Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.931537

53 (2015) 2831–2838
March

Characterization of hydrochar prepared from hydrothermal carbonization of peels of *Carya cathayensis sarg*

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Received 16 July 2013; Accepted 10 March 2014

ABSTRACT

Hydrothermal carbonization of peels of *Carya cathayensis sarg* (PCCS) by subcritical water or acetone- and ethanol-modified subcritical water was carried out at the temperature from 280 to 360˚C and coal-like hydrochar was obtained. The hydrochar yield decreased with increasing of treatment temperature, but the higher heating value (HHV) and carbon content of hydrochar were promoted at higher treatment temperature. The HHV of hydrochar was in range of 30–46 MJ/kg with an increase from 52.4 to 127.6%, compared to the original PCCS. The HHVs of hydrochars obtained at 360˚C could be comparable with those of heavy fuel oil (42.9 MJ/kg) and diesel oil (45.7 MJ/kg). The O/C and H/C values of hydrochar were similar to those of lignite and subbituminous, except the ash content. Especially, the O/C and H/C values of hydrochars prepared at 360˚C could be compatible with those of bituminous. When treated with acetone- or ethanol-modified subcritical water, a synergistic effect of acetone–water or ethanol–water for hydrothermal carbonization was observed; the liquefaction rate with acetone–water or ethanol–water mixture was larger than that of water or acetone or ethanol only. There was no significant change on the O/C and H/C values and HHV on the hydrochar, although more PCCS, was decomposed when using acetone–water or ethanol–water mixture.

Keywords: Hydrothermal carbonization; Organic solvent-modified subcritical water; Hydrochar; Peels of *Carya cathayensis sarg* (PCCS)

1. Introduction

Biomass is an important and abundant resource in the world; the annual production was eight times to the total annual world fossil energy consumption [1]. The advantages of low sulfur content, carbon dioxide capture capability, and regenerable ability make biomass to become a promising biofuel for taking the place of fossil fuel in the future. However, most of biomass was directly combusted as a fuel in the past decades. The high moisture content, hygroscopic feather, low-energy value, high volatile content, and high oxygen content make biomass define as a low-grade fuel. Therefore, it is necessary to improve the

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Presented at 2013 International Environmental Engineering Conference and Annual Meeting of the Korean Society of Environmental Engineers (IEEC 2013) Seoul, Korea, June 11–13, 2013

fuel value of the biomass. There are many methods to improve the fuel value of the biomass, one of them is to convert the biomass to biochar because biochar presents many advantages compared with the biomass feedstock such as high carbon content, high energy density, recalcitrant nature, and its ability to lower emission of greenhouse gases [2–4].

In recent years, conversion of biomass to biochar (hydrochar) by hydrothermal carbonization method using subcritical water has become a popular topic. Comparing with other biochar preparation method hydrothermal carbonization method gives some advantages such as: (1) hydrothermal carbonization employs relatively lower temperatures (150–350℃), (2) the biomass does not need a predried process which costs more, (3) the gases generated during hydrothermal carbonization process could dissolve in water and it makes no further pollution to the air, and (4) water in a reactor could dilute the acidic property of bio-oil generated during hydrochar production process and thus decreases the corrosion to the equipment [2,5]. Most researchers have focused on preparing hydrochar using pure subcritical water and there was no research about preparing hydrochar by organic solvent-modified subcritical water, where the relative dielectric constant could be changed by the addition of organic solvent [2,6,7]. It was known that the liquefaction of lignocellulosic biomass with methanol- or acetone-modified subcritical water could be significantly changed when compared with that of sole solvent [8]. Additionally, the critical value could be reduced when water was mixed with acetone or ethanol whose critical value was lower than that of water and the organic solvent could be recycled.

Therefore, in this study, organic solvent (acetone and ethanol)-modified subcritical water was used for hydrothermal carbonation of peels of *Carya cathayensis sarg* (PCCS) in order to investigate the effects of dielectric constant on the properties of prepared hydrochar. The prepared hydrochar would be used as a solid fuel or composed with liquid fuels to make slurry fuels.

