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Upgrading the characteristics of biochar from cellulose, lignin, and xylan for solid biofuel production from biomass by hydrothermal carbonization

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ABSTRACT

In this study, hydrothermal carbonization of the main lignocellulosic components was investigated as a method of renewable solid biofuel production from biomass. Hydrothermal carbonization of cellulose, xylan, and lignin was experimentally conducted between 150 °C and 280 °C, and the chemical and fuel properties of the resulting biochars were investigated. The properties of each of the three biomass components were greatly improved by hydrothermal carbonization and were similar to coal-like fuel substances; an increase in fixed carbon and carbon contents was also observed. Furthermore, by assessing carbon recovery and energetic retention efficiency, we could establish the optimum condition for hydrothermal carbonization of biomass to produce energy. The C/O and C/H ratios of all of the obtained biochars were decreased and found to be similar to those of lignite and sub-bituminous coal. The calorific values of the biochars were between 23–26 MJ/kg at a reaction temperature of 220 °C. The results of this study indicate that hydrothermal carbonization can be used as an effective method to generate highly energy-efficient renewable fuel resources from biomass.

Introduction

Renewable energy can help solve the current global energy issues caused by depletion of fossil fuel reserves and the large impact of CO_2 emissions on climate change [1–5]. Biomass is an increasingly popular renewable energy source, and it is predicted to become integral to the total renewable energy supply [1,2]. Biomass resources for biofuel production include various natural and derived materials, such as woody and herbaceous species, wood wastes, bagasse, agricultural and industrial residues, waste paper, municipal solid waste, sawdust, biosolids, grass, waste from food processing, animal wastes, aquatic plants, and algae [1–6].

Most of the available biomass includes a slowly degradable lignocellulose consisting of three major chemical components: cellulose, hemicellulose, and lignin [7,8]. Cellulose is difficult to convert into biofuel because it is an insoluble polysaccharide and a component of approximately 50% of all cell materials. Hemicellulose is easily depolymerized by acids to form polysaccharides. Xylan comprises up to 10% and 30% of all hemicelluloses found in softwoods and hardwoods, respectively [7,8]. Lignin is a highly substituted mononuclear aromatic polymer and is often found bound to adjacent cellulose fibers to form a lignocellulosic complex. The lignin content of various biomasses, including both softwoods and hardwoods, generally ranges from 10% to 40% of total dry mass [7–11]. Therefore, due to its complexity, pretreatment is necessary to convert lignocellulose into a biofuel.

Due to convenience, direct combustion of biomass for heating purposes has been used for ages; however, direct combustion of biomass is no longer favorable because the moisture content of biomass is too high for stable combustion. Furthermore, direct combustion has low energy recovery and emits environmentally unfriendly gases such as CO_2 and SO_2 [12–16]. Therefore, several alternative technologies have attempted to convert biomass into biofuel; these include biological, chemical, and thermochemical conversion processes. Biological processes require long treatment periods and highly refined systems [13]. Chemical processes convert biomass into bio-oils. Thermochemical processes involve pyrolysis, liquefaction, gasification, and supercritical fluid extraction methods [14–17]. The products of thermochemical processes are categorized as biogas and carbon-rich solid residue (such as biochar).

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Among thermochemical processes, hydrothermal carbonization (HTC) has gained widespread interest in recent years because of its efficiency and convenience [17–22]. HTC technology is based on the use of water at high temperatures and under high-pressures (also known as subcritical water: $180 < T < 373\ ^{\circ}C$, $1.5 < P < 22$ MPa). Several studies have shown that by using HTC, a biomass with a low calorific value and high water content can become a carbon-rich-solid with chemical properties similar to those of lignite coal [18–24].

The HTC conversion of each component of lignocellulosic biomass influences the overall quality of biochar. HTC can be used to improve the fuel properties of cellulose, hemicellulose, and lignin present in lignocellulosic biomass. However, few studies have performed HTC treatment on lignocellulosic components to produce high quality biochar. In this work, the objective was to test and compare the effects of HTC at different reaction temperatures for each of the three main lignocellulosic biomass components. We also investigated how the properties of the resulting biochars could affect the value of using lignocellulosic biomass as a viable energy source.

Materials and methods

Materials

In our experiments, we evaluated the change in biomass characteristics after HTC for three biomass components. Pure cellulose (α-Cellulose-fiber form, purchased from Nacalai Tesuque Inc., Kyoto, Japan); xylan (Beachwood, purchased from SIGMA), which is the main component of hemicellulose [7]; and lignin (purchased from Kanto Chemical Co., Inc., Japan) were subjected to HTC to evaluate if and how the contents of these materials could be improved for solid fuel production. Table 1 shows the original properties of each biomass component.

