and decreased oxygen and water content of bio-oil from copyrolysis of microalgae and low-density polyethylene (LDPE). Similar results were reported in copyrolysis of newspaper and high-density polyethylene (HDPE), where the bio-oil yield increased by 17.50 wt % when the mass ratio of feedstocks = 1:1 as compared to pyrolysis of newspaper alone under the same conditions. The higher heating value (HHV) of the bio-oil from copyrolysis was also comparably higher owing to the decrease of moisture and oxygen contents. The bio-oil yield of the process was also affected by the mass fraction of feedstocks. Biochar is another value-added product obtained from copyrolysis. Due to the high carbonaceous residue in biochar, the heterogeneous reaction of solid C with O is slower than homogeneous oxidation. Consequently, it is relatively stable compared to bio-oil. Unfortunately, biochar typically has a low heating value ranging between 13.4 and 17.40 MJ/kg compared to the heating value of commercial charcoal, which is ~30 MJ/kg. For this reason, biochar is not attractive for use as an energy resource. The main reason for the low heating value of biochar is that it is inherited from the low heating value properties of the raw biomass itself. Consequently, this work aims to evaluate a feasible method to improve biochar quality through copyrolysis between biomass and a material with a higher heating value such as plastic (41.7–46.4 MJ/kg). Research on biochar from copyrolysis of biomass and plastic waste, however, is still limited. The present study aims to produce and characterize high-quality biochar through copyrolysis of RH and HDPE. The impacts of plastic fraction and pyrolysis temperature and duration on the yield and physicochemical properties of biochar were investigated. The synergistic effects of RH and HDPE during copyrolysis were also revealed.

2. MATERIALS AND METHODS

2.1. Materials. RH and recycled HDPE pellet (4 × 4 mm²) were obtained from a local agricultural area in Maha Sarakham Province, Thailand and Union J. Plus (Thailand) Co., Ltd., respectively. RH was ground by a blender and then sieved to a particle size range of 0.5–1.0 mm. To break down the polymer chain, the HDPE pellet was initially dissolved in hot toluene at ~110 °C (the boiling point of toluene is 110.6 °C). After the pellet was almost completely dissolved, RH was added to the plastic–toluene solution. The mixture was stirred to ensure that each rice husk particle was completely wetted by the solution and then air-dried under a hood overnight (described
in Kositkanawuth et al.\textsuperscript{34}). The targeted mass fraction of RH varied from 50 to 90 wt %.

### 2.2. Pyrolysis and Copyrolysis Experiments

The pyrolysis tests were conducted using a 316 stainless steel fixed-bed reactor of 600 mm height and 23.4 mm inner diameter (i.d.). The reactor was externally heated by a resistance heater connected to a PID temperature controller and K-type thermocouple (Figure 1). A 316 stainless steel tube with 0.4 mm i.d. was connected to the top of the reactor allowing volatiles to flow into the cold traps containing isopropyl alcohol to collect condensable products. The noncondensable gaseous products were collected in Tedlar gas sampling bags (New Devex bag and PC valve 1 L, HEDETech) at the final outlet. Both pyrolysis and copyrolysis tests were conducted at three temperatures (400, 500, and 600 °C) and holding periods (15, 30, and 45 min), with three replicates under each condition (the result was reported as arithmetic mean). About 15 g of sample was loaded into the reactor and purged with nitrogen gas for 15 min. The reactor was then heated from room temperature to a given temperature at a heating rate at 10 °C/min and held for a targeted period. The solid biochar was collected and weighed after cooling the reactor to room temperature. The biochar product was labeled as RHxx-TEMP-TIME, where xx, TEMP, and TIME are the RH mass fraction, pyrolysis temperature, and hold time, respectively. For instance, RH100-400-15 refers to the biochar obtained from 100% rice husk pyrolyzed at 400 °C with 15 min holding time.

#### 2.3. Material Characterizations

All samples were dried in an oven at 105 ± 1 °C for at least 24 h before analysis. Proximate, ultimate, and heating value analyses were performed for the raw materials and biochar samples using a LECO TGA801 macro thermogravimetric analyzer, LECO CHN628 elemental analyzer, and LECO AC350 calorimeter (LECO Corp., St. Joseph, MI), respectively. The surface morphologies, surface areas, and chemical structures of four selected biochar samples, i.e., RH100-400-15, RH100-500-15, RH50-400-15, and RH50-500-15, were determined using a JEOL SEM analyzer JSM-6610 LV (JEOL Ltd., Tokyo, Japan), Belsorp mini II BET analyzer (MicromacBEL Corp., Osaka, Japan), and PerkinElmer KBr FTIR (PerkinElmer Corp., Waltham, MA), respectively. Thermogravimetric analysis (TGA) was conducted using a PerkinElmer Pyris 1 TGA (PerkinElmer Corp., Waltham, MA). About 20 mg of sample was heated from 30 to 900 °C at a heating rate at 10 °C/min under a nitrogen atmosphere for analysis of moisture content (M), volatile matter (VM), and fixed carbon (FC) and under air for analysis of ash (A) (50.0 mL/min gas flow rate) according to ASTM D3172,\textsuperscript{35} D3173,\textsuperscript{36} and D3175.\textsuperscript{37}