2. Material and methods

2.1. Materials

PCCS, which used as a raw material in all the experiment, were produced in Lin’an, China. The cellulose, hemicellulose, lignin, and ash contents of PCCS were 13.1, 22.3, 56.2, and 5.1%, respectively. PCCS were milled using a milling machine (WB-1 Osaka Chemical Corporation, Osaka, Japan) and then the powder was screened with the diameter below 0.3 mm. The powder was dried at 105℃ for 24 h before experiment. Ethanol and acetone were purchased from Wako Pure Chemical Industries (Osaka, Japan).

2.2. Biochar preparation

Hydrothermal carbonization of PCCS was performed in a batch reactor (Taiatsu Technology Corporation, Osaka, Japan) which was made from SUS316 stainless steel with the volume of 10 mL. On each experiment, 200 mg of the powder was mixed with 8 mL of ultrapure water or water–organic solvent in the volume ratio from 0 to 100% at ambient temperature. Afterward, the mixture was transferred to the batch reactor and the reactor was tightly closed. The reactor was set in a ceramic furnace (ARF-40K, Asahi-Rika, Chiba, Japan) with a temperature controller (TXN-700, Asone, Osaka, Japan). Hydrothermal carbonization was carried out at 280–360℃ with various organic solvent volume ratios for 15 min and at 280 and 360℃ for 15–45 min. It took 14–21 min to make the temperature inside the reactor reach to the desired temperature. In order to stop the reaction rapidly, the reactor was immersed into an ice bath as soon as the reaction time elapsed. The mixture in the reactor was then filtered using a G-4 glass filter (Vidtec, Fukuoka, Japan). The hydrochar (remained solid) was dried at 110℃ until the weight reached to a constant value. Each experiment was conducted three times.

2.3. Element analysis

The carbon, hydrogen, and nitrogen contents of the hydrochar were measured using a PerkinElmer 2400 II elemental analyzer (Kanagawa, Japan). The ash content was evaluated by burning the PCCS at 550℃ for 4 h. It was assumed that all the ash was remained in hydrochar during the hydrothermal carbonization process. Therefore, the ash content could be calculated for each hydrochar from the overall mass yield.

2.4. Calorific value determination

The higher heating value (HHV) of hydrochar was calculated by a partial least squares regression (PLS) method provided by Friedl et al. [9]. The equation is as follows:

$$\begin{aligned}\mathrm{HHV\,(PLS)} = {} & 5.22\,\mathrm{C}^2 - 319\,\mathrm{C} - 1647\,\mathrm{H} + 38.6\,\mathrm{CH} \\ & + 133\,\mathrm{N} + 21028 \end{aligned} \qquad (1)$$

where C = carbon, H = hydrogen, and N = nitrogen content expressed on a dry ash-free mass percentage.

2.5. Thermogravimetric analysis

The thermogravimetric analysis (TGA) was carried out by a thermogravimetry (TG-60A, Shimadzu, Kyoto, Japan). A platinum crucible loaded with 5–7 mg of hydrochar was first heated to 105℃ at the room temperature at the heating rate of 20℃/min and held for 10 min in order to remove the moisture, and then continuously heated to 600℃. N_2 was used as carrier gas with the flow rate of 100 mL/min.

2.6. Functional groups on biochar

The functional groups on the hydrochar were analyzed by a Jasco 4100 Fourier transform infrared spectroscopy (FT-IR, Jasco, Tokyo, Japan).

3. Results and discussion

3.1. Effect of hydrothermal carbonization temperature on hydrochar yield

The effect of hydrothermal carbonization temperature and treatment time on hydrochar yield is shown in Fig. 1. The hydrochar yield was 44.9% at 280℃ for 15 min and it decreased to 27.9% when the temperature increased to 360℃ (Fig. 1(a)). The hydrothermal carbonization temperature had more effect on hydrochar yield than that of treatment time (Fig. 1(b)). The decrease of hydrochar yield at higher temperature was due to the continuous decomposition of cellulose and a portion of lignin, because hemicellulose was almost volatilized and carbonized below 250℃ and volatilization of cellulose became faster at a temperature higher than 250℃ [10–12]. The reduction of hydrochar yield at longer treatment time was probably due to the decomposition of less reactive components of cellulose and a portion of lignin.

3.2. Effect of organic solvent volume ratio on hydrochar yield

The critical values of organic solvent–water mixture were obtained by linear fitting of the data obtained from Yuan et al. and Bicker et al. and the critical values are shown in Table 1 [13,14].

