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Characteristics of Hydrothermal Treatment of Woody Biomass and Features of Upgraded Solid

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Abstract

Heat treatment in hot-compressed water (hydrothermal treatment) at 250 °C upgrades woody biomass to solid with particular features by converting a major portion of carbohydrate (cellulose and hemicellulose) into water soluble matter and solvent-soluble lignin-like material, removing more than 90% of the alkali and alkaline earth metallic (AAEM) species. The upgraded biomass is available in production of metallurgical coke that has mechanical strength higher by more than six times than that of conventional one from coals, and activated carbon with specific surface area well above 2,000 m² g⁻¹ without any additives/chemicals. Repeated use of product water enables to maximize the yield of upgraded biomass, maintaining its ability of leaching of AAEM species.

1. Introduction

Heat treatment of biomass in hot-compressed water at 150–350 °C is normally termed hydrothermal treatment (HT). HT has been studied by a number of researchers,^{1–8} who putting main focal points of characteristics such as (i) conversion of carbohydrates (i.e., cellulose and hemicellulose) into sugar monomers/oligomers, furans and/or lower acids,^{4–6} and/or (ii) removal of oxygen from the biomass that results in production of solid fuel with increased calorific value as high as coal.

The upgrading of biomass into coal-equivalent solid fuel may be, unfortunately, economically infeasible in the fuel industry in consideration of expensiveness of HT as a high-pressure multi-phase process together with inexpensiveness of solid fuel. The present authors propose application of hydrothermally upgraded biomass to production of value-added carbon based material taking most advantage of particular properties of HUB. During HT, the water becomes acidic due to formation of acids (acetic and other lower acids), given an ability of leaching of the inherent metallic species that are represented by AAEM species. The absence of AAEM species enables gasification free from such species, which needs no syngas cleaning, and also production of clean activated carbon and other materials.

The present authors⁹ recently reported that acid-washed (i.e., near AAEM-free) chars from the pyrolysis of biomass are excellent starting materials of high surface area active carbon. The absence of AAEM species allowed steam gasification to develop micro-/meso-porous structures of char to its specific surface area even over 2,500 m² g⁻¹. HT, if operated at temperature around 240–260 °C, eliminates a substantial portion of the carbohydrate, transform its another portion into organic-solvent-soluble aromatic solid, while partially depolymerize the lignin. The chemical composition of thus upgraded biomass is expected to be an excellent raw material of metallurgical coke, which is produced through a sequence of hot briquetting to form high-density coke precursor and its carbonization.

The present study investigated characteristics of HT of woody biomass at 250 °C in terms of the yield, chemical composition (including contents of AAEM species) and thermochemical properties (in gasification and carbonization), and formation of water-soluble products. Investigation was also made on the effects of the repeated use of water (i.e., HT with recycling of

water), which avoids or minimizes the wastewater, on the performance of HT. It was also expected that accumulation of acids, if occurred, promoted acid-catalyzed hydrolytic decomposition of the carbohydrate lowering the temperature for HT.

2. Material and Methods

2.1 HT

The first run of HT (HT1) was performed with a mixture of cedar (*cryptomeria japonica*, particle size; 40 – 850 μm , 15 g-dry) and deionized water (105 ml) that was charged in an autoclave together with 1.0 MPa N_2 . The autoclave was immersed in a bath of fluidizing sand at 250 °C for 60 min, and then quenched in iced water. The resulting slurry was taken out of the autoclave and subjected to filtration at ambient temperature. The filtrate (LIQ-1) was recovered and used for the next run while the solid was washed with 20 g deionize water under ultrasonication, and then filtered while the filtrate (washing) was recovered as LIQ-2. The solid (upgraded cedar) was dried at 50 °C under vacuum until its mass became constant. In the second run (HT2), a 75 ml portion of LIQ-1, 15 g-dry of the fresh cedar and 30 ml makeup water were charged in the autoclave. The procedures of HT and the post treatments were the same as the HT1. HT runs were repeated up to HT4, simulating the recycling of product water by that of LIQ-1's. Analyses determined elemental and chemical compositions of the upgraded cedar, the concentrations of organic carbon (TOC) and lower acids and furans in LIQ-1 and LIQ-2. Details of the analyses are reported elsewhere.¹⁰

2.2 Steam Gasification

The original cedar and upgraded one from HT1 (cedar-HT1) were pyrolyzed upon heating at 10 °C min^{-1} to 900 °C in an atmospheric flow of N_2 (purity > 99.9996 vol%). The resulting char samples, hereafter referred to as Char-I and Char-II, respectively, were subjected to steam gasification. Other char samples were also prepared. Another char sample, Char-IIa, was prepared through washing of the cedar-HT1 with 3N HCl and the subsequent pyrolysis in the same way as above. Char-IIa was loaded with K_2CO_3 at 0.95 or 4.6 wt%-K/dry for preparation of K-catalyst-loaded chars (Char-IIa-K1 or Char-IIa-K, respectively). These L-loaded chars were prepared for investigating the effect of AAEM species on the pore development of char during the gasification.

