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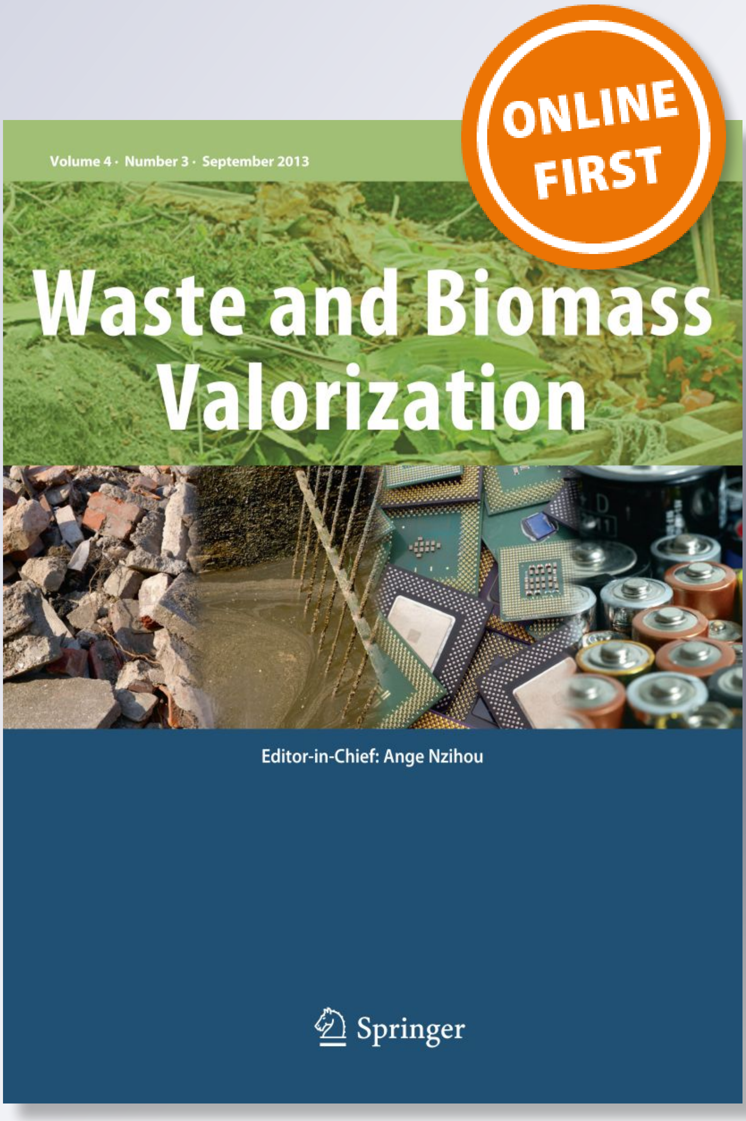
Waste and Biomass Valorization

ISSN 1877-2641

Waste Biomass Valor
DOI 10.1007/s12649-017-9898-9



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ORIGINAL PAPER

Characterization and Production of Solid Biofuel from Sugarcane Bagasse by Hydrothermal Carbonization

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Received: 7 December 2015 / Accepted: 7 March 2017

Abstract Hydrothermal carbonization of sugarcane bagasse using hot-compressed-water was investigated for the treatment of solid material to understand the occurring decomposition reactions. The experiments were performed in 14 ml of batch type reactor in the range of temperatures 200–300 °C and reaction times 3–30 min. After separation of solid residues from liquid material, approximately 34–88 wt% of raw material was recovered as solid products. Characterizations show that increased treatment temperature and reaction time causes structural changes of the sugarcane bagasse. When the temperature and reaction time was increased, hemicellulose and cellulose gradually dissolved, leaving a lignin-like acid insoluble residue. The presence of the residue increases the fixed carbon and decreases the volatile matter content of the solid product. Dehydration significantly decreases the oxygen content and slightly decreases the hydrogen content of the treated material. With these changes, the caloric value and of the solid product increases by 1.1–1.9 times that of the raw material. Higher temperature treatment (300 °C) produces a material with high caloric value and fixed carbon, with a composition comparable to typical solid fuels such as lignite (or low rank-coal). The hydrothermal carbonization of sugarcane bagasse could be a solution to reduce environmental pollution caused by the combustion of wet stockpiled sugarcane bagasse in the sugar industry. The treated sugarcane bagasse reduces energy loss, smoke and water vapor during the combustion process.

Keywords Sugarcane bagasse · Lignocellulosic biomass · Hydrothermal carbonization · Hot-compressed-water · Solid biofuel

Introduction

Biomass has potential for use as transportation fuel, feedstock for chemical products and renewable power generation. It is abundant, renewable and environmentally friendly. Biomass has been considered as an alternative to fossil fuels. Biomass from agricultural waste is particularly suitable as it does not compete with animal feedstock or the food industry [1].