#### 2.4. Data Processing

The biochar yield \(Y\) was calculated by eq 1.

\[
Y(\text{wt}%) = \frac{\text{weight of the product after experiment (g)}}{\text{weight of the original sample (g)}} \times 100
\]  

\[\text{(1)}\]

For copyrolysis, the synergistic effect, \(\Delta Y\) of RH and HDPE was determined by comparing the differences of product yields between the theoretical and experimental values. Positive and negative values of \(\Delta Y\) illustrate positive and negative effects of copyrolysis, respectively.

\[
Y_{\text{theo}} = Y_1 \times W_1 + Y_2 \times W_2
\]  

\[\text{(2)}\]

where \(Y_{\text{theo}}\) and \(Y_{\text{ex}}\) are the theoretical and experimental biochar yields, respectively, and \(Y\) and \(W\) are the experimental biochar yield and the mass fraction of each feedstock.

The energy yield \((\eta_{fi})\) and fixed carbon yield \((Y_{fi})\) were calculated using the following equations as indicators of process performance.

\[
\text{energy yield(}\eta_{fi}) = Y \times \frac{\text{HHV}_{bc}}{\text{HHV}_{dry}}
\]  

\[\text{(4)}\]

\[
\text{fixed carbon yield(}Y_{fi}) = Y \times \frac{\text{FC}}{100 - \text{feed ash}}
\]  

\[\text{(5)}\]

where HHV\(_{bc}\) and HHV\(_{dry}\) are the higher heating values (MJ/kg) of the feedstock and the corresponding biochar product, respectively, and FC (%) is the fixed carbon content of the biochar product.

### 3. RESULTS AND DISCUSSION

#### 3.1. Raw Material Characterizations

Table 1 illustrates the results of proximate and ultimate analyses of raw RH and HDPE.

| Property                        | RH                | HDPE              |
|--------------------------------|-------------------|-------------------|
| moisture (wt %, ar)             | 7.04 ± 0.02       | 0.22 ± 0.04       |
| volatile (wt %, daf)            | 61.70 ± 0.74      | 97.14 ± 0.52      |
| fixed carbon (wt %, daf)        | 15.31 ± 2.21      | 0.00 ± 0.00       |
| ash (wt %, daf)                 | 15.95 ± 1.47      | 2.64 ± 0.25       |
| ultimate analysis (wt %, daf)   |                   |                   |
| C                               | 46.75 ± 0.64      | 83.69 ± 0.45      |
| H                               | 6.66 ± 0.11       | 15.23 ± 0.25      |
| N                               | 0.66 ± 0.15       | 0.21 ± 0.01       |
| O (daf)\textsuperscript{6}      | 45.94             | 0.88              |
| O/C                             | 0.74              | 0.01              |
| H/C                             | 1.71              | 2.18              |
| higher heating value (MJ/kg\textsuperscript{-1}, db) | 15.59 ± 0.02 | 43.89 ± 0.10 |

\textsuperscript{6}O = 100-C-H-N.

HDPE. The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the samples under a nitrogen atmosphere are shown in Figure 2 and exhibit significantly different thermal behaviors owing to their composition differences. RH mass loss behavior is similar to other biomass materials, as it is mainly comprised of cellulose, hemicellulose, and lignin (Figure 2A). The decomposition of RH primarily occurs between 240 and 400 °C, with a maximum mass loss rate of 1.80% /min at 316 °C (Figure 2B). The shoulders of the DTG curve (202–345.5 °C) indicate simultaneous degradation of cellulose and hemicellulose decomposition,\textsuperscript{38} and the mass loss after 400 °C is associated with lignin degradation and material carbonization.\textsuperscript{39} In contrast, the thermal decomposition of HDPE only has a single sharp peak (398–473 °C) with a maximum mass loss rate of 6.47% /min at 443 °C, which is similar to the reported values, 398–474 °C.\textsuperscript{38,40,41} The decomposition of HDPE starts at a temperature, 398 °C, at which the RH already lost 57.38 wt % mass. As HDPE is mainly polymerized ethylene, only ~21.5 wt % remains as...
residue at 900 °C, whereas the value for RH is 33.19 wt % due to its high ash content (~16%) and more complex molecular structure.