Fig. 2 shows the effect of ethanol and acetone volume ratios on hydrochar yield at 280, 320, and 360℃. The hydrochar yield decreased with increasing of ethanol volume ratio from 0 to 50% and then increased at the volume ratio from 75 to 100% (Fig. 2(a)). The variation tendency of hydrochar yield was coincident with that of sub-and supercritical liquefaction of rice straw in the presence of ethanol– or 2-propanol–water mixture, and the hydrogen donor solvent (ethanol) probably responded for this phenomenon [13]. However, the hydrochars obtained at the ethanol volume ratio from 75 to 100% were lower than that at 0% and it was different with that of rice straw. When the experiment was carried out with acetone, the hydrochar yield formation was slight decreased when the acetone volume ratio increased from 0 to 75% and then promoted (Fig. 2(b)).

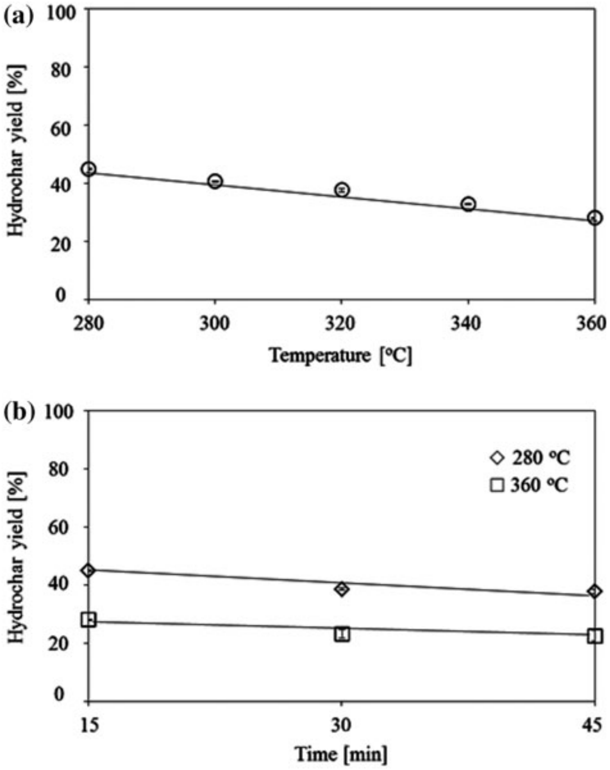

Fig. 1. The yield of hydrochar from hydrothermal carbonization of PCCS prepared (a) at various treatment temperatures for 15 min and (b) at (◇) 280℃, and (□) 360℃ for various treatment times.

Judging from all the results, a synergistic effect of water–acetone or water–ethanol for hydrothermal carbonization was observed. The liquefaction rate with acetone–water or ethanol–water mixture was larger than that of water or acetone or ethanol only. Therefore, it was considered that the addition of organic solvent could promote both hydrolysis and pyrolysis reactions during the hydrothermal carbonation process. It is known that the liquid phase (bio-oil) after hydrothermal carbonization would be a good source for producing liquid fuel or hydrogen [15,16]. Therefore, higher bio-oil yield could also be obtained even

Table 1
The critical value (T_c, P_c) of the used solvents

Volume ratio (%)	Ethanol–water		Acetone–water	
	T_c (℃)	P_c (MPa)	T_c (℃)	P_c (MPa)
0	374.00	22.10	374.00	22.10
25	342.13	17.65	339.08	17.73
50	313.72	11.67	304.15	13.36
75	278.40	8.74	269.23	8.99
100	243.00	6.30	235.00	4.60

