

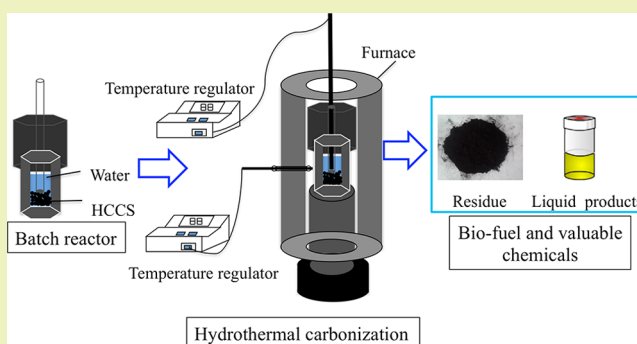
# Characterization of the Residue and Liquid Products Produced from Husks of Nuts from *Carya cathayensis* Sarg by Hydrothermal Carbonization

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**ABSTRACT:** Hydrothermal carbonization is considered to be an environment-friendly method to pretreat biomass. Therefore, hydrothermal carbonization of the husks of nuts from *Carya cathayensis* Sarg, at various temperatures and pHs were performed and the fuel properties of the obtained residue, water-soluble products (WSP) and acetone-soluble products (ASP) were characterized. It was found that the residue yield decreased with increasing hydrothermal carbonization temperature while the yield of total soluble products (WSP and ASP) was nearly the same. The residue and total soluble products yields had no large changes in the pH range of 4.0–10.0, but fewer residues and more total soluble products were obtained at pH 13.0. It was confirmed that hemicellulose was more reactive than cellulose and lignin during hydrothermal carbonization and that lignin could be effectively hydrolyzed/decomposed at pH 13.0. The higher heating values (HHVs) of residues were in the ranges of 22.0 to 28.2 MJ kg<sup>-1</sup> at temperatures from 180 to 260 °C and pH from 4.0 to 10.0. The HHVs of these residues could be comparable with those of some commercial coals, such as lignite. However, the HHVs of residues decreased when the pH reached to 13.0. The WSP and ASP showed lower HHVs compared with heavy fuel oils, which meant the HHVs of WSP and ASP should be increased before being applied as bio-fuels.

**KEYWORDS:** Hydrothermal carbonization, husks of nuts from *Carya cathayensis* Sarg, pH, residue, fuel property



## INTRODUCTION

Biomass, as an important and abundant renewable resource in the world, is considered to be a promising energy alternative to fossil fuels in the future because it is more environment-friendly than fossil fuels in many aspects. Namely, it captures carbon dioxide through photosynthesis, which can offset the carbon dioxide emitted during combustion of biomass, and it also emits less sulfur than fossil fuels when it is combusted. However, biomass is regarded as a low-grade fuel because of its inherent properties such as high moisture content, high volatile content, low energy density and high oxygen content.<sup>1</sup> It is necessary to apply pretreatment processes to overcome these drawbacks.

There are several methods to pretreat biomass: fast and slow pyrolysis to obtain bio-oil and gasification to obtain bio-gases.<sup>2,3</sup> However, all of these treatments are carried out at high temperatures and with a carrier gas throughout the process in order to isolate oxygen and/or carry bio-gases and volatile materials out of the reactor. In addition, all existing treatments require predrying of the biomass in order to improve the quality of the product.

Compared with the methods described above, hydrothermal carbonization using subcritical water has some advantages.<sup>4,5</sup> Lower treatment temperatures (180–260 °C) and the elimination of both a predrying step and the need for a carrier gas should make hydrothermal carbonization a lower-cost

treatment option. Additionally, this method can avoid the noxious air pollution caused by nitrogen and sulfur oxides and corrosion to the treatment equipment from the acidic properties of the generated products in the liquid phase. Taken together, hydrothermal carbonization is a promising method for biomass pretreatment. Up to now, much information could be obtained about hydrothermal carbonization of various biomasses by subcritical water.<sup>6–12</sup> For example, Yan et al. and Reza et al. pretreated loblolly pine with hot compressed water to upgrade the fuel properties of loblolly pine.<sup>4,6,7</sup> Chen et al. performed hydrothermal carbonization of sugarcane bagasse via wet torrefaction for biofuel production.<sup>5</sup> In all of the above research studies, the fuel properties of raw biomass were significantly elevated after hydrothermal carbonization and a solid char with high energy density and calorific value was obtained. However, to our knowledge, there has been no report about the influence of pH on the hydrothermal carbonization of biomass, a key issue because the ion product of subcritical water would be changed with the addition of acid or alkali. It is known that cellulose and hemicellulose are hydrolyzed/decomposed during subcritical water hydrothermal liquefaction<sup>13,14</sup> and that the addition of acid could accelerate

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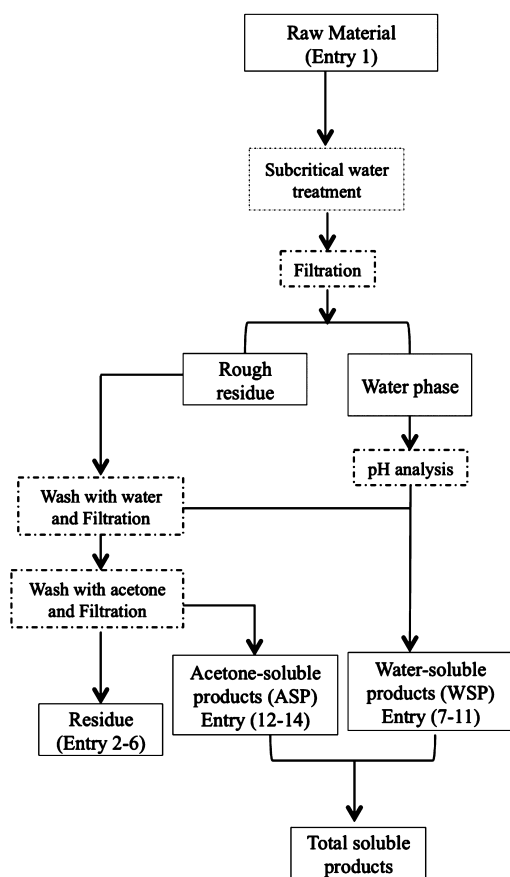
the hydrolysis/decomposition rates, but the effect of pH on hydrothermal carbonization of biomass is still unclear, given its more complex structure than pure cellulose and hemicellulose.