3.2. Biochar Yields. 3.2.1. Pyrolysis of RH. Figure 3 displays the yields of biochar from RH pyrolysis under different operating conditions. As expected, the biochar yields decrease with an increase of pyrolysis temperature, as the higher temperature usually leads to increased cracking of organic constituents of biomass.42 The biochar yield at 400 °C, 53.14–55.06 wt %, is higher than those obtained at 500 and 600 °C, 47.54 and 40.20 wt %, respectively. This may result from the secondary decomposition of the biochar or biomass under elevated temperature conditions, 400–600 °C.43 The temperature has less impact on the yield when increased from 500 to 600 °C, as the major fraction of hemicellulose and cellulose and part of the lignin already degraded when the temperature reaches 500 °C. This is also demonstrated by the TGA analysis, i.e., no significant mass loss after 500 °C.

The holding time exhibits only minor impacts in the biochar yield, i.e., the change of yields is not significant when the holding time was extended from 15 to 45 min. Approximately 3 wt % decreases of biochar yield were observed in RH100-500 and RH100-600 tests when the holding time was increased from 30 to 45 min. Theoretically, the degradation of the feedstock increases with the holding time.44,45 The TG curves in Figure 2A exhibit limited mass loss above 450 °C, and this could be thought to equate to extended hold time as the temperature increases for an additional 40 min from 500 to 900 °C.

3.2.2. Copyrolysis of RH and HDPE. The temperature and holding time have similar impacts on biochar yields as those of RH pyrolysis for copyrolysis of RH and HDPE. Thus, the mass fraction of HDPE becomes the dominant factor in biochar yields (Figure 4). As the biochar yield from 15 min holding is similar to that from 30 and 45 min, only data obtained from 15 min are included in Figure 4. Overall, different trends are observed for copyrolysis temperatures of 400 and 500/600 °C.
The increase of HDPE mass fraction initially results in decreased biochar yields when the pyrolysis temperature is at 400 °C, i.e., the yield decreases from 41.36 to 33.02 wt % when the HDPE mass fraction increased from 10 to 30 wt % (RH90 to RH70). The yields, however, increase to 42.24 and 49.29 wt % when the HDPE fraction is 40 and 50 wt %, respectively, which may result from the incomplete degradation/reaction of HDPE, as the pyrolysis temperature is not high enough. Similar results were reported by Caglar and Aydinli\textsuperscript{46} that a wax of ultrahigh-molecular-weight polyethylene (UHMWPE) formed inside the reactor when copyrolysis was conducted with hazelnut shell and UHMWPE at 425 °C, which was lower than the maximum decomposition temperature of UHMPE, 485 °C. In addition, the incomplete degradation of HDPE is also demonstrated by the proximate analysis, i.e., the volatile matter contents of the solid products obtained at 400 °C using RH60 and RH50 feedstocks are both >50 wt %. The increased yield of solids is associated with the melting of HDPE and RH is coated by melted HDPE, which possibly hinders the escape of VM from the RH and leads to coking\textsuperscript{47}.

Opposite trends are observed when the copyrolysis temperature is at 500 and 600 °C. A lower solid yield is obtained from feedstock with a lower RH content, as most HDPE in the sample already evaporated when the temperature went beyond its main decomposition temperature (at ∼474 °C according to TGA in this study). When the HDPE mass fraction increased from 10 to 50 wt %, the biochar yields decreased from 36.53 to 22.91 wt % at 500 °C and from 36.95 to 22.42 wt % at 600 °C. Similar results were also reported by Caglar and Aydinli\textsuperscript{46} on copyrolysis of hazelnut and UHMWPE at different weight ratios. With an increase of plastic fraction, the solid yield decreased from 26.0 to 5.0 wt % at 515 °C\textsuperscript{46}. The yields of gas-phase products also increased with an increase of plastic fraction and pyrolysis temperature, resulting in a lower char yield. Abnisa et al.\textsuperscript{48} quantified bio-oil production from copyrolysis of palm shell and PS with different ratios (PS decomposition temperature >350 °C\textsuperscript{46}) and found that oil yield continuously increased from ∼45 to >60 wt % with an increase of PS fraction from 20 to 60 wt % at 400 °C, whereas the char yield decreased from ∼27 to 14 wt %.

3.2.3. Synergistic Effects. The difference in theoretical and experimental yields, ΔY, is used to evaluate the synergistic effect of mixing the RH and HDPE (Figure 5). The copyrolysis generally exhibits negative impacts on biochar production, as indicated by the negative values of ΔY. As the primary target of copyrolysis is to improve the yield and quality of bio-oil,\textsuperscript{26,27,29,50–52} the negative synergistic effect on biochar production can be attributed to the interaction between biomass and polymer that tends to produce more volatile products. The free radicals derived from RH decomposition initially promote the degradation of HDPE and the formation of hydrocarbon radicals. This interaction involves initiation and secondary radical formation via depolymerization, H transfer, and reaction between radicals\textsuperscript{36,53}. Similar results were reported by Chen et al.\textsuperscript{54} on the copyrolysis of waste newspaper (WP) and HDPE, and the negative synergistic effects on biochar production were observed.