A thermogravimetric analyzer was used for measuring the kinetics of steam gasification of the char samples at 850 °C and steam concentration of 20 vol%. More details of the procedure of the steam gasification are found elsewhere.¹¹

2.3. Preparation of Coke

Experimental examination was made on the production of metallurgical coke from the original cedar and cedar-HT1. These solids (after pulverized to sizes smaller than 100 μm) were briquetted upon heating at 200 °C and at a mechanical pressure of 114 MPa. The briquettes, which were in a form of disk (diameter; *ca.*, 14 mm, thickness; *ca.* 5 mm) were carbonized to coke by heating at a rate of 3 °C min^{-1} up to 900 °C (briquettes from the cedar-HT1) or 1000 °C (those from the original cedar). The tensile strengths of the coke samples were measured at ambient temperature. Details of the experimental procedures, which have been developed originally by the present authors, are reported elsewhere.^{12,13}

3. Results and Discussion

3.1. Characteristics of HT

Fig. 1 shows changes in the product yields with the run number (n) of HT, i.e., with the progress of recycling of water. The yield is defined on a carbon basis by the following equation.

$$\text{Yield at } n\text{-th run} = \frac{\text{Amount of product from } n\text{-th run}}{\text{Amount of cedar fed in } n\text{-th run}} \quad (1)$$

The yield of the cedar-HT seems to become steady at ca. 85% even at $n = 2$. This steady yield is higher by 12% than the yield at $n = 1$. The increase in the yield of upgraded biomass is explained by conversion of the water-soluble matter (WS) into a part of cedar-HT. Though not shown in the figure, an assumption of steady conversion, around 43%, of the recycled WS explains well the observed trend of the WS and predicts a steady yield of 35%.

Fig. 2 presents the change in the chemical composition of the cedar within the range of run number up to 4 where the cedar-HT yield is already stable. There are three clear trends. First, HT removes more than 85% of the original carbohydrates. Second, HT hardly changes the net fraction of lignin. Third, HT forms substantial amount of material that is extractable with benzene/ethanol (2/1 in vol.). It is reasonably concluded from these trends that HT converts the carbohydrates into water-soluble matter and the benzene/ethanol extract.

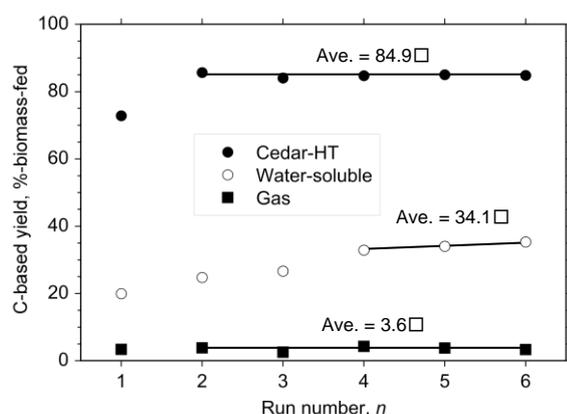


Fig. 1. Yields of solid (cedar-HT n), gas and liquid as a function of run number n . The yields are defined for each run based on carbon of cedar charged in autoclave.

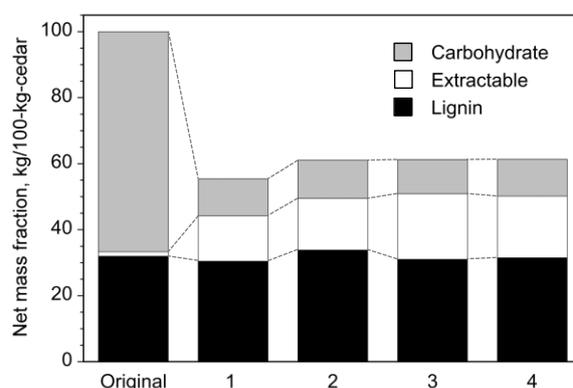


Fig. 2. Net mass fractions of carbohydrate (cellulose and hemicellulose), lignin and benzene/ethanol extractable matter in the original cedar and cedar-HT at different run number (n).

It is known that the primary products from the hydrolysis of carbohydrates are sugar monomers and oligomers, and these are further converted to furans, acid and gas. It is believed that the benzene-ethanol extract originates from the carbohydrates via sugars and/or furans under catalysis of the *in-situ* formed acids.¹⁰ The analysis of LIQ-1 and LIQ-2 demonstrated formation of glycolic, succinic, acetic and formic acids as well as that of sugars and furans (furfural and 5-hydroxymethyl furfural). The recycling of water increased the concentration of those four major acids until the third run, and stabilized later. The concentration of the acid catalysts seemed to be high enough to cause the substantial formation of the benzene/ethanol extractable.