In this study, subcritical water was applied to hydrothermal carbonization of husks of nuts from *Carya cathayensis* Sarg (HCCS, in other words, HCCS is husks of hickory nuts) as a model waste biomass. Roughly 7000 tons of this biomass are generated annually in China, and an effective treatment method for this resource has been anticipated. The purpose of this research is to upgrade the value of HCCS as a fuel source including carbon content, energy value and water-resisting property. The effect of pH on hydrothermal carbonization of HCCS was also investigated in order to determine the optimal conditions for hydrothermal carbonization of HCCS. Further, the fuel properties of obtained liquid products were characterized to evaluate their potential for application as resource for bio-fuel production.

## MATERIALS AND METHODS

**Materials.** HCCS, as the raw material in all the experiments, came from Lin'an, China. The husks were milled and screened using a milling machine (WB-1, Osaka Chemical Corp., Osaka, Japan) to obtain powder with a diameter under 0.3 mm, and the powder was dried at 105 °C for 24 h before the experiments. The reagents used here were all purchased from Wako Pure Chemical Industries (Osaka, Japan).

**Hydrothermal Carbonization of Husks of *Carya cathayensis* Sarg (HCCS).** Figure 1 shows the flow scheme of HCCS treatment during hydrothermal carbonization.



**Figure 1.** Flow scheme of HCCS treatment during hydrothermal carbonization.

Hydrothermal carbonization of HCCS was carried out in a batch reactor (Taiatsu Technology Corp., Osaka, Japan) made from SUS 316 with the volume of 10 mL. A mixture of 200 mg of HCCS and 8 mL of ultrapure water with a pH of 4.0, 5.9, 7.0, 10.0, or 13.0 (pH was adjusted by HCl or NaOH; the pH of ultrapure water was 5.9) was loaded into the batch reactor, and the reactor was tightly sealed. The reactor was then set in a ceramic furnace (ARF-40K, Asahi-Rika, Chiba, Japan) with a digital temperature controller (TXN-700, ASONE, Osaka, Japan). Hydrothermal carbonization was carried out from 180 to 260 °C with the treatment time of 10 min at various pH values. The reactor was immersed in an ice bath as soon as the reaction time elapsed. The mixture was filtered with a G-4 glass filter (Vidtec, Fukuoka, Japan). The pH of obtained filtrate was measured by a HM-25R pH meter (DKK-TOA Crop. Tokyo, Japan). The remaining solid (rough residue) was first washed with 20 mL of ultrapure water and then with 20 mL of acetone. After that, all of the obtained filtrates were dried at 60 °C and the remaining liquid products were designated as water-soluble products (WSP) and acetone-soluble products (ASP), respectively. The residue was dried at 105 °C to reach a constant weight. It should be noted that the partition of the sodium ions (in the case of pH 13) between residue and WSP would be affected by the ion exchange of the sodium ions with the HCCS and neutralization of generated organic acid by NaOH during hydrothermal carbonization. Our X-ray fluorescence (XRF) measurement revealed that the residue contained low amount of sodium ion (less than 0.02 wt %), which was similar to that of raw HCCS. Therefore, to simplify the calculation, we assumed that these sodium ions were primarily present in the residue and all the sodium ions from NaOH were remained in the WSP. We did not consider about the hydroxide ion from NaOH because it might be contained in all of the hydrothermal carbonization products, including water and other volatile products that were difficult to calculate. We also assumed that no ash was dissolved in the subcritical water during hydrothermal carbonization. The yields of the residue, WSP, ASP and total soluble products were calculated by the following equations:

$$\text{yield}_{(\text{residue})} (\%) = \frac{(\text{mass of dry and ash} - \text{free residue})}{(\text{mass of dry and ash} - \text{free HCCS})} \times 100\% \quad (1)$$

$$\text{yield}_{(\text{WSP})} (\%) = \frac{(\text{mass of WSP})}{(\text{mass of dry and ash} - \text{free HCCS})} \times 100\% \quad (2)$$

$$\text{yield}_{(\text{ASP})} (\%) = \frac{(\text{mass of WSP})}{(\text{mass of dry and ash} - \text{free HCCS})} \times 100\% \quad (3)$$

$$\text{yield}_{(\text{total soluble products})} (\%) = \text{yield}_{(\text{WSP})} + \text{yield}_{(\text{ASP})} \quad (4)$$

**Analysis of the HCCS, Residue, WSP and ASP.** The lignin contents of the HCCS and residue were determined by a 72% sulfuric acid method, and the holocellulose and cellulose were measured by the method described by Yokoyama et al.<sup>15,16</sup> The hemicellulose content was calculated by the weight difference between holocellulose and cellulose. The weight of each component was calculated by the following equation:

$$\text{component weight} = C \times \text{weight of the residue} \quad (5)$$

where C is the cellulose, hemicellulose or lignin content in the residue.

The Fourier transform infrared (FTIR) spectra of WSP and ASP were analyzed by Fourier transform infrared spectroscopy (Jasco 4100, Jasco, Tokyo, Japan). The spectra were acquired in the range of 4000–1000  $\text{cm}^{-1}$ .