The ΔY at 400 °C is much lower than that at 500 and 600 °C, indicating that the impact of radical interaction on solid product yields is much less when the copyrolysis temperature exceeds the HDPE decomposition temperature. ΔY is found to decrease with an increase of HDPE mass fraction, reach the minimum value with RH70, and then increase with the HDPE fraction for RH60 and RH50 when the copyrolysis temperature is at 400 °C. This may relate to both the heat transfer in the reactor and the interactions between RH and HDPE radicals. As higher plastic ratios can cause more agglomeration of particles in the blended samples, the heat transfer across the entire sample becomes poor. Furthermore, the amount of free radicals generates from RH decomposition for activating the HDPE degradation decreases with the RH fraction in the samples, resulting in the incomplete conversion of HDPE in RH60 and RH50 samples at 400 °C. Activated hydrocarbon radicals may also react with the free radicals from RH and form stable species, which are then adsorbed on the RH residue,\textsuperscript{55} leading to a slight increase in ΔY values.

3.3. Biochar Characterizations. 3.3.1. Proximate, Ultimate, and HHV Analyses. The results from proximate, ultimate, and HHV analyses for both individual and blended biochars are illustrated in Figures 6 and 7 and listed in Table 2. As the influences of temperature and holding time on RH biochars (RH) and copyrolysis biochars (RH50 to RH90) are relatively similar, they are discussed together. The impacts of feedstock ratios are discussed separately.

The VM contents are greatly decreased from 25.46–26.64 to 7.01–9.57 wt % in RH biochars and from 8.57–65.21 to 4.35–19.53 wt % in blended biochars when the pyrolysis temperature increases from 400 to 600 °C. More volatiles and gases are released under high-temperature conditions,
resulting in increases of FC (from 42.27–43.03 to 52.18–54.27 wt % in RH biochars and from 18.95–55.21 to 46.44–58.23 wt % in blended biochars) and ash (from 31.08–31.53 to 37.84–40.81 wt % in RH biochars and from 15.85–37.95 to 34.04–39.50 wt % in blended biochars) contents. The changes in product compositions are associated with the decompositions of hemicellulose, cellulose, and some lignin in raw RH. Further decomposition of the lignocellulosic structure would be responsible for a lower VM content at 600 °C, and FC is gradually formed through volatilization, char rearrangement, and deactivation reactions. Small changes in RH proximate analysis results are observed for different holding times (<4% absolute) at the same pyrolysis temperature. The impacts of holding time, however, are more significant for blended biochars, especially when the plastic fraction is high. For instance, more than 8 and 6 wt % changes in combustible fractions (i.e., VM and FC) of RH60 biochars produced at 500 °C are observed when the holding time is extended from 15 to 30 and 30 to 45 min, respectively. A longer holding time generally diminishes the amount of solid product via secondary biochar cracking, leading to changes in their proximate compositions. Moreover, Ronsse et al. and Pecha and Garcia-Perez reported that the primary volatile products can be further cracked or repolymerized via secondary reactions if the vapor holding time is more than 1 s. Thus, more vapor phase homogeneous reactions occurred with an increased holding time, i.e., a longer holding time provided more chances for the hot biochar to react with volatile products generated. Although temperature and holding time
both influence proximate analysis of biochars, the temperature has more significant impacts. There is a significant improvement in the C content of all biochars as compared to that of raw RH. A slow pyrolysis process mainly induces bond breaking between C and functional groups on the biomass surface, such as −OH, aliphatic C−O, and aliphatic C−H groups. Thus, an increase in C content in the solid products is expected from the pyrolysis process. The C content of the RH biochars produced at 400 °C is ∼1.5 times higher than that of the original RH under all holding times. When the temperature increases from 400 to 600 °C, the C content increases from ∼70 to ∼80 wt % for RH biochars and ∼80 to 88 wt % for blended biochars. A maximum of 6.78 wt % increase of C content can be achieved by increasing the holding time. Besides, the decrease of H and O contents is observed. Similar to biochar yields, the holding time seems to have less impact on the biochar element compositions than temperature. The C content is in a range of other agricultural biochar products, i.e., empty fruit bunch, corncob, oak slabs, and Leucaena wood, 60 and 95 wt %, respectively.63,64

Table 2 presents the sample HHV data. Values increase from ∼14 MJ/kg for raw RH to 19−20 MJ/kg for RH biochars and 19−31 MJ/kg for blended biochars. Angin65 suggested that HHV in biomass is typically upgraded as a function of pyrolysis temperature. No significant changes of HHV are observed with temperature change for RH biochars, whereas the HHV of blended biochars with the highest HDPE blending rates decreases by ∼36% (relative) when the temperature increases from 400 to 600 °C. The holding time is found to have less influence on the HHV of biochars.