Among agricultural wastes, sugarcane bagasse is abundant and has the potential to be transformed into energy and chemical feedstocks. Bagasse is the fibrous residue obtained after sugarcane juice is extracted. Generally, 280 kg or 30–32% of wet bagasse is produced from 1 t of sugarcane [2]. In many sugar mills, sugarcane bagasse is used to generate heat and power for the milling process. Though sugarcane bagasse can be used as fuel, a significant amount of bagasse remains stockpiled. The stockpiled bagasse has low economic value and is an environmental problem for mills and surrounding districts, especially if stockpiled for long periods, which increases the risk of spontaneous combustion [3]. The conversion of sugarcane bagasse to chemical and energy sources is a viable option

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to considerate for reducing environmental pollution and fossil fuel consumption.

To increase the economic value of sugarcane bagasse, numerous conversion methods have been proposed. The conversion methods consist of either biochemical/biotechnology methods or thermochemical methods. These techniques include pyrolysis [4, 5] and hydrothermal methods [6, 7], for producing energy, pulp and paper, chemicals and fermentation-based products [8]. Hydrothermal treatment is a method that has generated widespread interest in recent years [1, 6, 7], as it is able to convert low-carbohydrate biomass into materials with a high energy content or directly into biofuel.

Hydrothermal treatment, particularly using hot-compressed-water (HCW), is suitable for materials with high moisture content [9–11]. It has also been acknowledged as an efficient technique to selectively decompose biomass. The HCW acts as a solvent and can also be applied as a reactant, catalyst or product [12]. It enhances the hydrolysis reaction, decomposing the lignocellulosic polymer into valuable chemicals that dissolve into liquid products. Any remaining solid product has a high caloric value [9–11, 13].

Although hydrothermal treatment for the conversion of sugarcane bagasse has been studied, previous literature focuses mainly on the pre-treatment and saccharification processes for monomeric sugar and bioethanol production [7, 14–17]. Few studies are concerned with the treated sugarcane bagasse being converted to solid biofuel and valuable chemical compounds. Chen et al. [18] reported a wet torrefaction or hydrothermal carbonization of sugarcane bagasse at a fixed temperature of 180 °C using water and dilutes sulfuric acid. In this study, they addressed the effects of acid concentration, heating time and solid-ratio on hydrothermal carbonization performance. The study reported that the sugarcane bagasse chemical formula lost H and O atoms under dehydrogenation, deoxygenation and dehydration processes. However, this study did not clearly describe the mechanism of the decomposition reaction under hydrothermal carbonization.

In our previous paper, the decomposition reaction of cellulose and hemicellulose under hydrothermal treatment for production of valuable chemicals such as furans and organic acids from sugarcane bagasse has been investigated and described in detail [19]. Therefore, in order to utilize sugarcane bagasse effectively, the main objective of the present study was to obtain the best condition for production of solid biofuel. The solid product obtained from hydrothermal carbonization has been investigated and characterized in order to comprehensively understand the decomposition reaction mechanism. The hydrothermal carbonization experiment is carried out over a temperature range of 200–300 °C and reaction times of 3–30 min. The effect of temperature and reaction time on the material decomposition was determined based on physicochemical changes to the surface morphology, elemental composition, or functional groups. A mechanism for the decomposition reaction under hydrothermal carbonization is proposed and discussed based on the characterizations of the solid product under various conditions. Distribution of solid characteristics product such as ultimate and proximate values, heating value, energy density and energy yield are also evaluated and discussed with regard to the feasibility of using treated sugarcane bagasse as a solid biofuel. Sugarcane bagasse can be used for valuable chemical production, and can also produce carbonaceous material for solid biofuel.

Materials and Methods

Material Preparation

Sugarcane bagasse which is used in this study provided by sugar industry. It was pulverized using a cutting mill into maximum particle size of 1.0 mm, and then dried in an oven at 60 °C for 24 h before hydrothermal carbonization treatment.

Hydrothermal Carbonization Treatment Experiment

The hydrothermal carbonization were carried out following the methodology described in [19, 20]. In hydrothermal carbonization experiments, 1.2 g of sugarcane bagasse and 10 ml water were mixed in a batch cylindrical reactor. All the experiments have been carried out in the batch process using a cylindrical reactor (SUS 316, 14 ml) equipped with a K-thermocouple to measure the reaction temperature. N_2 gas was used to replace air in the reactor and to adjust the initial internal pressure at 0.5 MPa. The operating pressure of the reactor was retained at or above the saturated water vapor pressure, in order to maintain the water in the liquid form. The reactor was heated to the target temperature by immersion into a pre-heated salt bath at the desired reaction time. After heating, the reactor was then immediately cooled by immersion into a water bath to room temperature.