As seen in Table 1, pH of water after each run was between 3.0 and 3.1 regardless of the run number. The acidification of the water was undoubtedly due to the formation of lower organic acids. It was then expected that leaching of the inherent AAEM species occurred extensively during HT. The removal rates are in a range of 90–96%. Table 1 shows the removal rates of K, Mg and Ca from the cedar for the first to fourth runs. Measurement of Na removal rates was not successful due to elution (leaching) of Na from glass bottles used in the analytical process. It was, however, believed that the removal rate of Na was as high as that of K, according to the present authors' recent investigation on the leaching of AAEM species from biomass.¹⁴

Table 1 also shows that the leaching ability of the water is maintained at least until the fourth run. The ability will be lost eventually after many runs of HT, but it is expected from the result that the recycling of water is rather durable.

Table 1. Removal rates of AAEM species from the solid for HT1–HT4.

<i>n</i>	pH of water (after run)	removal rate, %		
		K	Mg	Ca
1	3.05	95.8	94.4	90.9
2	3.09	94.9	81.2	92.1
3	3.12	94.0	90.7	89.6
4	3.10	95.8	94.0	89.1

The removal rate is defined as the fractional amount of metallic species leached out of the cedar to that contained initially.

The results of from HT with repeated use of the water thus demonstrated its effectiveness in simultaneous maximization of the yield of upgraded cedar (cedar-HT), elimination of a major portion of the carbohydrates, their chemical transformation into a portion of the upgraded cedar, and then removal of AAEM species.

3.2 Coke Production from Upgraded Biomass

Coke samples were prepared from the original cedar and cedar-HT's from the first and fourth runs. Table 2 summarizes the result. The mass yield of coke from the original cedar is only 27.5 wt%-briquette. Such a low yield arises from high volatility of the carbohydrates, in particular, cellulose. Substantial release of volatiles during the pyrolysis and carbonization makes the resulting coke more macro-porous and thereby lowering its mechanical strength. The tensile strength of the coke from the original cedar is slightly higher than average strength of commercially available blast furnace coke. However, this does not directly mean feasibility of the coke to the use in blast furnace. Its reactivity with CO₂ at elevated temperature, which is often represented by a particular measure, CRI (coke reactivity index), is extraordinary high due to the catalysis of the inherent AAEM species. Such a high CRI will make the operation of blast furnace difficult.

HT greatly improves the yield and properties of the coke. The coke yields near 50 wt% is attributed to the elimination of the highly volatile carbohydrates. It was found in the present authors' recent study¹⁰ that the benzene/ethanol soluble material of the hydrothermally upgraded biomass contributed to the coke (in terms of its mass) near-equally to the lignin. The presence and/or abundance of this material also enhance the plasticization of the upgraded biomass and its densification during the hot briquetting. The cokes from the cedar-HT's have much higher bulk densities than that from the original cedar. The micrographs of Fig. 3 show that the dense matrix formed at the briquetting has been maintained in the carbonization. Pores are seen on the fractured surface but their sizes are well below 10 μm.

The bulk density as high as 1.2 g cm⁻³ gives tensile strengths as high as 40 MPa, which is even higher than those of cokes from lignites that were prepared by the same procedure as in the present study.^{12,13} Another importance with the cokes from the cedar-HT's is that HT has removed the major portion of AAEM species. Though not reported here in detail, the reactivity with CO₂ of the cokes from the cedar-HT was slightly higher but similar to that of a commercially used blast furnace coke.

Table 2. Yield and properties of coke samples.

Precursor of coke	yield, wt%-briquette	tensile strength, MPa	bulk density, g cm ⁻³
Cedar	27.5	8.6	0.87
Cedar-HT1	48.6	39.6	1.21
Cedar-HT4	48.8	36.6	1.22
Reference ^{a)}	-	5 - 6	-

a) commercially available blast furnace coke.

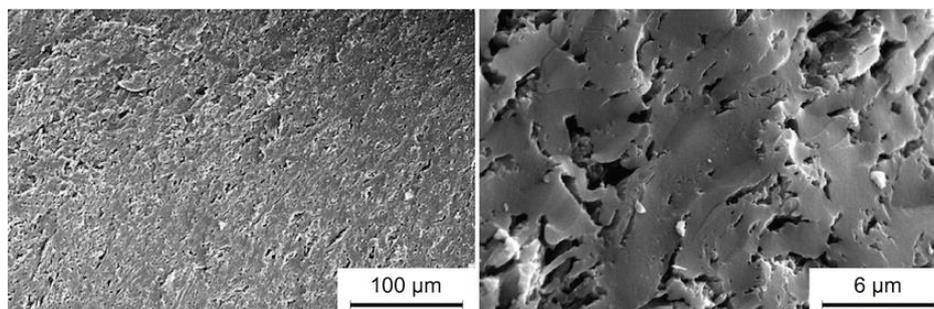


Fig. 3. Scanning electron micrographs of fracture surfaces of a coke sample from cedar-HT1.