The feedstock ratio is the dominant factor in co-pyrolysis. Two different trends are observed from proximate analysis at 400 °C and at 500/600 °C when HDPE is added. At 400 °C, VM sharply increases from 16.25 to 66.28 wt % when the HDPE ratio increased from 10 to 50 wt % (RH90 to RH50), resulting in a decrease in FC and ash content. As the ash content of HDPE is almost 0 wt %, a higher HDPE fraction in feedstock leads to a lower ash content in the final biochars. At 500 and 600 °C, fewer variations in VM (between 5.06 and 14.65 wt %), FC (between 52.04 and 58.23 wt %), and ash content (between 33.31 and 37.83 wt %) are observed, except for the feedstocks with high plastic ratios, i.e., RH60 and RH50.

The addition of HDPE noticeably affects the elemental composition of biochar. In comparison with the RH biochars obtained under the same conditions, an increased C content (i.e., 5.14−17.29, 2.90−15.82, and 0.85−5.22 wt %) and a decreased O content (i.e., 7.97−15.66, 3.19−13.23, and 0.24−4.13 wt %) are observed in blended biochars obtained at 400, 500, and 600 °C, respectively. Changes in the H content depend on the HDPE fraction in the raw samples. An increase in the HDPE fraction from 0 to 20 and 30 wt % results in an increased C content of the blended biochar pyrolyzed at 400 and 500/600 °C. The C content then reduces due to the further increase of HDPE fraction (i.e., RH60−500−15 = 88.37 wt % C; RH50−500−15 = 87.85 wt % C). An opposite trend, however, is observed for the H content, except for a sharp reduction of the H content of the blended biochar obtained at 500 and 600 °C (i.e., RH60−500−15 = 4.94 wt % H; RH50−500−15 = 3.11 wt % H) when the HDPE fraction increased from 40 to 50 wt %. One possible explanation for the reduction in the H content would be the interaction between plastic materials and hot biochars, releasing more H into gas-phase products such as CH4 and H2, resulting in a lower H content. Similar results were reported by Chen et al.,66 wherein a 4.81 wt % (absolute) increase in C (59.00−63.81 wt %) and a 5.1 wt % (absolute) decrease in O (38.88−33.78 wt %) due to the addition of 50 wt % HDPE in newspaper waste for co-pyrolysis were found. The improvement in biochar quality may associate with the presence of reactive H, transferring from polyethylene chains to RH-derived radicals, resulting in secondary cracking of RH-derived biochar.66 The addition of 10 wt % HDPE leads to a sharp reduction of the O content, resulting in an increase in C content. No significant change in the O content is observed for the feedstocks with higher HDPE contents (20−50 wt %).

It is worth noting that the HDPE fraction has more significant impacts on proximate and ultimate analysis results at 400 °C rather than that at 500 and 600 °C, at which HDPE decomposition is completed, as the decomposition of HDPE begins at 400°C. Incomplete degradation of HDPE is observed at 400 °C, ∼25 wt % HDPE is degraded. A higher plastic fraction can result in agglomeration of particles inside the reactor and hinder the heat transfer across the entire sample, as the heat flow is influenced by the particle size and heterogeneity of samples and pyrolysis products.67 Less variation of chemical composition, therefore, is observed at 500 and 600 °C, as HDPE is mostly volatilized.

To assess the graphitization and aromatization of the biochar products, their H/C and O/C ratios are compared to other conventional solid fuels on a van Krevelen diagram (Figure 8). In comparison with raw RH (O/C = 0.74), the O/C values for

Table 2. Higher Heating Value (HHV) for the Biochar Produced in This Study

| temperature (°C) | RH100 | RH90 | RH80 | RH70 | RH60 | RH50 |
|------------------|-------|------|------|------|------|------|
| Holding Time of 15 min |       |      |      |      |      |      |
| 400              | 19.38 ± 0.39 | 20.95 ± 0.21 | 21.92 ± 2.88 | 21.21 ± 0.18 | 28.87 ± 0.92 | 30.01 ± 3.00 |
| 500              | 19.44 ± 0.43 | 20.68 ± 0.52 | 19.78 ± 0.17 | 20.95 ± 0.11 | 22.95 ± 0.86 | 20.62 ± 0.79 |
| 600              | 20.27 ± 0.47 | 19.86 ± 0.42 | 20.18 ± 0.11 | 20.57 ± 0.30 | 18.90 ± 0.41 | 19.56 ± 0.27 |
| Holding Time of 30 min |       |      |      |      |      |      |
| 400              | 19.48 ± 0.26 | 20.66 ± 0.42 | 20.86 ± 1.77 | 22.29 ± 1.53 | 28.32 ± 0.81 | 31.40 ± 2.28 |
| 500              | 19.65 ± 0.65 | 19.88 ± 0.57 | 20.00 ± 0.17 | 20.07 ± 0.17 | 21.41 ± 0.76 | 19.17 ± 0.61 |
| 600              | 20.19 ± 0.22 | 19.58 ± 0.18 | 20.50 ± 0.00 | 20.22 ± 0.38 | 20.15 ± 0.35 | 20.21 ± 0.23 |
| Holding Time of 45 min |       |      |      |      |      |      |
| 400              | 19.10 ± 0.36 | 21.55 ± 0.37 | 19.86 ± 2.02 | 19.47 ± 1.19 | 26.52 ± 1.98 | 30.70 ± 1.88 |
| 500              | 19.41 ± 0.27 | 19.83 ± 0.47 | 19.95 ± 0.28 | 20.03 ± 0.20 | 21.18 ± 0.83 | 19.41 ± 0.54 |
| 600              | 19.88 ± 0.11 | 18.75 ± 0.28 | 20.30 ± 0.25 | 19.87 ± 0.38 | 20.62 ± 0.27 | 19.63 ± 0.09 |
both individual and blended biochars are quite low, ranging between 0.07 and 0.23 for RH biochars and 0.03 and 0.13 for blended biochars, and the value tends to decrease with an increase of pyrolysis temperature. The decrease in O/C indicates a higher degree of carbonization owing to the removal of hydrophilic functional groups from original RH feedstock structures. A different trend of the O/C ratio is observed at high HDPE ratios (RH60 and RH50). The O/C ratio first increases slightly and then decreases with the change in the temperature from 400 to 500 °C and then 500 to 600 °C, respectively.