A temperature range of 200–300 °C, and a reaction time (including heating period i.e. 3 min) from 3 to 30 min was used. The treated slurry was then collected and filtered using a GP 16 glass filter under vacuum to separate the solid and liquid products for further analysis. The compositions of the liquid product and water soluble fraction were analyzed using HPLC where equipped with a KC-811 column (JASCO) and refractive index detector (RI-2031, JASCO). The solid or water insoluble product was dried at 105 °C until constant weight to yield the final solid product.

$$\text{Yield of solid product (wt\%)} = \frac{\text{mass of solid product (g)}}{\text{mass of raw material (g)}} \times 100\% \tag{1}$$

Analysis Methods

The composition of raw sugarcane bagasse was determined using the procedure recommended by the US National Renewable Energy Laboratory (NREL) [21]. Before analyzing the composition of the raw material, a sample was extracted using ethyl alcohol to determine the wax content using a soxhlet extractor over 8 h at 80 °C. 150 mg of the de-waxed sample was then dried and treated with 1.5 ml of 72 wt% H_2SO_4 at 30 °C for 1 h. 42 ml of water was added to the treated sample and hydrolyzed for 1 h in an autoclave at 121 °C. The hydrolyzed sample was cooled, and then filtered using a GP 16 glass filter under vacuum and washed several times with hot water. The residue was noted as a Klason lignin (i.e. acid insoluble solid residue) and was dried at 105 °C overnight. The concentration of sugars, such as xylose, arabinose and glucose, and other chemicals from the filtrate, were analyzed by high-performance liquid chromatography (HPLC). The chromatograph was equipped with a KC-811 column (JASCO) and refractive index detector (RI-2031, JASCO). The HPLC was operated under the following conditions: oven temperature 50 °C, 2 mM $HClO_4$ used as the mobile phase, delivered at a flow rate of 0.7 ml/min. Cellulose and hemicellulose were determined by the following correlations [21]:

$$\text{Cellulose (wt \%)} = \text{glucose (wt \%)} \times 0.9 \tag{2}$$

$$\text{Hemicellulose (wt \%)} = (\text{xylose} + \text{arabinose}) \text{ (wt \%)} \times 0.88 \tag{3}$$

The ash content was determined by measuring the weight of raw bagasse before and after heating a 1.0 g sample at 575 °C for 5 h. The solid products were further characterized by several methods. A Yanaco CHN Corder MT-5 elemental analyzer was used to measure the elemental composition of the solid products. Chemical components, ultimate, proximate and heating values of sugarcane bagasse presented in Tables 1 and 2, respectively.

The elemental compositions or ultimate values were used to calculate the higher heating value, energy density and energy yield. The higher heating value (HHV) was calculated according to Dulong's formula [22]:

$$\text{HHV}\left(\text{MJ kg}^{-1}\right) = 0.3383\text{C} + 1.442\,(\text{H} - \text{O}/8) \tag{4}$$

where C, H, and O are the percentages of carbon, hydrogen, and oxygen, respectively.

The energy density ratio and energy yield were calculated using the following Eq. [23]:

$$\text{Energy density ratio} = \frac{\text{HHV of solid product}}{\text{HHV of raw material}} \tag{5}$$

$$\text{Energy yield(wt \%)} = \text{Yield of solid product (wt \%)} \times \text{energy density ratio} \tag{6}$$

$$\text{Recovery ratio} = \frac{\text{(chemical component in treated material)}}{\text{(chemical component in raw)}} \times \text{yield of solid product} \tag{7}$$

The solid products were analyzed by scanning electron microscopy (SEM KEYENCE/VE-9800) to determine the effect of hydrothermal carbonization on the sugarcane bagasse morphology. The samples were pre-treated for SEM analysis by sputter-coating with a thin layer of gold. Fourier transforms infrared (FTIR) spectrometer (JASCO 670 Plus) using the KBr disk technique was also performed to identify the chemical structure and functional groups of the untreated and treated samples. The samples for analysis were prepared by mixing with KBr and pressing into pellets (1 mg of sample/100 mg of KBr).

Proximate analyses of untreated and treated material were conducted using a thermogravimetric analyzer (TGA) (Bruker TG DTA 2000SA). The experiments were conducted following conditions set in the JIS Standard method (JIS M 8812:2004) for proximate analysis of coal and coke. The TGA analyzer was monitored by computer to determine the weight change and the temperature/time curve.

Table 1 Chemical components of sugarcane bagasse

Chemical component (wt% d.b.)					
Cellulose	Hemicellulose		Klason lignin	Wax	Ash
	Arabinan	Xylan			
43.4	1.7	20.0	20.3	2.3	5.6

d.b. dry basis

Table 2 Ultimate, proximate and heating values of sugarcane bagasse

Ultimate values (wt% d.a.f.)				Proximate values (wt% d.a.f.)		Heating value (MJ/kg)
C	H	O (diff.)	N	VM	FC	GCV
44.2	5.8	49.7	0.2	86.6	13.4	14.4

d.a.f dry ash free basis, *diff.* difference, *VM* volatile matter, *FC* fixed carbon, *GCV* gross caloric value

Prior to TGA testing, approximately 5 mg of a solid sample was placed in a platinum crucible. The experiment was conducted in four-step control program with conditions as presented in Table 3. The moisture content is determined by the mass loss after heating period at 107 °C. Mass evolved between 107 and 900 °C represented volatile matter content, while the remaining was the fixed carbon content. The remaining after heating sample at 900 °C was considered to be ash. Thermogravimetric experiments were carried out under a nitrogen atmosphere with a constant flow of 100 ml/min over steps 1–3, and oxygen in step 4 to completely burn out the chars. The analysis was repeated two times to check for repeatability.