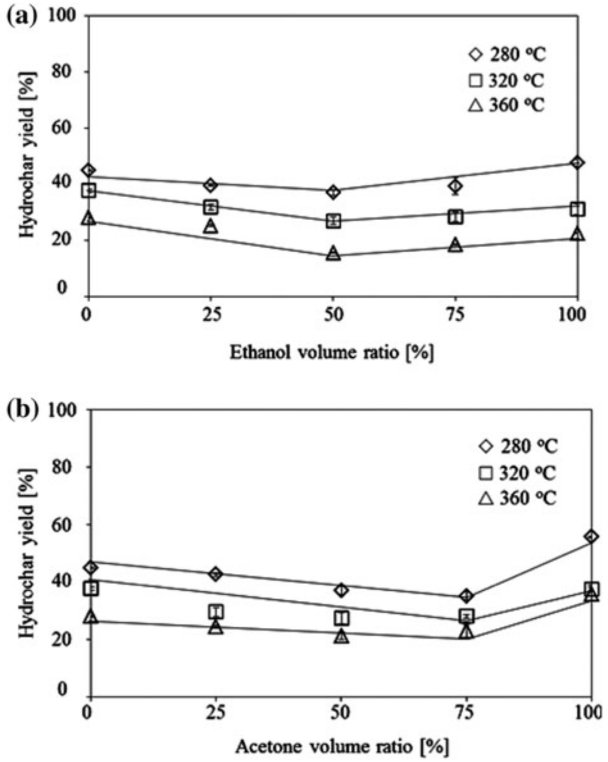

Fig. 2. Effect of (a) ethanol and (b) acetone volume ratio on hydrochar yield at (◇) 280℃, (□) 320℃, and (△) 360℃ for 15 min.

though lower hydrochar yield was obtained when using acetone–water or ethanol–water mixture. Besides, it cost less energy during the evaporation of organic solvent containing liquid phase to obtain bio-oil than that of containing water only, because acetone and ethanol have lower boiling point compared with water. Additionally, the evaporated acetone or ethanol could be reused and it made no further pollution. The research about the production of bio-oil by subcritical liquefaction of biomass will be investigated in the future.

3.3. Elemental analysis of hydrochar

Fig. 3 shows the influence of various hydrothermal carbonization conditions on the elemental contents of hydrochar at ash-free basis. The carbon, hydrogen, nitrogen, and oxygen contents of original PCCS were 51.5, 4.8, 0.9, and 42.8%, respectively. The carbon content of hydrochar was concentrated from 51.5 to 84.8% with increasing of hydrothermal carbonization temperature, along with significant decreasing of oxygen content. However, the hydrogen and nitrogen contents were nearly the same. Meanwhile, the ash content was increased when the hydrothermal carbonization temperature increased (Fig. 3(a)). These results were due to the dehydration, decarbonation, and demethanation during the hydrothermal carbonization process. The spectra peak of FT-IR which would be discussed later also demonstrated that the aforementioned reactions occurred during the hydrothermal carbonization process. Additionally, dehydration was more drastic than decarbonation and demethanation during hydrothermal carbonization (Fig. 4).

The carbon content was also increased when PCCS were treated at longer times at 280 and 360℃, respectively. The oxygen content was even decreased to as low as 1.31% at 360℃ for 45 min (Fig. 3(b)). The low oxygen content was due to the decomposition of hemicellulose and cellulose which contained high oxygen content at that treatment temperature. This result was in accordance with the low hydrochar yield which was due to the decomposition of hemicellulose and cellulose during the subcritical water treatment at 360℃ (Fig. 1(b)).

The carbon, hydrogen, oxygen, or nitrogen content should be changed with hydrochar yield. However, the carbon, oxygen, nitrogen, and ash contents of hydrocahrs were almost the same and only the hydrogen content was changed with hydrochar yield when PCCS treated with acetone- and ethanol-modified subcritical water (Fig. 3(c) and (d)). Therefore, we considered that polymerization reaction or other reactions