The C, H and N contents of the residue, WSP and ASP were analyzed using a PerkinElmer 2400 II elemental analyzer (Kanagawa, Japan). The elemental content of the residue was further corrected for ash content to give the elemental content of the residue on an ash-free basis, and the element content of WSP was corrected for the sodium ion content to express the element content on a sodium ion-free basis.

The HHVs of the residue, WSP and ASP were determined from their elemental contents and they were calculated by the equation as follows:<sup>17</sup>

$$\text{HHV (MJ kg}^{-1}\text{)} = 5.22\text{C}^2 - 319\text{C} - 1647\text{H} + 38.6\text{CH} + 133\text{N} + 21028 \quad (6)$$

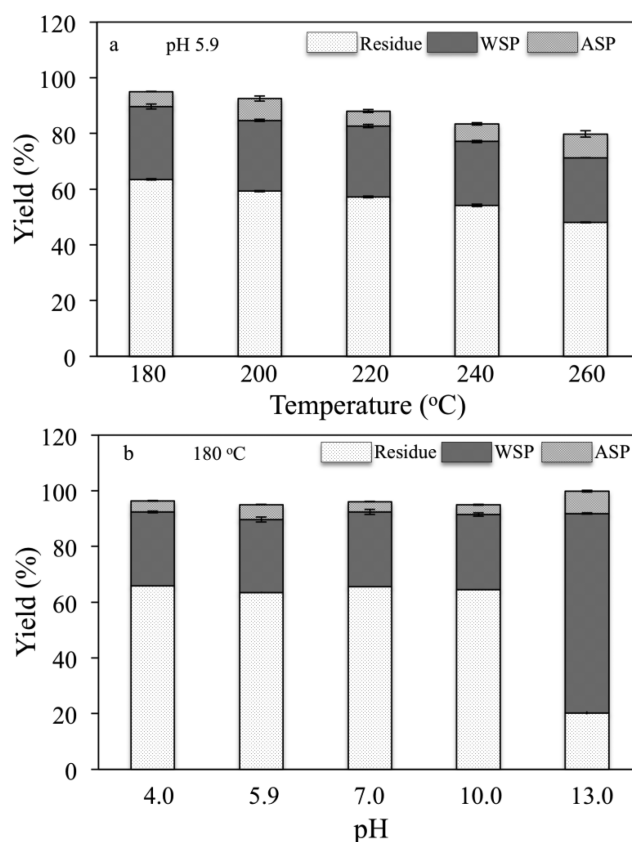
where C = carbon, H = hydrogen and N = nitrogen content expressed on mass percentage.

The method to evaluate equilibrium moisture content (EMC) of the HCCS and residue was as follows: About 100 mg of HCCS or the residue was placed in a plastic dish and then into a big plastic bottle containing a saturated salt solution at the experimental temperature of 30 °C. Each experiment was performed in triplicate. Potassium acetate, magnesium nitrate and sodium chloride with relative humidities (RH) of 23%, 53% and 75%, respectively, were used to control the relative humidity in the plastic bottle. It took 20–30 days for the HCCS and residue to reach equilibrium. The EMC was calculated by the weight difference before and after treatment.

## RESULTS AND DISCUSSION

**Effect of Treatment Temperature and pH on the Yields of the Residue, WSP and ASP.** Figure 2a, b show the effect of hydrothermal carbonization temperature and pH on the yields of residue, WSP and ASP for the treatment time of 10 min, respectively. The yield of the residue was drastically reduced with increasing of hydrothermal carbonization temperatures, and it reached about 48.1% of the initial HCCS when the temperature was 260 °C (Figure 2a), probably due to the hydrolysis/decomposition of cellulose, hemicellulose and apportion of lignin. The yield of WSP showed a slight decrease with the increase in the hydrothermal carbonization temperature and the yield of ASP increased as the hydrothermal carbonization temperature increased to 260 °C. However, the yield of total soluble products hardly changed as the temperature increased from 180 to 260 °C, which revealed that the HCCS hydrolysis/decomposition rate and total soluble products hydrolysis/decomposition rate reached an equilibrium state in the 180–260 °C temperature range. Therefore, the optimal temperature for liquefaction of HCCS to obtain total soluble products in the conditions of our study (e.g., milled input, 10 min treatment time) was 180 °C.

The yields of the residue, WSP and ASP were nearly the same when the pH was increased from 4.0 to 10.0 at each hydrothermal carbonization temperature. However, the yields of WSP and ASP, especially the yield of WSP increased when the pH was 13.0, resulting the yield of total soluble products reached to over 80% even at 180 °C. Meanwhile, the residue yield fell steeply to 20% (Figure 2b). The similar results were



**Figure 2.** Effect of (a) temperature and (b) pH on yields of residue, WSP and ASP. ( $n = 3$ ). Treatment time: 10 min.

obtained when evaluation of the effect of pH on the yields of residue, WSP and ASP at the temperatures of 220 and 260 °C (data not shown). These results suggested that higher pH could effectively liquefy the HCCS during the hydrothermal carbonization process. As reported by Lynam et al., more cellulose could be reacted with large amounts of acetic acid (concentration: 1.79 and 2.31 M), and acetic acid at those concentrations appeared to perform a catalytic role in hydrothermal carbonization.<sup>18</sup> Likewise, in this study, the weights of cellulose, hemicellulose and lignin showed no significant changes in the pH range from 4.0 to 10.0 but were steeply decreased when the pH was 13.0. These phenomena (Table 1), discussed below, indicate that HCl or NaOH at concentrations of  $10^{-4}$  M (pH 4.0–10.0) are not high enough to accelerate the hydrolysis/decomposition of cellulose whereas NaOH at 0.1 M (pH 13.0) did effectively promote the hydrolysis/decomposition of cellulose in the hydrothermal carbonization process.