Similarly, H/C decreases as the temperatures increase from raw RH (H/C = 1.71) to RH biochars (H/C = 0.38–0.88) and blended biochars (H/C = 0.28–1.54). A reduction in the H/C ratio usually indicates higher structural stability in biochar due to the increase in aromaticity. Similar results were reported by Kaewtrakulchai et al. on the influences of temperature on fuel characteristics of biochars obtained from corn stalk, pineapple residue, and cassava cake, in which H/C and O/C were found to decrease from 0.61–0.80 to 0.38–0.43 and 0.22–0.30 to 0.14–0.16, respectively, with an increase of pyrolysis temperature from 400 to 600 °C. Overall, variations in H/C and O/C among biochar samples decrease under higher reaction temperatures, indicating that aromaticity and polarity in biochars become more homogeneous through dehydration and decarboxylation reactions.

Biomass loses more O and H than C in the pyrolysis process (Figure 8). The changes in biochar properties, therefore, are associated with an increase of C content, resulting in an increase of HHV and the energy density of the biochar produced. The H/C and O/C of most biochars obtained in this study are close to coal and anthracite, whereas the RH60 and RH50 biochars are comparable to the broader range of coal types, indicating that copyrolysis improves biochar when plastic addition is <40 wt %, especially at low temperatures, i.e., <450 °C. For other applications, Schimmelpenning and Glaser suggested that biochars with <0.6 H/C and <0.4 O/C would be suitable for soil amendment and carbon sequestration, as biochars with low atomic O/C could endure in soil for hundreds of years (long-term stability).

The addition of HDPE has positive impacts on the HHV of biochars in most cases, especially in RH50 biochars. The higher HDPE fraction generally results in an increased heating value of blended biochars obtained at 400 °C, whereas only small HHV changes are observed for blended biochars obtained at 500 and 600 °C. The increase of HHV is associated with changes in proximate compositions. RH50 has the lowest initial ash content and the biochar obtained at 400 °C is with the highest VM and FC content, leading to the highest HHV, ~30–32 MJ/kg, whereas blended biochars produced at 500 and 600 °C are with lower combustible fractions. Most volatiles from HDPE are released to the gas phase when the temperature is greater than the main decomposition temperature of HDPE, resulting in lowered HHV of blended biochars obtained at 500 and 600 °C. For instance, ~30% reduction in HHV of RH50 biochar is found when the temperature increases from 400 to 500 °C (from 30.01 to 20.62 MJ/kg) and from 400 to 600 °C (from 30.01 to 19.56 MJ/kg), which is also reflected by the decrease of combustible fractions in the biochar: from 85.19 to 62.51 and 60.51 wt % when the temperature is increased from 400 to 500 and 600 °C, respectively.

3.3.2. Structural Analysis. The chemical structure analysis results from FTIR, BET, and SEM on the selected biochars are shown in Figures 9–11 and listed in Table 3. The functional

![Figure 8](https://doi.org/10.1021/acsomega.1c03874) van Krevelen diagram for biochar productions under a constant holding time of 15 min (green markers represent biochars produced at 400 °C, blue markers represent biochars produced at 500 °C, and yellow markers represent biochars produced at 600 °C) (Figures S5 and S6 refer to van Krevelen diagrams for biochar productions under constant holding times of 30 and 45 min, respectively).