Table 3 Thermogravimetric program for proximate analysis

Step	Heating rate (°C/min)	Temperature indicated (°C)	Period (min)	Atmosphere
1	0	20	15	N_2
2	30	107	10	N_2
3	80	900	10	N_2
4	0	900	15	O_2

Results and Discussion

Thermal Characterization of Treated Sugarcane Bagasse

Proximate and ultimate parameters are important to establish the energy contained in coal and other solid fuels for potential thermal conversion. Figure 1 shows the proximate analysis of the treated material. Changes of the volatile and fixed carbon content are mainly caused by the thermal decomposition of biomass components. Similar to other lignocellulosic biomasses, sugarcane bagasse has a high volatile matter content of 86.6 wt% and low fixed carbon of 13.4 wt%. As shown in Fig. 1, at 200 °C, the proximate values were not significantly altered. At temperatures above 240 °C, the treatment causes a decrease in volatile matter content but increases the fixed carbon of the material. The proximate values were affected by temperature as well as reaction time. Figure 1 suggests that long retention time could decrease the volatile matter and increase the fixed carbon of a treated material. However, at 300 °C, (>20 min) the proximate values tended to remain constant.

Analysis of elemental composition of solid product yielded at different temperatures and reaction times is

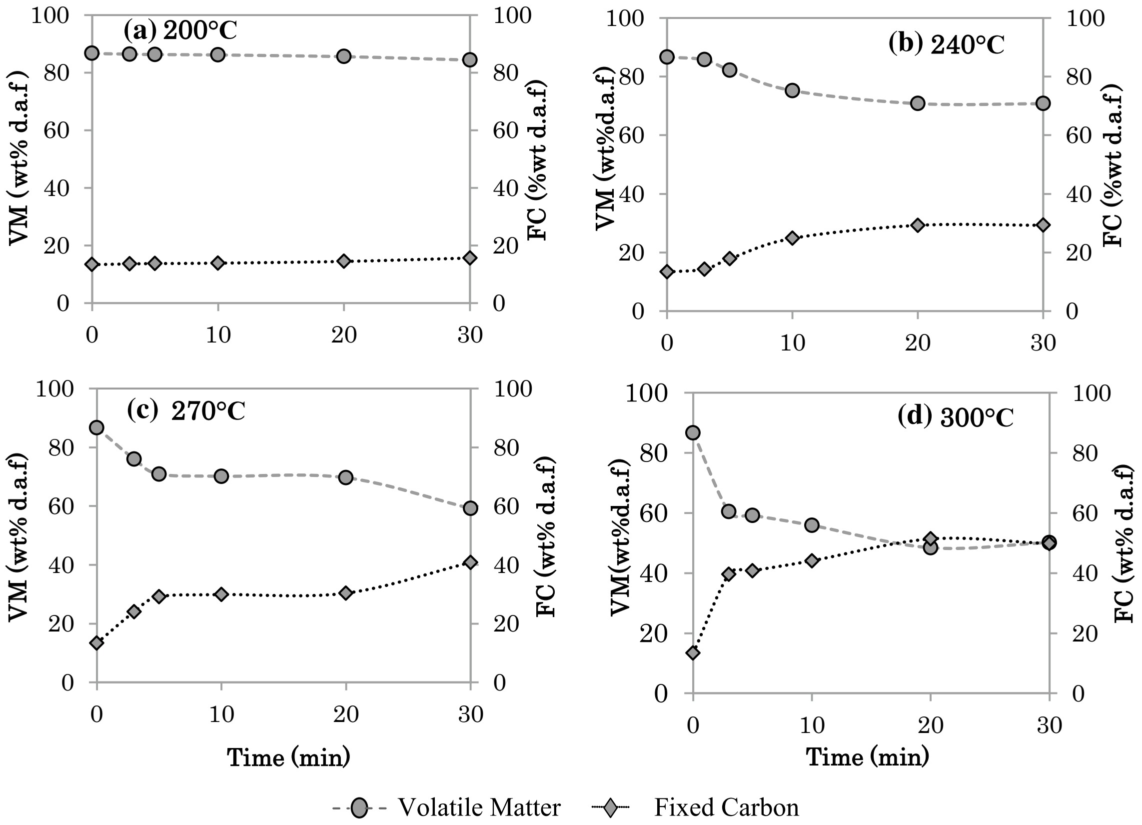

Fig. 1 Proximate values of raw and treated sugarcane bagasse data under HCW treatment in various reaction conditions

shown in Table 4. As expected, the treatment significantly affects the elemental composition of the solid product. Treated material shows higher carbon content and lower oxygen content than the raw materials.