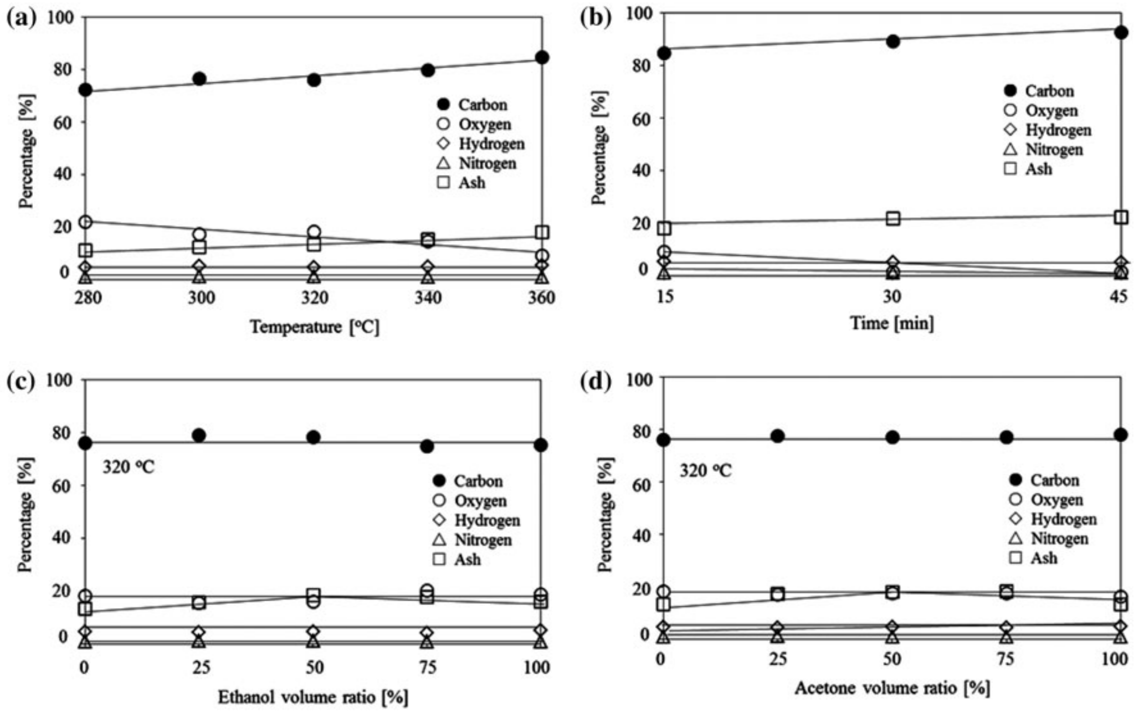

Fig. 3. Effect of (a) various treatment temperatures, (b) various treatment times at 360˚C, (c) ethanol volume ratio at 320˚C, and (d) acetone volume ratio at 320˚C on the (●) carbon, (○) oxygen, (◇) hydrogen, (△) nitrogen, and (□) ash contents of hydrochar.

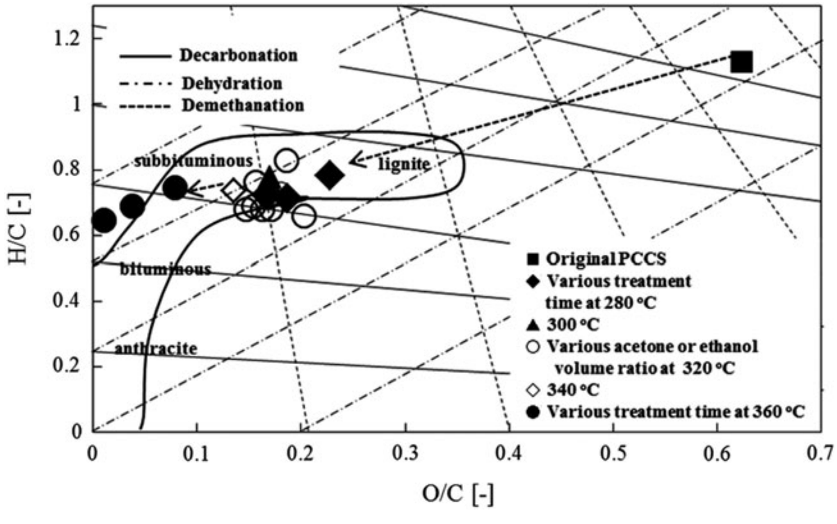

Fig. 4. Van Krevelen diagram of (■) original PCCS, hydrochars prepared at (◆) 280˚C for various treatment times, (▲) 300˚C, (○) 320˚C for various acetone or ethanol volume ratios, (◇) 340˚C, (●) 360˚C for various treatment times as well as coal band.

had been occurred between acetone/ethanol and cellulose or lignin in the hydrochar and these reactions supplemented the qualities of carbon and oxygen lost during hydrothermal carbonization. The results described above suggested that acetone- and ethanol-modified subcritical water could effectively stabilize the carbon, oxygen, and hydrogen contents in hydrochar.