Figure 9. FTIR spectra of selected biochars (RH100-400-15, RH50-400-15, RH100-500-15, and RH50-500-15).

| Biochar Sample | Surface Area (m²/g) | Pore Volume (×10⁻⁹ cm³/g) | Average Pore Size (nm) |
|----------------|----------------------|----------------------------|------------------------|
| RH100-400-15   | 1.546                | 88.576                     | 22.913                 |
| RH100-500-15   | 2.585                | 75.832                     | 117.330                |
| RH50-400-15    | 0.286                | 5.580                      | 8.137                  |
| RH50-500-15    | 2.036                | 107.30                     | 210.860                |
The band at 3400 cm\(^{-1}\) is attributed to stretching vibrations of O–H. Distinct peaks are observed at 2915 and 2850 cm\(^{-1}\); indicating asymmetric and symmetric stretching of C–H in CH\(_2\) groups from the polyethylene matrix. The absorption peak at around 1600 cm\(^{-1}\) relates to deformation vibrations of the water molecules (δ-H\(_2\)O) and the aromatic groups in lignin (C=C stretching) that are normally found in biochars. The peak at 1470 cm\(^{-1}\) is the C–H bending band of CH\(_2\) groups. In addition, the peak at ∼1435 cm\(^{-1}\) is defined as CH deformation in the lignin and carbohydrates (cellulose and hemicellulose). Moreover, the most intense band at 1099 cm\(^{-1}\) corresponds to the vibration of silicon–oxygen tetrahedrons (SiO\(_4\)) and the main vibrations of the C–OH bond in cellulose. The absorption peak at 790 cm\(^{-1}\) represents the presence of symmetric vibration of the Si–O–Si bond. Finally, the peak at ∼720 cm\(^{-1}\) is also attributed to the CH\(_2\) rocking mode.

The impacts of temperature can be identified from the O–H functional group at 3400 cm\(^{-1}\) in RH and blended biochars. The increase of temperature leads to more release of free and intermolecular-bonded hydroxyl groups –OH between cellulose chains. Thus, the peak is more significant in RH100-400-15 and RH50-400-15 samples but almost disappears in RH100-500-15 and RH50-500-15 samples. The decrease in O–H stretching illustrates an improvement in hydrophobicity of the biochar due to dehydration, resulting in improved fuel stability during fuel storage and handling in humid environments.\(^{57,64}\) The RH biochars (RH100-400-15 and RH100-500-15) have a significant peak at 1600 cm\(^{-1}\), representing the remnants of some lignin fragments and intermediate structures. The intensity of this peak, however, is weakened in copyrolysis of biochars (RH50-400-15 and RH50-500-15) owing to the decreased lignin content of the feedstocks replaced by HPDE. Moreover, the presence of the peaks at 2915, 2850, 1470, and 720 cm\(^{-1}\) is associated with the addition of HDPE in RH50-400-15, but these peaks almost disappear in RH50-500-15. Peaks at 1435, 1099, and ∼790 cm\(^{-1}\) derived from the chemical structure of RH still exist in the blended sample at 500 °C (RH50-500-15), indicating that the addition of HDPE has fewer impacts on the biochar chemical structure under the higher pyrolysis temperature conditions, as HDPE is mostly evaporated (especially when the pyrolysis temperature is higher than the decomposition temperature of plastic).

As biochar can be also utilized as low-cost natural adsorbents, the surface area, pore volume, pore size, and morphology of the biochar obtained are characterized and shown in Table 3 and Figures 10 and 11. Overall, the BET surface area of biochar increases with pyrolysis temperature due to the decomposition of hemicellulose, the depolymerization of cellulose, and the partial degradation of lignin. The VM, therefore, is released from the biochar matrix, forming voids or pores.\(^{57,64,66}\) An increased surface area is observed in both RH biochar and blended biochar when the temperature is increased from 400 to 500 °C. The surface area of RH100-500-15 is ∼1.67 times higher than that of RH100-400-15 but with a smaller pore volume due to the destruction of pore walls under higher pyrolysis temperature conditions.\(^{64,67}\) Similar phenomena are also observed in blended biochars except for the larger average pore size in RH50-500-15. Moreover, the pore type increases from mesopore (2–50 nm) to macropore (>50 nm) when the temperature is increased from 400 to 500 °C.

A drastic reduction of surface area, more than five times, is observed when 50 wt % HDPE is added to the feedstock (RH50-400-15), as HDPE in RH50 melted rather than evaporated at 400 °C. A different trend, however, is observed...
when comparing the RH biochars to blended biochars obtained at 500 °C (RH100-500-15 and RH50-500-15), i.e., a slightly reduced surface area of RH50-500-15, 20% (relative). The pore volume and size, however, both increase in blended biochar at 500 °C due to the release of volatiles from HDPE via thermal decomposition, resulting in a higher pore volume and larger pore size. Thus, the pyrolysis temperature is crucial for the production of biochars through copyrolysis of biomass and plastics.