Figure 2 shows the changes of atomic H/C and O/C ratios of the raw and treated materials plotted according to the Van Krevalen diagram [24]. The raw sample has high ratios of H/C and O/C, but the values decrease with increasing treatment temperature and time. The most significant change occurs in the temperature range of 240–300 °C where the trajectory slope is parallel to the dehydration line. This suggests that the dehydration reaction prevails during hydrothermal carbonization treatment. It was also observed that a slight carboxylation occurred at 270–300 °C (>10 min). The resulting solid product had elemental compositions comparable with typical solid fuels such as lignite. A solid product or fuel with low H/C and O/C ratios is favorable to reduce the energy loss, smoke and water vapor produced during the combustion process [25].

Table 4 Elemental composition of solid residue after treatments

Treatment conditions		Ultimate analysis (wt%, d.a.f.)			
Temperature (°C)	Time (min)	C	H	O (diff.)	N
200	3	45.3	6.0	48.5	0.2
200	5	45.2	5.7	48.7	0.4
200	10	45.3	5.6	48.6	0.4
200	20	46.9	5.9	47.0	0.2
200	30	48.6	5.8	45.3	0.2
240	3	46.1	6.0	47.7	0.2
240	5	48.9	5.9	44.8	0.3
240	10	51.1	5.8	42.7	0.3
240	20	53.1	5.7	40.8	0.3
240	30	54.6	5.7	39.4	0.3
270	3	49.6	5.7	44.3	0.2
270	5	54.1	5.7	40.0	0.3
270	10	60.3	5.2	34.1	0.4
270	20	64.8	5.0	29.7	0.4
270	30	67.8	5.0	26.6	0.5
300	3	60.2	5.4	34.0	0.4
300	5	64.5	5.1	30.0	0.4
300	10	68.2	5.2	26.1	0.4
300	20	70.2	5.3	24.1	0.4
300	30	70.0	5.1	24.5	0.4

Thermal qualities and energy yields are presented in Fig. 3 as follows: (a) gross caloric value, (b) energy density, (c) solid product yield and (d) energy yield. Hydrothermal treatment increases the carbon content of sugarcane bagasse and significantly increases its higher heating value. As presented in Fig. 3a, the higher heating value of the treated material increases with increased treatment temperature and time. Optimal conditions were obtained at temperatures of 300 °C. Compared with the untreated sample of 14.4 MJ/kg-dry feed base, the higher heating value of the bulk product at optimum conditions increased to 27.0 MJ/kg-dry base feed. With the increased heating value, the treatment also increases the energy density of the solid product. The energy density increased with reaction temperature and time from a low of 1.1 at 200 °C (3 min) to a high of 1.9 at 300 °C (20 min). This trend is reversed when concerning the energy yield and mass yield, the hydrothermal carbonization causes a reduction of these yields. As can be seen in Fig. 3c, d, the initial mass and energy yields decreased rapidly with increasing temperature from 200 to 270 °C over a

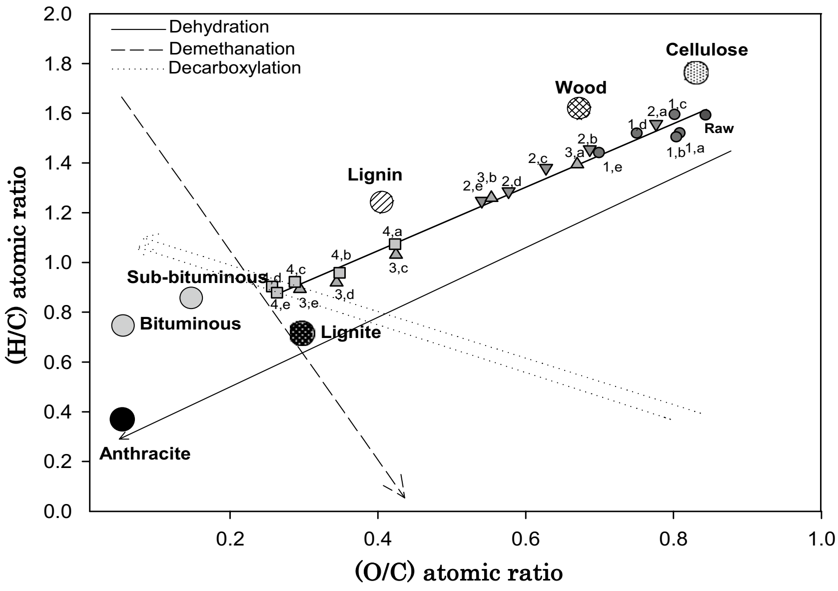

Fig. 2 Atomic H/C and O/C ratios of treated material in different treatment conditions (*1* 200 °C; *2* 240 °C; *3* 270 °C; *4* 300 °C; *a* 3 min; *b* 5 min, *c* 10 min; *d* 20 min; *e* 30 min)