The mass yield after hydrothermal carbonization was reduced from 95.1% to 79.8% as the temperature increased from 180 to 260 °C. This phenomenon meant that 4.9% to 20.2% of volatile products (i.e., formic acid, acetic acid furfural and water)<sup>13,14</sup> and bio-gases such as  $\text{CO}_2$  and  $\text{NO}_x$  were generated during hydrothermal carbonization.<sup>19</sup> The pH ranging from 4.0 to 10.0 had no effect on the mass yield. However, there was an increase in mass yield when the pH reached 13.0 (Figure 2b) and the same results were obtained at 220 and 260 °C (data not shown). This fact means that a higher NaOH concentration inhibited the generation rates of volatile products and bio-gases.

**Final pH of the WSP.** Organic acids were generated during hydrothermal carbonization of biomass and they would change

Table 1. Effect of Temperature or pH on the Compositions, Elemental Content and HHVs of HCCS and Residues

entry	temperature (°C)	pH	main components <sup>a</sup> (mg)			element content (%)				heating value HHV (MJ/kg)
			cellulose	hemicellulose	lignin	C	H	N	O <sup>b</sup>	
1	25	HCCS	24.7 ± 0.2	41.8 ± 0.3	106.4 ± 0.6	51.5	4.8	0.9	42.8	20.2
2	180	4.0	19.3 ± 0.3	16.3 ± 0.6	83.7 ± 0.7	56.1	5.1	1.1	37.7	22.3
		5.9	18.2 ± 0.6	16.1 ± 2.0	84.7 ± 2.4	55.2	5.3	1.0	38.5	22.0
		7.0	19.6 ± 1.2	15.0 ± 0.2	83.9 ± 0.2	56.3	5.0	1.1	37.6	22.4
		10.0	21.9 ± 0.5	12.9 ± 0.8	82.1 ± 1.0	56.8	5.1	1.1	37.0	22.7
		13.0	9.4 ± 1.4	7.5 ± 1.7	23.7 ± 0.7	42.5	4.7	0.4	52.3	16.9
3	200	5.9	20.7 ± 0.7	10.3 ± 0.8	84.8 ± 0.9	58.6	5.0	1.1	35.4	23.4
		4	220	4.0	23.6 ± 1.3	6.1 ± 0.9	83.8 ± 1.0	61.3	4.5	0.9
4	220	5.9	19.3 ± 0.4	7.6 ± 0.2	88.6 ± 0.2	61.8	4.9	1.0	32.3	25.0
		7.0	19.9 ± 0.8	7.1 ± 0.3	87.9 ± 0.3	61.3	4.8	0.8	33.2	24.6
		10.0	18.7 ± 0.5	8.5 ± 1.2	82.4 ± 3.5	61.0	4.5	0.8	33.7	24.3
		13.0	10.0 ± 0.7	0.6 ± 0.1	10.6 ± 0.7	40.8	3.5	0.0	55.6	16.5
		5	240	5.9	15.1 ± 0.1	7.9 ± 1.2	80.1 ± 1.3	63.1	4.8	0.9
6	260	4.0	10.1 ± 2.6	7.3 ± 0.1	78.9 ± 0.1	67.2	4.4	0.7	27.8	27.4
		5.9	10.2 ± 0.7	7.5 ± 1.3	77.6 ± 1.2	67.2	4.7	0.9	27.2	27.7
		7.0	8.5 ± 0.8	5.9 ± 1.7	76.5 ± 1.5	68.2	4.6	0.7	26.5	28.2
		10.0	8.1 ± 0.4	6.2 ± 1.1	80.2 ± 1.0	67.7	4.6	0.7	27.0	27.9
		13.0	3.5 ± 0.3	0.1 ± 0	5.4 ± 0.1	38.5	9.3	0.8	51.4	15.1

<sup>a</sup>All the experiments were carry out in triplicate. <sup>b</sup>Calculated by difference.

the final pH of water phase. We thus measured the pH of WSP obtained after hydrothermal carbonization of HCCS, and the results are shown in Figure 3. The final pH of WSP decreased

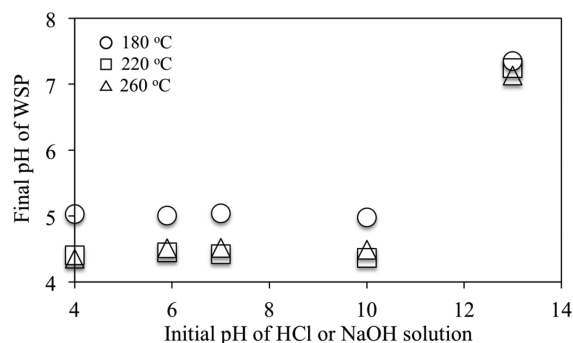


Figure 3. Effect of initial pH on the final pH of WSP obtained at various temperatures.

with the increase in the hydrothermal carbonization temperature and it reduced to 4.4 at 260 °C and initial pH 5.9. Changing the pH from 4.0 to 10.0 had no dramatic effect on the final pH of WSP obtained at the temperature of 180 °C and the final pH of WSP was around 5.0. However, the final pH was 7.4, which was still maintained at the weak alkali value when the initial pH was 13.0. The similar results were also obtained during evaluating the final pH values of WSP in other temperatures. The decrease of final pH during hydrothermal carbonization was mainly caused by the formation of carboxylic acids, including acetic acid, lactic acid and formic acid,<sup>13</sup> whereas the remaining of final pH in a weak alkali value revealed that the generated carboxylic acids were all neutralized by NaOH during hydrothermal carbonization.