The morphology of RH biochar (RH100-400-15) analyzed by SEM exhibits an amorphous structure with some irregular-shaped holes due to dehydration and devolatilization of cellulose. The regular pore structures, however, all disappear in blended biochar (RH50-400-15). The surface is smoother with almost no developed pores, which is similar to the SEM image of plastic waste materials presented by Zhou et al.21 Melted HDPE may cover and block existing holes and voids in the biochar. Besides, the RH biochar is also capable of adsorbing some volatile species (VOCs) from HDPE.26 As RH50-400-15 biochar has a relatively low surface area and porosity, it cannot be employed as an adsorbent. The copyrolysis biochar obtained at higher temperatures (e.g., RH50-500-15), however, may be applied for adsorption.

3.4. Energy and Fixed Carbon Yields. The energy (η_E) and fixed carbon yield (Y_{fc}) are calculated and plotted as a function of the HDPE fraction in the feedstocks in Figure 12 to evaluate the feasibility of blended biochar to be used as a solid fuel. η_E represents the amount of energy retained in biochars after the pyrolysis process, whereas Y_{fc} is an economic parameter to evaluate the performance of the carbonization process.77 The higher the η_E and Y_{fc} of biochars, the greater the economic feasibility for biochar to be used as a solid fuel.

In general, η_E mainly depends on biochar yields and biomass types.78 The maximum η_E >70%, is achieved for RH biochar produced at the lowest pyrolysis temperature, i.e., 400 °C, whereas the lowest η_E is found for RH biochar obtained at the highest temperature with the longest holding time, only ∼55% (RH110-600-45), resulting from the increased degradation of hemicellulose, cellulose, and lignin under elevated temperatures. Similar results were reported by Matali et al.79 on torrefaction of woody biomass. About 28 wt % reduction in the η_E was observed from 99.20 to 71.20% when the temperature was increased from 200 to 300 °C.

The η_E drops continuously with an increase of HDPE fraction in feedstock for the copyrolysis process, except for RH60 and RH50 biochars at 400 °C, for which the HHV of the blended biochars is greater than that of the corresponding RH biochars owing to the existence of HDPE residues. The η_E values for these RH60 and RH50 biochars, however, are still lower than those for RH100 biochars obtained under the same pyrolysis conditions. Although the HHV of the blended biochars does not change significantly with the HDPE fraction in feedstocks, the η_E continuously decreases with an increase of pyrolysis temperature and reaches the minimum value of ∼15%.

The impact of feedstock HDPE ratios on Y_{fc} is similar to that on η_E. A continuous decrease in Y_{fc} is observed, from 28 to 12%, when the HDPE fraction increases from 0 (RH100) to 50 wt % (RH50), which is also associated with the decrease of FC content and biochar yield. Operating parameters (temperature and holding time) slightly affect the Y_{fc}. Although higher temperatures usually result in biochars with higher FC contents, the Y_{fc} only slightly changes, in a range of 25.3−28.5% under all testing conditions. Thus, the copyrolysis of biomass and plastic would not offer economic feasibility when only considering solid fuel production.

4. CONCLUSIONS

Biochar yields and properties from copyrolysis of RH and HDPE were investigated in the temperature range of 400−600 °C with 15−45 min holding periods. The operating parameters exhibited similar impacts on both RH pyrolysis and copyrolysis. The yields and physicochemical properties of biochar were mainly affected by pyrolysis temperature, and the impact of holding time is very limited. The biochar yields decrease with an increase of temperature for RH pyrolysis with 53−55 wt % maximum yield at 400 °C, but no significant impact of temperature on the HHV of biochar was observed. A similar trend was observed for the copyrolysis process, and the highest blended biochar yields were also obtained at 400 °C, 33−56 wt %.

The fraction of HDPE was found to significantly affect both the quality and quantity of blended biochars produced. Blended biochar yields gradually decrease with an increase of HDPE fraction in the feedstock (from 10 to 50 wt %) at 500 and 600 °C but increase with the HDPE fraction at 400 °C, which is associated with the incomplete degradation at 400 °C. Negative synergistic effects on blended biochar production, however, were observed. The addition of 10−20 wt % HDPE improves the quality of biochar based on FC and C analyses, but a further increase of plastic fraction (30−50 wt %) would have negative impacts on the biochar quantity, especially under low-temperature conditions, e.g., 400 °C, at which the heat transfer of the blended samples was hindered due to the agglomeration of particles. Although the HHV was improved at 400 °C with a maximum value of 30 MJ/kg for RH50 biochars, it mainly results from an increase in volatile matter from melted HDPE. The η_E and Y_{fc} analyses, however, illustrate that solid fuel application of the blended biochars from copyrolysis has lower economic benefits in comparison with those of RH pyrolysis. Thus, the solid-, liquid-, and gas-phase products should all be considered for process evaluation in future studies.
**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c03874.

Additional data on biochar yields, Van Krevelen diagrams, energy yields, and fixed carbon yields for 30 and 45 min holding times; nature of materials: recycled graded HDPE pellet of 4 × 4 mm² and ground raw rice husk of 0.5−1.0 mm (PDF)

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