The H/C and O/C values were one of the important properties for the characterization of solid fuels. Therefore, the H/C and O/C values of hydrochars prepared at various conditions as well as coal bands on the van Krevelen diagram are shown in Fig. 4. The O/C and H/C values significantly decreased after hydrothermal carbonization. It was due to the dehydration, decarbonation, and demethanation reactions during the hydrothermal carbonization process. The H/C and O/C values of all the hydrochars could be compatible with those of subbituminous and lignite coal, except the ash content. The H/C and O/C values of hydrochars obtained at 360°C for various treatment times could even be compatible with that of bituminous coal. These results suggested that the hydrothermal carbonization process, using subcritical water, would be an effective method to lower the H/C and O/C values of hydrochar which are intended to be used as a fuel.

3.4. Calorific value of biochar

HHV is another important property to evaluate solid fuels and the HHVs of hydrochars were calculated from the element contents of carbon, hydrogen, and nitrogen on dry ash-free basis. The HHV of hydrochar increased from 30.8 to 40.2 MJ/kg with the temperature increasing from 280 to 360°C. It was an increase of 52.4 to 127.6% compared to the original PCCS (20.2 MJ/kg) (Fig. 5(a)). The HHV was continuously elevated at the longer treatment time on 280 and 360°C, respectively (Fig. 5(b)). The HHVs of hydrochars were much higher than those of methanol (22.7 MJ/kg) and pyrolytic oil (24.7 MJ/kg) and they could also be compatible with those of lignite char (31.3 MJ/kg) and charcoal (34.4 MJ/kg). Additionally, the HHVs of hydrochars prepared at 360°C could even be compatible with those of diesel oil (45.7 MJ/kg) and heavy fuel oil (42.9 MJ/kg) [17].

The HHVs of hydrochars obtained from acetone- and ethanol-modified subcritical water carbonization at 320°C were almost the same although acetone– and ethanol–water mixture accelerated the liquefaction rate of PCCS (Fig. 5(c)).

The results aforementioned suggested that hydrothermal carbonization of biomass would be an effective method to get energy-dense hydrochars from biomass.

3.5. Thermogravimetric analysis

TGA of hydrochars prepared at various conditions is shown in Fig. 6. The weight loss mainly occurred at the temperatures between 200 and 500°C. The thermal stability was promoted with the increasing of hydrothermal carbonization temperature (Fig. 6(a)). Higher ash and lower volatile matter content probably responded to the thermal stability of hydrochars. The thermal stabilities of hydrochars obtained at the ethanol volume ratio from 0 to 75% were more stable than that prepared at 100% (Fig. 6(b)). However, the thermal stability of hydrochars prepared by