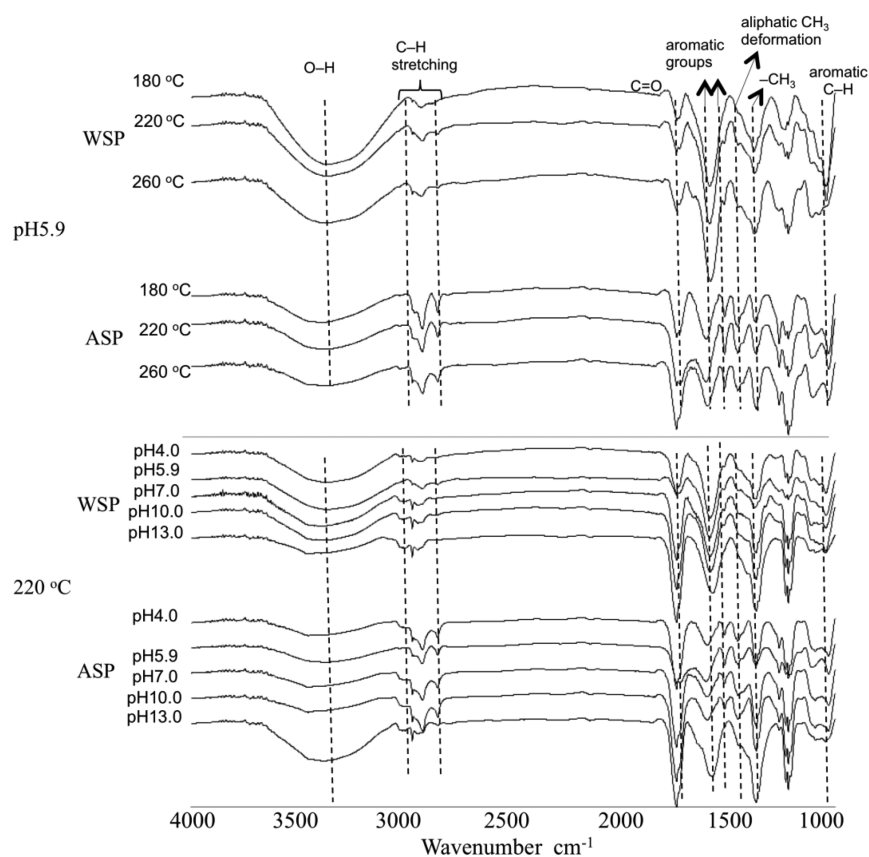
**Determination of Compositions of HCCS and the Residue.** Cellulose, hemicellulose and lignin are the primary components of biomass. In this study, the main components of the residue prepared at various conditions were analyzed to help elucidate the reaction mechanism in hydrothermal carbonization. As shown in Table 1, the weights of cellulose,

hemicellulose and lignin in 200 mg of HCCS before hydrothermal carbonization were 24.7, 41.8 and 106.4 mg, respectively (entry 1). Hemicellulose was dramatically decreased to 10.3 with hydrolysis/decomposition of 75% even at 200 °C (entry 3), and showed further slight reductions at higher temperatures. It seemed more difficult to hydrolyze/decompose cellulose than hemicellulose and the weight of cellulose was reduced from 19.3 to 10.2 mg with the decrease of 11.9% to 58.3% as the temperature increased from 180 to 260 °C (entries 2–6) at the pH of 5.9. The weight of lignin decreased from 83.7 to 77.6 mg with the decline of 21.4% to 27.1% in the temperature range of 180–260 °C (entries 2–6) at pH 5.9. Therefore, cellulose and hemicellulose were more reactive than lignin during hydrothermal carbonization of HCCS, and it was confirmed that this reduction of residue yield was primarily due to the hydrolysis/decomposition of hemicellulose and cellulose in HCCS.

The variation of pH within the range of 4.0–10.0 had no significant effect on the weights of cellulose, hemicellulose and lignin in the residue, resulting the constant values of residue yield. However, all of the solid components, especially the lignin, were dramatically decreased at pH 13.0 (entries 2–5) and almost all of them were hydrolyzed/decomposed at 260 °C (entry 6). It was previously reported that, the addition of H<sub>2</sub>SO<sub>4</sub> to a final concentration of 0.1 M could remove a large amount of hemicellulose at 180 °C in 5 min hydrothermal carbonization of bagasse<sup>5</sup>. In contrast, all of the compositions were effectively liquefied when NaOH was employed at a concentration of 0.1 M (pH 13.0). Therefore, NaOH may be more effective for liquefying biomass than H<sub>2</sub>SO<sub>4</sub> at 180 °C.

**FTIR Results of WSP and ASP.** The mass corresponding to the reduction of HCCS over the hydrothermal carbonization process should be included in the water and acetone solutions, as shown in Figure 1. The fractions recovered by water and acetone were called water-soluble products (WSP) and acetone-soluble products (ASP), respectively. We used FTIR to characterize these fractions according to the temperature and pH of the hydrothermal carbonization (Figure 4). The spectra showed that temperature and pH had no effect on the