Lab-scale hydrothermal carbonization reactor

A laboratory-scale HTC reactor was used to investigate the effects of hydrothermal reaction temperatures on cellulose, xylan (hemicellulose), and lignin. The experiments were performed using a 1-L reactor consisting of a reactor body, heater, and a steam condenser operated under N_2 gas. A compound sample (40 g) of each biomass component was mixed with an equal amount of water and loaded into the reactor. The operating temperatures (and pressures) of the HTC reactor were 150 °C (1.3 MPa), 180 °C (1.8 MPa), 200 °C (2.0 MPa), 220 °C (2.4 MPa), 250 °C (3.8 MPa), and 280 °C (6.5 MPa), and the reaction time was set at 30 min with an agitation speed of 200 rpm. After completing the hydrothermal reaction, the pressure and temperature were allowed to decrease to atmospheric pressure and room temperature, respectively, and the products were taken out of the reactor.

Table 1
Properties of each biomass component.

	Cellulose	Xylan	Lignin
Proximate analysis (wt.%, d.b.[a])			
Volatile matter	93.4	79.8	54.8
Fixed carbon	6.1	15.2	27.4
Ash	0.5	5.1	17.8
Ultimate analysis (wt.%, d.b.[a])			
C	43.0	41.9	51.6
H	6.4	6.0	4.3
N	0.0	0.0	0.0
O	50.1	47.0	26.3
Calorific value (MJ/kg, d.b.[a])	16.5	13.9	20.4

[a] Is on dry basis.

Analytical procedures

Powders were prepared from all samples: pure biomass components and their biochars. All powders were sieved and the fraction with a particle size between 177 and 250 μm was used for fuel property analysis. Elemental composition analysis of cellulose, xylan, lignin, and their solid products (as biochar) was carried out using a PerkinElmer 2400 Series II CHN organic elemental analyzer (PerkinElmer, Waltham, MA, USA). Proximate analysis was conducted using a SHIMADZU D-50 simultaneous TGA/DTA analyzer. Calorific value was determined using a bomb calorimetric standard method according to JIS M-8814 (JPN ISO1928:1995). The functional groups were analyzed by Fourier transform infrared (FTIR) spectroscopy (Nicolet iS 10, SCINCO CO.) in the range of $4000\ cm^{-1}$–$400\ cm^{-1}$ with each spectrum generated from the spectral average of at least five scans. These data were used to calculate carbon and energy-related properties associated with the recovered solids, including carbon recovery efficiency, fixed carbon recovery efficiency, energy densification, and energetic retention efficiency (see Table 2 for parameter definitions and equations [25,26]).

Results and discussion

Effect of hydrothermal carbonization on biomass components

HTC changed the properties of cellulose, hemicellulose, and lignin. Fig. 1 and Table 3 show the analysis of the biomass components produced by varying the hydrothermal reaction temperature. The fixed carbon content of cellulose increased from 6.1% to 35.0% in response to HTC at 220 °C. This result suggests that the cellulose began to decompose at 220 °C. The fixed carbon and carbon contents of xylan increased from 15.2% to 33.5% and from 41.9% to 61.3%, respectively, at 180 °C (Figs. 1 and 2). Below 180 °C, the compositions of the products were not different from the raw material. This result is not surprising because the hydrolysis of hemicellulose occurs at 180 °C [18]. As the fixed carbon content and carbon content increased due to HTC, the calorific value increased. However, the results for lignin were different from those of cellulose and hemicellulose. Lignin started to decompose at temperatures exceeding 250 °C (Fig. 1). This is likely due to the decomposition or pyrolysis of lignin at temperatures slightly below 250 °C. Thus, when HTC is applied to treat biomass, the increase in the fixed carbon content of biomass is mainly due to the increase in the fixed carbon content of cellulose and hemicellulose. Additionally, the ash content of lignin was higher than that of cellulose.

Fig. 3 shows the calorific values of cellulose, hemicellulose, and lignin. Pure lignin had a higher calorific value (20.4 MJ/kg) than

Table 2
Equations used to estimate the effects of hydrothermal carbonization.

Term	Equation
Solid recovery (=product yield)	$\frac{\text{Mass of dried biochar}}{\text{Mass of dried initial feedsock}}$
Carbon recovery efficiency	$\frac{\text{Carbon (\%) in biochar}\cdot\text{Biochar weight}}{\text{Carbon (\%) in feedstock}\cdot\text{feedstock weight}}$
Fixed carbon recovery efficiency	$\frac{\text{Fixed carbon (\%) in biochar}\cdot\text{Biochar weight}}{\text{Fixed carbon (\%) in feedstock}\cdot\text{feedstock weight}}$
Energy densification	$\frac{\text{Calorific value of biochar}}{\text{calorific value of feedstock}}$
Energetic retention efficiency (=energy recovery)	$\frac{\text{Calorific value of biochar}}{\text{Calorific value of feedstock}}\times\text{Solid recovery}$
HHV improvement	$\frac{\text{HHV of biochar} - \text{HHV of feedstock}}{\text{HHV of feedstock}}$