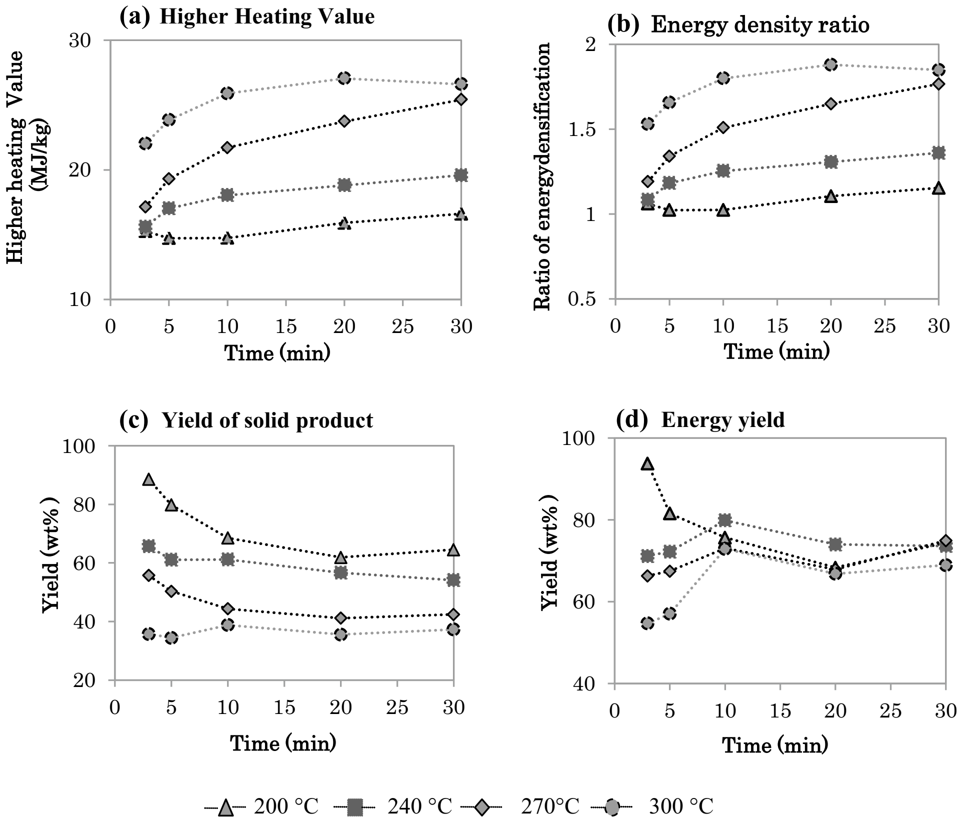

Fig. 3 Distributions of **a** higher heating value, **b** energy density ratio, **c** yield of solid products, and **d** energy yield undergoing hydrothermal carbonization

range of treatment times (<10 min). The mass and energy yield of the solid product remained constant at temperature of 300 °C with the lowest energy yield of 54.6 wt%.

The proximate, ultimate and thermal analysis results suggest that the hydrothermal carbonization can convert biomass from a low quality energy material to a high quality energy material. These results indicate that hydrothermal carbonization could be a solution to reduce environmental pollution caused by the combustion of wet stockpiled sugarcane bagasse in the sugar industry. The treated sugarcane bagasse reduces energy loss, smoke and water vapor during the combustion process and also produces valuable chemical compounds such as furans and organic acids [19]. It also has suitable characteristics for use as a solid biofuel for thermal conversion.

Solid Product Chemical Composition

The chemical composition of the solid products were measured and presented in Fig. 4. The recovery ratio of each chemical component remaining in the solid products was given. The recovery ratio of the treated sugarcane bagasse is defined by Eq. (7).

Figure 4 compares the percentage of chemical compounds remaining in the treated material with the raw material. The cellulose and hemicellulose content in the solid product gradually decreases with increasing temperature and reaction time. Hemicellulose is more susceptible to hydrolysis than other polymers because of its branched structure and lower degree of polymerization [25]. Hemicellulose begins to decompose at 200 °C (3 min) with a recovery ratio of only 85.1 wt%. It is completely decomposed and undetectable in the solid residue at 200 °C (20 min) and 240 °C (5 min). Garrote et al. [26] reported that hydrolysis of lignocellulosic material causes decomposition in the presence of ion hydronium at 150–230 °C. Ion hydronium is generated by water auto-ionization and acts as a catalyst, leading to the generation of oligosaccharide and splitting of the acetyl group of hemicellulose, which generates acetic acid [27]. The analytical results indicate that the acetyl group starts splitting at 200 °C (3 min). The hydronium ion from the acetic acid also acts as a catalyst in the next reaction step for the degradation of polysaccharides [26, 28, 29].