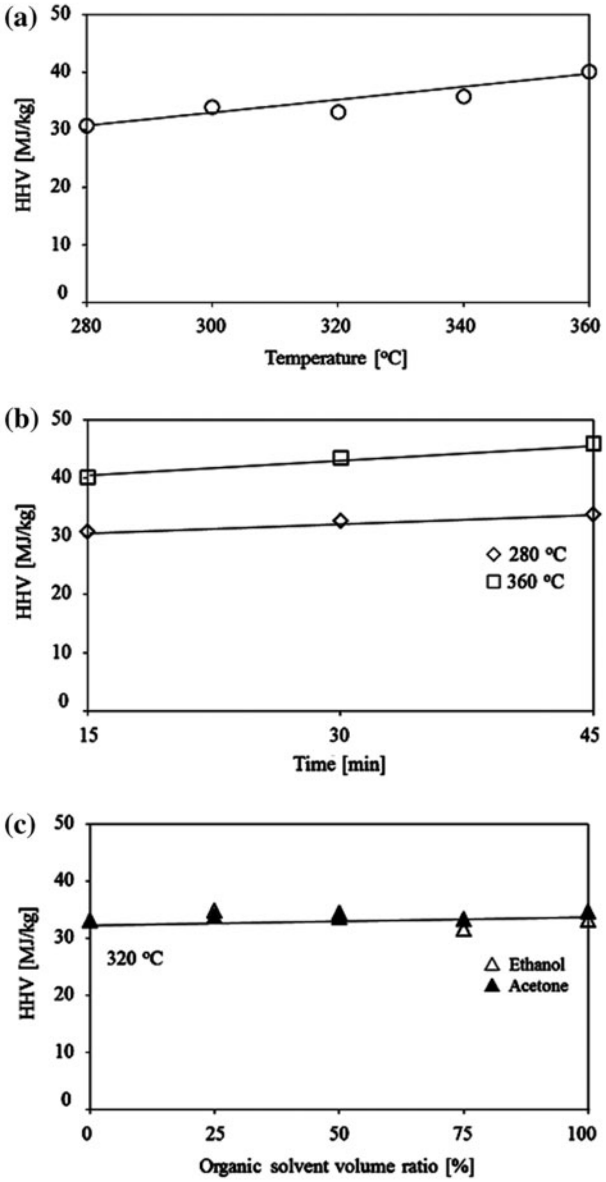

Fig. 5. Effect of (a) treatment temperature, (b) treatment time (□) 280°C and (◇) 360°C, and (c) organic solvent volume ratios (▲) acetone and (△) ethanol at 320°C on the HHV of hydrochar.

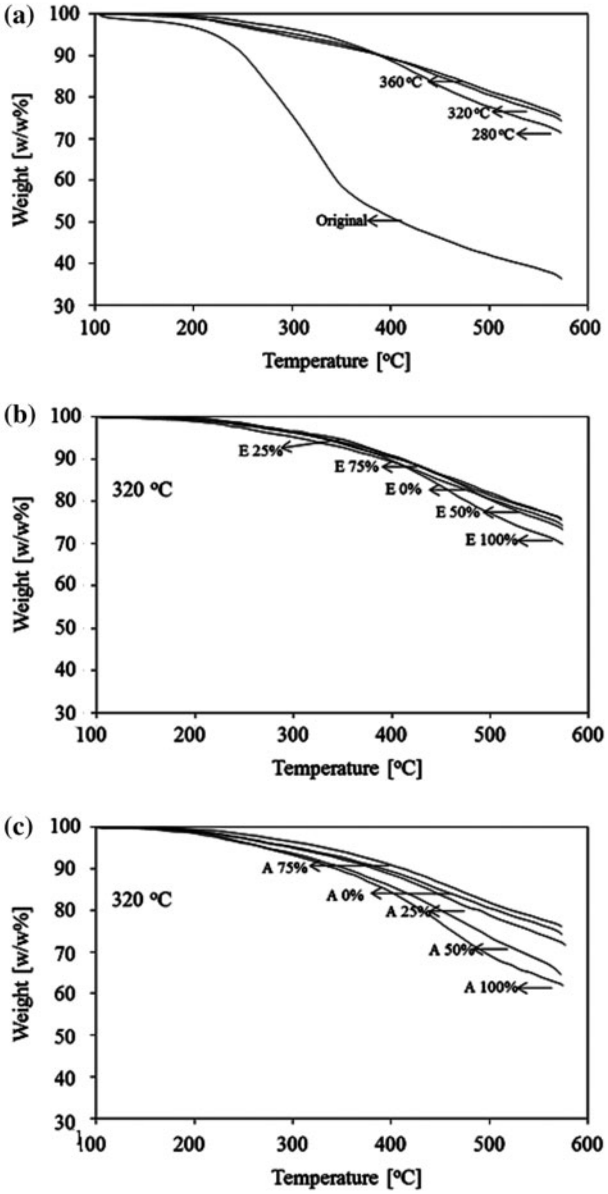

Fig. 6. TGA curves of hydrochars prepared at (a) various hydrothermal carbonization temperatures and various, (b) ethanol, and (c) acetone volume ratios at 320°C. A (E) 50% = acetone (ethanol) volume ratio of 50%.

acetone-modified subcritical water had no regulation. The thermal stability of hydrochars did not change a lot at the acetone volume ratio of 0, 25, and 75%, but it was decreased at the ratio of 50 and 100% (Fig. 6(c)).

From all the results described above, it was found that hydrochar with high thermal stability could be obtained by the hydrothermal carbonization method.