**Figure 4.** FTIR spectra of WSP and ASP prepared at various temperatures (above) and pH values (below) at 220 °C.

**Table 2.** Effect of Temperature or pH on the Elemental Contents of WSP and ASP, and HHVs of WSP, ASP

entry	temperature (°C)	pH	WSP					entry	ASP				
			C (%)	H (%)	N (%)	O <sup>a</sup> (%)	HHV (MJ/kg)		C (%)	H (%)	N (%)	O <sup>a</sup> (%)	HHV (MJ/kg)
7	180	4.0	35.2	4.7	0.6	59.4	15.0	12	53.5	6.3	0.7	39.6	21.6
		5.9	39.5	4.3	0.6	55.7	16.1		62.9	4.9	0.9	31.3	25.6
		7.0	33.4	5.1	0.6	60.9	14.5		48.0	6.3	0.6	45.2	19.1
		10.0	34.7	4.5	0.6	60.2	14.9		51.8	5.6	0.7	42.0	20.6
		13.0	25.6	2.7	0.6	71.1	14.6		23.0	4.5	0.4	72.1	13.1
8	200	5.9	34.7	4.2	1.0	60.1	15.1	13	63.7	6.0	1.0	29.4	26.9
9	220	4.0	34.1	4.9	1.2	59.8	14.8	14	59.4	6.1	1.0	33.6	24.5
		5.9	33.7	4.2	1.2	60.9	14.9		61.9	5.1	1.2	31.9	25.2
		7.0	32.1	5.2	1.1	61.6	14.2		56.6	5.8	1.0	36.6	23.0
		10.0	32.1	5.0	1.1	61.8	14.3		60.7	6.3	1.0	31.9	25.5
		13.0	31.4	3.1	0.5	65.1	14.9		23.1	5.4	0.4	71.1	12.4
10	240	5.9	32.4	4.0	1.5	62.2	15.1	15	63.0	5.3	1.2	30.5	26.0
11	260	4.0	32.1	5.4	1.5	61.1	14.2	16	64.4	6.0	1.1	28.5	27.3
		5.9	34.2	4.3	1.6	59.9	15.0		63.5	5.2	1.2	30.1	26.2
		7.0	32.5	5.0	1.5	61.0	14.4		63.5	5.7	1.1	29.7	26.6
		10.0	36.3	5.4	1.6	56.7	15.2		64.0	5.9	1.3	28.9	27.0
		13.0	26.2	3.6	0.4	69.8	14.0		24.6	6.2	0.4	68.8	12.1

<sup>a</sup>Calculated by difference.

adsorption bands of WSP and ASP. The main adsorption bands from WSP were quite similar to those of ASP, indicating that WSP and ASP contained similar functional groups. The O–H stretching vibration around 3300 cm<sup>-1</sup> indicated the presence of phenols and alcohols in WSP and ASP. The O–H stretching vibration of WSP was stronger than that of ASP because phenols, which have lower O–H content than alcohols, were more prevalent in ASP.<sup>20</sup> This peak in ASP became stronger at

pH 13.0, probably due to the hydrolysis/decomposition of phenols. The absorption bands between 2840 and 2960 cm<sup>-1</sup> corresponding to the C–H stretching indicated that hydrocarbon alkyls were one of the products during hydrothermal carbonization. The C=O stretching band at 1740 cm<sup>-1</sup> indicated the presence of esters, carboxylic acids, ketone, aldehydes and/or phenol compounds in the WSP and ASP. The absorption bands around 1600 and 1510 cm<sup>-1</sup> related to

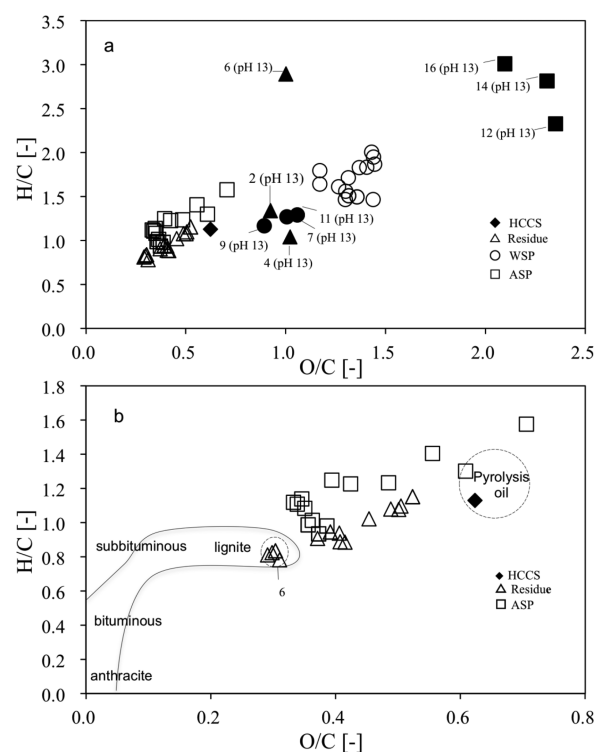
the mono- and polycyclic and substituted aromatic groups due mainly to the decomposition of lignin. The disappearance of the  $1510\text{ cm}^{-1}$  peak in ASP at pH 13.0 suggested that some of the aromatic compounds decomposed at this pH. The absorbance at  $1376\text{ cm}^{-1}$  corresponding to the  $-\text{CH}_3$  bond and the aromatic C–H in-plane plus C–O in the primary stretching band at around  $1050\text{ cm}^{-1}$  indicated the appearance of arone chemicals.<sup>21</sup> We attempted to use gas chromatography–mass spectrometry (GC–MS) as another analytic method to identify the compounds present in the WSP and ASP, but neither the WSP nor the ASP could dissolve in the organic solvents. Therefore, the compounds in WSP and ASP could not be identified in this study (data not shown).

**Elemental Contents and HHVs of Residue, WSP and ASP.** The elemental content of the residue shown in Table 1 helps to illustrate the decomposition progression of HCCS during hydrothermal carbonization. At pH 5.9, the carbon content of the residue increased from 55.2% to 67.2% with the increase of temperature from 180 to 260 °C, and its oxygen content decreased at the same time (entries 2–6 in Table 1). There was no great change in hydrogen or nitrogen contents. The pH range from 4.0 to 10.0 seemed to have no effect on the carbon and oxygen contents. However, lower carbon content and higher oxygen content were obtained in the residue at pH 13.0. The decrease of residual carbon content at pH 13.0 was due to the lignin content of the HCCS because lignin, having the highest carbon content among the main components of the biomass, hydrolyzed/decomposed at pH 13.0.