In contrast with hemicellulose, the decomposition of cellulose at 200 °C remained undetected, even after a longer reaction time. Cellulose starts to degrade at 240 °C (5 min) with a recovery ratio of 85.7 wt%. It gradually degrades and is undetectable at 270 °C (20 min). Cellulose is a long un-branched glucose polymer, linked by strong β-(1,4)-glycoside bonds. Its regular structure gives it greater thermal stability than hemicellulose. It is reasonable that

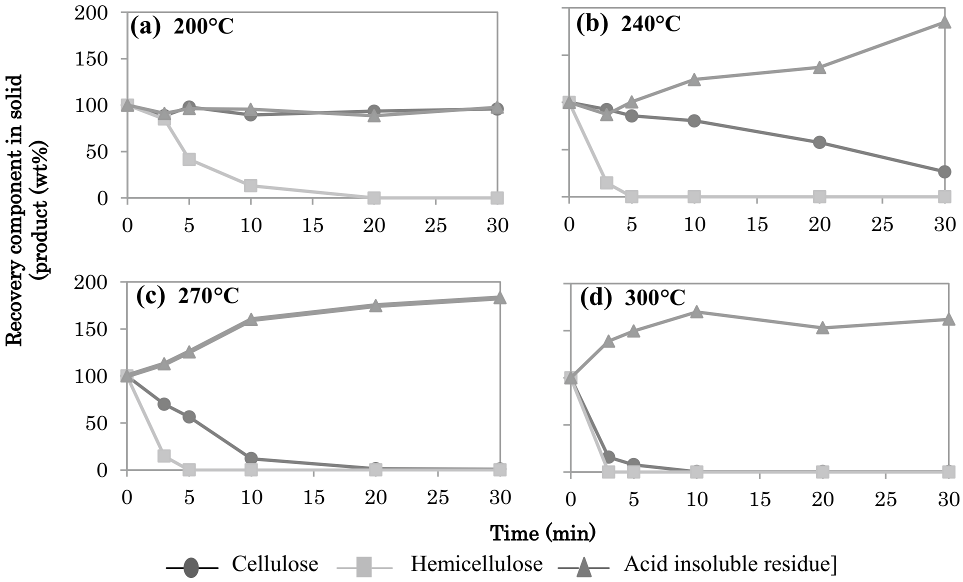

Fig. 4 Recovery ratio of each component in solid product in various conditions

cellulose would require more severe treatment conditions to decompose than hemicellulose.

Based on the composition data of the solid products, hemicellulose and cellulose decompose under treatment from complex polymers into smaller molecular weights of simpler substances (such as xylose, arabinose, and glucose). These monosaccharides undergo dehydration and fragmentation (i.e., ring-opening and C–C bond breaking) processes and produce different soluble product such as furan compounds (furfural, 5-HMF) and organic acids [19, 30]. Hydrothermal carbonization treatment removes the O and H content. Significant amounts of O are removed due to the rupture of glycosidic bonds of hemicellulose and cellulose.

At elevated treatment conditions, the solid products are mainly dominated by compounds that behave as acid insoluble solid residues (i.e. klason lignin). This was observed from the recovery ratios of acid insoluble solid residues in the solid product exceeding 100 wt%. There have been several studies regarding lignin behavior under hydrothermal carbonization treatment [26, 30, 31]. Garrote et al. [26] noted that re-polymerization of solubilized lignin by breaking lignin–carbohydrate bonds in the presence of the organic acids released under hydrothermal treatment causes an increase in the acid insoluble solid residue produced. However, complete solubilization of lignin is not possible because of the advent of re-condensation reactions. Sugar degradation products (such as furfural) also react with lignin by condensation reactions and generate insoluble lignin (called 'pseudolignin'). Cara et al. [30] confirms that increased acid insoluble content is also caused by extractive content material. Sevilla et al. [29] observed that aromatic or phenolic compounds can be generated by two-step decomposition reactions from polysaccharides and monosacharides. The first step decomposition reaction produced furfural-like compounds. These compounds then generated acid/aldehydes and phenol.

We have found in our studies that the recovery ratio of acid insoluble solid residue increases because of char, re-polymerization products, condensation reactions, and saccharide decomposition products. As we described in our previous study [19], the liquid product at low temperatures (200 °C), when furan-like compounds had not decomposed, the content of acid insoluble solid residues slightly increased. At mild treatment conditions, increased acid insoluble solid residue content is also likely to be affected by extractive material. Under more severe treatment conditions, furan degradation products increase the content of acid insoluble solid residue. The products deposited onto the surface of solid increase the content of the acid insoluble residue (klason lignin) in the treated material.

At 300 °C (>10 min), the recovery of acid insoluble solid residue tends to decrease. This suggests that under hydrothermal carbonization, lignin undergoes degradation and re-polymerization in an aqueous media. The dissolved fraction depends on the operational conditions. Complete solubilization of the lignin is not possible because of the advent of re-condensation reactions [32].