3.3 Steam Gasification of Char from Upgraded Biomass

Fig. 4 compares the kinetics of steam gasification of Char-I, Char-II and Char-IIa. Char-I from the original cedar undergoes very fast gasification, which was catalyzed by the inherent AAEM species. The gasification obeys zero-order kinetics, which occurs when the catalyst are highly dispersed in the gasifying carbonaceous matrix of char. The change in the rate of conversion around 15 min is due to transformation of the catalyst at which its concentration reaches a loading saturation level (LSL).¹¹ HT not only slows down the char conversion but also alter the mechanism by the elimination of AAEM species. The kinetic analysis revealed that the gasification of Char-II followed first-order kinetics over the entire range of char conversion, which was typical to non-catalytic gasification. In fact, the gasification of Char-IIa, in other words, the char from the HCl aq.-washed cedar-HT, takes place tracing a profile near-identical to that for Char-II. Thus, HT did not fully removed AAEM species, but eliminated the catalytic AAEM species completely.

Investigation of partially gasified Char-II revealed a value of upgraded cedar. Fig. 5 illustrates the change in the specific surface area (SSA) of Char-II with the progress of gasification in terms of conversion. SSA increases monotonically with the char conversion beyond 2,000 m² g⁻¹. Though not shown here, the gasification of K-loaded Char-II (i.e., Char-II-K1 and Char-II-K2) caused the development of SSA, but much less extensively than those of Char-II and Char-IIa. The maximum SSA was 1,200 – 1,400 m² g⁻¹. The substantial increase in SSA was thus attributed to the absence of AAEM species.⁹ The upgraded cedar is an excellent raw material of clean and high-surface-area carbon material, and also applicable to coproduction of such material and syngas.

4. Conclusion

The present study has demonstrated that HT with recycling of water maximizes the yield of upgraded cedar that is free from catalytic AAEM species. The upgraded cedar is

an excellent raw material of high-strength metallurgical coke and also that of high-surface-area carbon materials.

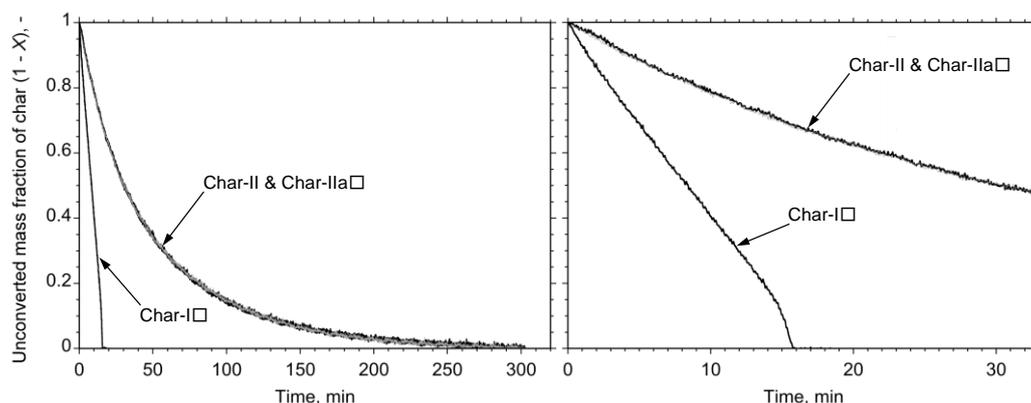


Fig. 4. Time profiles for steam gasification of Char-I, Char-II and Char-IIa. The left and right graphs are drawn with different time scales.

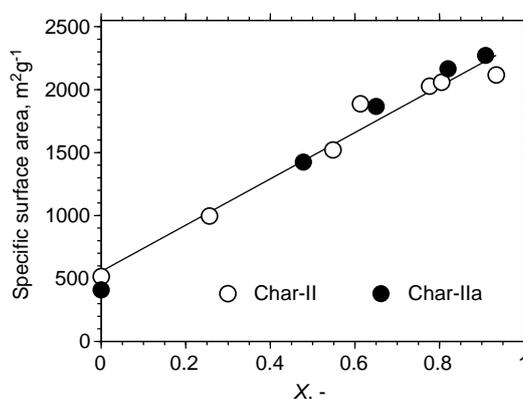


Fig. 5. Specific surface areas of Char-II and Char-IIa as a function of conversion.

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