The elemental contents of WSP and ASP are shown in Table 2. The temperature and pH seemed to have no significant effect on the elemental content of WSP. The elemental content of ASP showed no dramatic change at the pH range of 4.0–10.0 at various temperatures, and lower carbon content was obtained at pH 13.0. The carbon content of ASP was higher than that of WSP in the same conditions except at pH 13.0. This was consistent with the results obtained by direct liquefaction of woody biomass at 340 °C for 30 min.<sup>20</sup> The main components of the ASP in that study were phenolic compounds and derivatives, long-chain carboxylic acids/esters and hydrocarbons, and these compositions had higher carbon content than the carbohydrates, acetic acids, pyran derivatives and aldehydes in the WSP.

Next, in order to examine the fuel properties of the residue, WSP and ASP, the H/C vs O/C values of residue, WSP, ASP and flash pyrolysis oil (dry basis)<sup>22,23</sup> were plotted on a van Krevelen diagram, as shown in Figure 5. From Figure 5a, it is clearly seen that the residue and ASP had lower O/C and H/C values than those of WSP prepared under the same conditions except for the case of pH 13.0 (black keys in Figure 5a), where the residue and ASP had higher O/C values than those prepared at other conditions. This result indicated that the residue and ASP prepared at pH 13.0 had lower fuel properties than those prepared at other conditions, because a fuel with higher H/C and O/C ratios would lead to more energy loss, and more smoke and water vapor generation during the combustion process.<sup>8</sup> Therefore, it was not appropriate for hydrothermal carbonization of HCCS at high pH for bio-fuel production.

Figure 5b shows the H/C vs O/C values of residue and ASP at 180 to 260 °C for the pH range of 4.0–10.0. Compared with HCCS, residues with lower H/C and O/C values were obtained through hydrothermal carbonization. The H/C and O/C values of residue moved toward to those of commercial



**Figure 5.** van Krevelen diagram of (a) HCCS, residue, WSP and ASP prepared at 180–260 °C, pH 4.0–13.0 and (b) HCCS, residue and ASP prepared at 180–260 °C, pH 4.0–10.0 as well as areas of pyrolysis oils (dry basis) and coal band. The area of pyrolysis oils was referred from references 22 and 23.

coals with the increase in the hydrothermal carbonization temperature, and the H/C and O/C values of residues prepared at 260 °C (entry 6) could be comparable with those of lignite. The O/C and H/C values of ASP could also be comparable with those of pyrolysis oil.

The HHVs of residue, WSP and ASP are an important index to evaluate the performance of hydrothermal carbonization, we thus calculated the HHVs of residue, WSP and ASP from their elemental contents in this study. As shown in Table 1, the HHV of HCCS was  $20.2\text{ MJ kg}^{-1}$  and the HHV of residue prepared at pH 5.9 increased with the increase in the hydrothermal carbonization temperature. The increase in HHV was due to the decrease of low-energy chemical bonds (i.e., H–C and O–C) and the increase in a high-energy chemical bond (C–C) during hydrothermal carbonization.<sup>8</sup> The HHVs of these residues could be comparable with those of some commercial coals shown in Table 3, such as Northumberland No. 81/2

**Table 3.** Comparison of HHVs of the Present Residues with Those of Some Commercial Coals and Torrefied Biomass

biomass/commercial coal	HHV (MJ/kg)	reference
residue (entries 2–6, pH 5.9)	22.0–27.7	this study
Northumberland No. 81/2 Sem. Anth. Coal	24.7	24
Ggerman Braunkohole lignite	25.1	24
Jnanjra Bonbahal Seam Coal–R–VII	24.1	24
Green Ind. No. 3–hvBb coal	27.4	24
dry torrefied loblolly pine (300 °C, 80 min)	23.5	19
dry torrefied loblolly pine (300 °C, 30 min)	23.1	26
dry torrefied loblolly pine (25 °C, 8 h)	24.8	26

Sem. Anth. Coal (24.7 MJ kg<sup>-1</sup>), Jhanjra Bonbahal Seam Coal–R–VII (24.1 MJ kg<sup>-1</sup>) and German Braunkohole lignite (25.1 MJ kg<sup>-1</sup>). The HHV of residue prepared at 260 °C and pH 5.9 (27.7 MJ kg<sup>-1</sup>) that exhibited an elevation rate of 37% compared to that of the original HCCS could even be comparable with that of Green Ind. No. 3–hvBb coal (27.4 MJ kg<sup>-1</sup>).<sup>24</sup> This elevation rate of HHV was much higher than those for 15 min treatments of willow (17%) and beech (20%) at the mild pyrolysis temperatures of 270 and 280 °C, respectively.<sup>25</sup> It was also much higher than those of dry torrefied loblolly pine processed for 8 h at 250 °C, and 30 and 80 min at 300 °C, respectively, which had similar elemental content and HHV to those of HCCS<sup>19,26</sup> (Table 3). Therefore, it was considered that hydrothermal carbonization is better at elevating HHV than dry torrefaction. The pH range from 4.0 to 10.0 seemed to have no effect on the HHV of the residue because the composition and elemental content of the residue was nearly the same at this range; lower HHV was obtained at pH 13.0, which was due to the hydrolysis/decomposition of lignin as described above.