3.6. Functional groups on biochar

The FT-IR spectra of hydrochar prepared at various conditions are shown in Fig. 7. Fig. 7(a) shows the effect of temperature on the functional groups of hydrochar. The spectra peak of C–O linkage at the wave range from 1,120 to 1,050 cm^{-1} disappeared compared to the original PCCS. It indicated that the ether bond in hemicellulose and cellulose and the methoxy group in lignin that are easy to break in hydrothermal process were fractured during the subcritical water treatment [2]. The benzene peaks which were typically around 1,600, 1,510, and 1,440 cm^{-1} had no significant change. This result supposed that the lignin-derived aromatic structure was very stable even when the temperature reached to 360°C. The phenolic OH peak at 1,330 cm^{-1} was decreased or disappeared during the subcritical water treatment and the β-anomers or β-linked glucose polymers peak absorbed at around 893 cm^{-1} disappeared with the increasing of treatment temperature.

The phenomenon was in accordance with those described above when PCCS were treated by acetone– or ethanol-modified subcritical water except the peak at 893 cm^{-1} (Fig. 7(b)). The β-anomers or β-linked glucose polymers peak at 893 cm^{-1} was shifted to around 873 cm^{-1} after treatment.

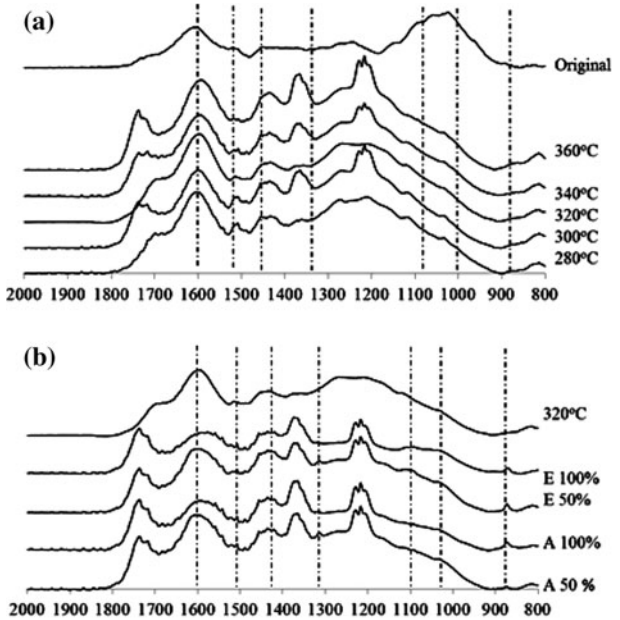

Fig. 7. FT-IR spectra of hydrochar prepared on (a) different temperatures and (b) various organic solvent volume ratios at 320°C. A(E) 50% = Acetone (ethanol) volume ratio of 50%.

4. Conclusion

Hydrothermal carbonization of PCCS by subcritical water or acetone- or ethanol-modified subcritical water at various treatment temperatures and times were carried out in this study and coal-like hydrochars were obtained. The hydrochar yield decreased with increasing of treatment temperature, but hydrochar with higher carbon content, higher HHV, lower volatile matter content, lower oxygen content, and O-containing functional groups was obtained at the same time. The carbon content and HHV of hydrochar were between 72.3–92.6% and 30–46 MJ/kg, respectively. The HHVs of hydrochars were much higher than those of methanol and pyrolytic oil and they could be compatible with those of lignite char and charcoal. These results indicated that hydrothermal carbonization could be an effective process to produce higher carbon content and higher energy-density hydrochar. The O/C and H/C values of hydrochars could be compatible with those of lignite and subbituminous. Especially, the O/C and H/C values of hydrochars prepared at 360°C were similar to that of bituminous except the ash content. When treated with acetone– or ethanol-modified subcritical water, a synergistic effect of acetone–water or ethanol–water for hydrothermal carbonization was observed; the liquefaction rate with acetone–water or ethanol–water mixture was larger than that of water or acetone or ethanol only. Although lower hydrochar yield was obtained when using acetone–water or ethanol–water mixture, more bio-oil, which was a good source for producing liquid fuel or hydrogen, could be obtained at the same time. Acetone- or ethanol-modified subcritical water could effectively stabilize the carbon and oxygen contents in hydrochar.

Acknowledgments

We thank Prof. Yoshiei Kato and Associate Prof. Azhar Uddin, Graduate School of Environmental and Life Science, Okayama University for lending us TGA for thermogravimetric analysis.

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