Changing the temperature and pH seemed to have no dramatic effect on the HHV of WSP. The HHVs of WSP were between 14.0 and 16.1 MJ kg<sup>-1</sup>, lower than those obtained from the liquefaction of woody biomass at 340 °C for 30 min.<sup>20</sup> The temperature also had no effect on the HHV of ASP and it seemed that changing the pH from 4.0 to 10.0 above 200 °C led to no great change in the HHV of ASP. It was interesting that a lower HHV of ASP was obtained at pH 13.0, under which conditions lignin was greatly hydrolyzed/decomposed. This could be due to the change of carbon content of ASP because the carbon content dominated the HHV as shown in eq 6. The HHVs of WSP and ASP were much lower than those of heave fuel oil, aviation gasoline and diesel oil.<sup>24</sup> Therefore, the HHVs of WSP and ASP should be improved before application by the means of lowering oxygen content.

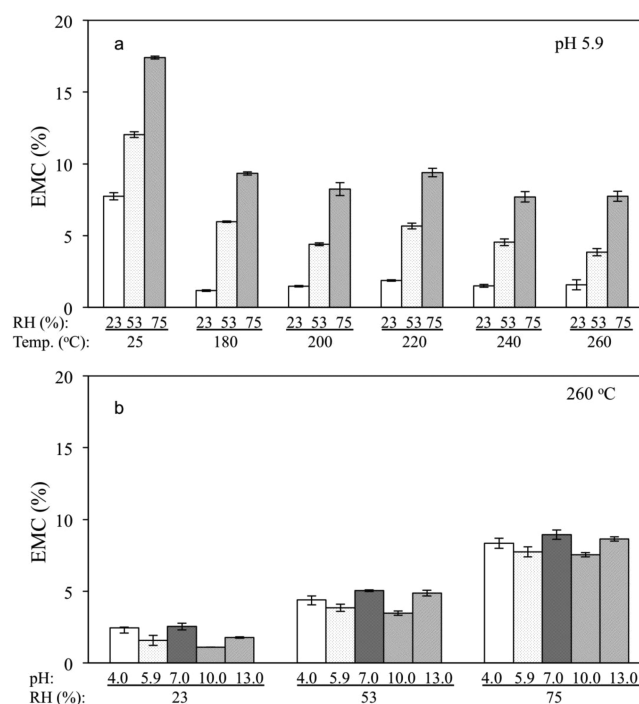
From all of the results described above, we considered that hydrothermal carbonization could effectively upgrade the fuel properties of biomass, and the optimal conditions for 10 min hydrothermal carbonization of HCCS are 260 °C, pH 5.9. A pretreatment was needed before application of WPS and APS as biofuels. The residue, WSP and ASP prepared at pH 13.0 were not appropriate for application as bio-fuels.

#### Equilibrium Moisture Content of HCCS and Residue.

The moisture content strongly affected the biodegradation of biomass. The relative humidity of the surrounding air was one of the parameters that affected the EMC.<sup>27</sup>

Figure 6a shows the effect of hydrothermal carbonization temperature on the EMC of the residue. The higher hydrothermal carbonization temperature made the residue more hydrophobic and the EMC was elevated at higher RH content. As shown in Table 1, the weights of cellulose, hemicellulose and lignin in the residue were reduced after hydrothermal carbonization. However, more cellulose and hemicellulose were hydrolyzed/decomposed than lignin, and hence the lignin content in the residue increased with the increase of hydrothermal carbonization temperature. Therefore, the EMC reduction at higher hydrothermal carbonization temperatures was due to the increase of lignin content in the residue as lignin is more hydrophobic than cellulose or hemicellulose.

Figure 6b shows the relationship between EMC and the residue prepared at various pH values. There was no significant change of the EMC at the same RH. The constant EMC of the



**Figure 6.** Equilibrium moisture content (EMC) of residue prepared at (a) various temperatures at pH 5.9 and (b) various pH values at 260 °C ( $n = 3$ ).

residue (pH 4.0–10.0) was due to its fairly constant composition since the composition of biomass affects the EMC of the biomass.<sup>27</sup> Although the composition of the residue changed at pH 13.0, the EMC of the residue was similar to those obtained at pH values from 4.0 to 10.0, probably due to the high ash content in the residue.

Therefore, hydrothermal carbonization was shown to be an effective process to improve the hydrophobicity of biomass; also, high ash content in the residue could affect the hydrophobicity of the residue.

## CONCLUSIONS

The residue, WSP and ASP produced from hydrothermal carbonization of HCCS at various temperatures and pH values were characterized in this study. The residue yield was decreased when the treatment temperature increased from 180 to 260 °C while the total soluble products yield was almost the same. Changes in pH within the range from 4.0 to 10.0 had no significant effect on residue and total soluble products yields. However, a lower residue yield and higher total soluble products yield were obtained at pH 13.0. At 260 °C and pH 5.9, more hemicellulose (82.1%) was hydrolyzed/decomposed than cellulose (58.3%) or lignin (27.1%), and it was confirmed that the reactivity order of the components of HCCS was hemicellulose > cellulose > lignin. The final pH value of WSP was lower than initial pH value and it decreased with increase in the hydrothermal carbonization temperature. Changing the initial pH from 4.0 to 10.0 had no dramatic effect on the final pH value of WSP. However, the final pH value increased to around 7.3 when the initial pH elevated to 13.0, which meant that the generated carboxylic acids were all neutralized by NaOH. The HHV ranges of residue were from 22.0 to 28.2 MJ kg<sup>-1</sup> for 10 min of treatment in the temperature range of 180–260 °C and pH range from 4.0 to 10.0, and the HHV of residue

decreased at pH 13.0. The HHVs of these residues were comparable with those of several commercial coals. The WSP and ASP had lower HHVs than those of heavy fuel oil and diesel oil, and they needed a pretreatment to increase their HHVs before application. The residue became more hydrophobic at higher treatment temperatures, indicating that hydrothermal carbonization could efficiently elevate the hydrophobicity of the biomass.

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### Notes

The authors declare no competing financial interest.

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