The Correlation Between Acid Insoluble Solid Residues and Fixed Carbon

It has also been observed that increased acid insoluble solid residue is associated with increased fixed carbon, as presented in Fig. 5. To determine the correlation between the acid insoluble and the percentage of fixed carbon, the content of acid insoluble in certain conditions was compared with the maximum content of acid insoluble. A similar

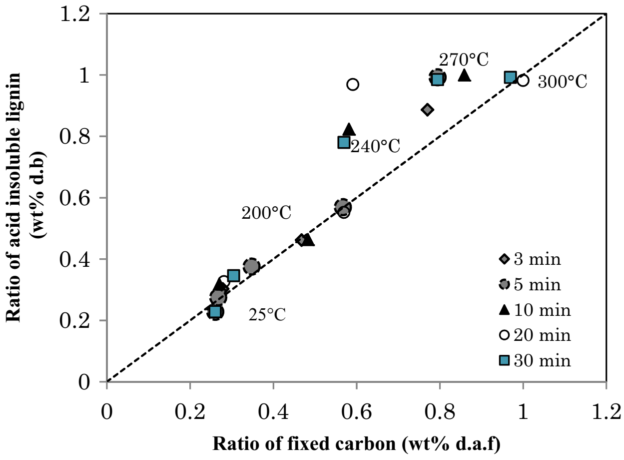

Fig. 5 Correlation between fixed carbon values and acid insoluble residue content

calculation method was applied to the fixed carbon ratios. A linear relation between the acid insoluble solid residues and the fixed carbon of the hydrothermal carbonization solid product was found. This relationship was found to have correlation coefficients (r^2) of 0.9622, 0.9496, 0.9167, 0.9821, and 0.9211 at 3, 5, 10, 20 and 30 min, respectively. These results suggest that increases of acid insoluble solid residue content in the solid product increases the amount of fixed carbon in the treated material.

These findings are consistent with the proximate values previously discussed. According to proximate analysis, the increased treatment temperature and time decreases the volatile matter and leaves the material with a high percentage of fixed carbon. The fixed carbon content increases with the decreased number of H–C and O–C bonds, and the remains of C=C bonds in the material. H–C and O–C bond are easily volatilized at high temperatures.

FTIR Analysis of Solid Product Functional Groups

To investigate the hydrothermal reaction conditions in more detail, FTIR analysis was conducted. Figure 6 presents the spectral data obtained from the FTIR analyzer. The spectral data give a simple characteristic comparison between the raw material and the hydrothermal product. All of the peaks were confirmed with literature data [31–35]. The FTIR spectral data showed a peak around 3300 cm^{-1} that is attributed to an –OH group. Comparing the FTIR spectra of the raw material and treated material, the –OH group peak decreased with increasing temperature. This indicates that the hydrogen-bonded –OH groups of cellulose were gradually ruptured. The peak changes were most apparent at temperatures above 240 °C, and almost disappeared at 300 °C (20 and 30 min). T hese conditions explain why the hydrothermal carbonization increases the hydrophobicity of the solid product.

The peak in the range of 2928–2940 cm^{-1} is attributed to the aliphatic CH_n groups and also weakens with increased temperature, indicating fragmentation and decomposition of the polymer chains. The peak in the range of 1720–1740 cm^{-1} represents C=O stretching vibrations of un-conjugated ketone, carbonyls, ester groups; and C=O of acetyl group in xylan (hemicellulose) become weaker with increasing temperature. This result is consistent with the data composition shown for the treated material, indicating the removal of a large part of hemicellulose. The peak intensity at around 1049 cm^{-1} represents C–O stretching vibrations of the cellulose and hemicellulose. This suggests that a large portion of hemicellulose and cellulose decomposes with increased temperature and reaction time. This feature is most noticeably observed above 240 °C (30 min) as the hemicellulose and cellulose were undetected at this temperature. The peak of the C–O–C aryl–alkyl ether linkages was detected around 1247 cm^{-1}. The peak of the β-glycosidic linkages between glucose in cellulose was observed in the range of 874–897 cm^{-1}, indicating a weakening presence of cellulose, which was completely undetected at temperatures above 270 °C. The peaks around 1608, 1500, and 1408 cm^{-1} correspond to the C=C stretching of aromatic groups in the lignin. The peaks around 1608 and 1408 cm^{-1} suggest that lignin in the feed material was almost stable during treatment and remained in the solid product. However, at 270 °C (20 min), the spectral data of peaks started to stretch slightly, indicating slight degradation of the lignin occurs at these high temperatures and treatment time.

SEM Analysis

SEM analysis was conducted to determine the effect of hydrothermal carbonization treatment on the material structure. The SEM images in Fig. 7 present the sugarcane bagasse surface before and after hydrothermal carbonization treatment at 10 and 30 min at varied temperatures. The sugarcane bagasse surface before treatment shows a basic and compact fiber surface structure. At 200 °C, the deformation of fibers and some cracks were apparent on the surface of the solid product. At 240 °C, the treated material surface was covered with 'debris' and a thin layer of deposits seemed to cover the whole surface. Under stronger conditions, structural rapture was observed and the surface was more cracked and covered with more small debris. This debris could be made up of the acid insoluble residue or lignin deposit, as reported by literature [26, 34]. This is consistent with the findings of acid insoluble solid residue in the solid product and from the FTIR results. It is evident that hydrothermal carbonization treatment ruptures

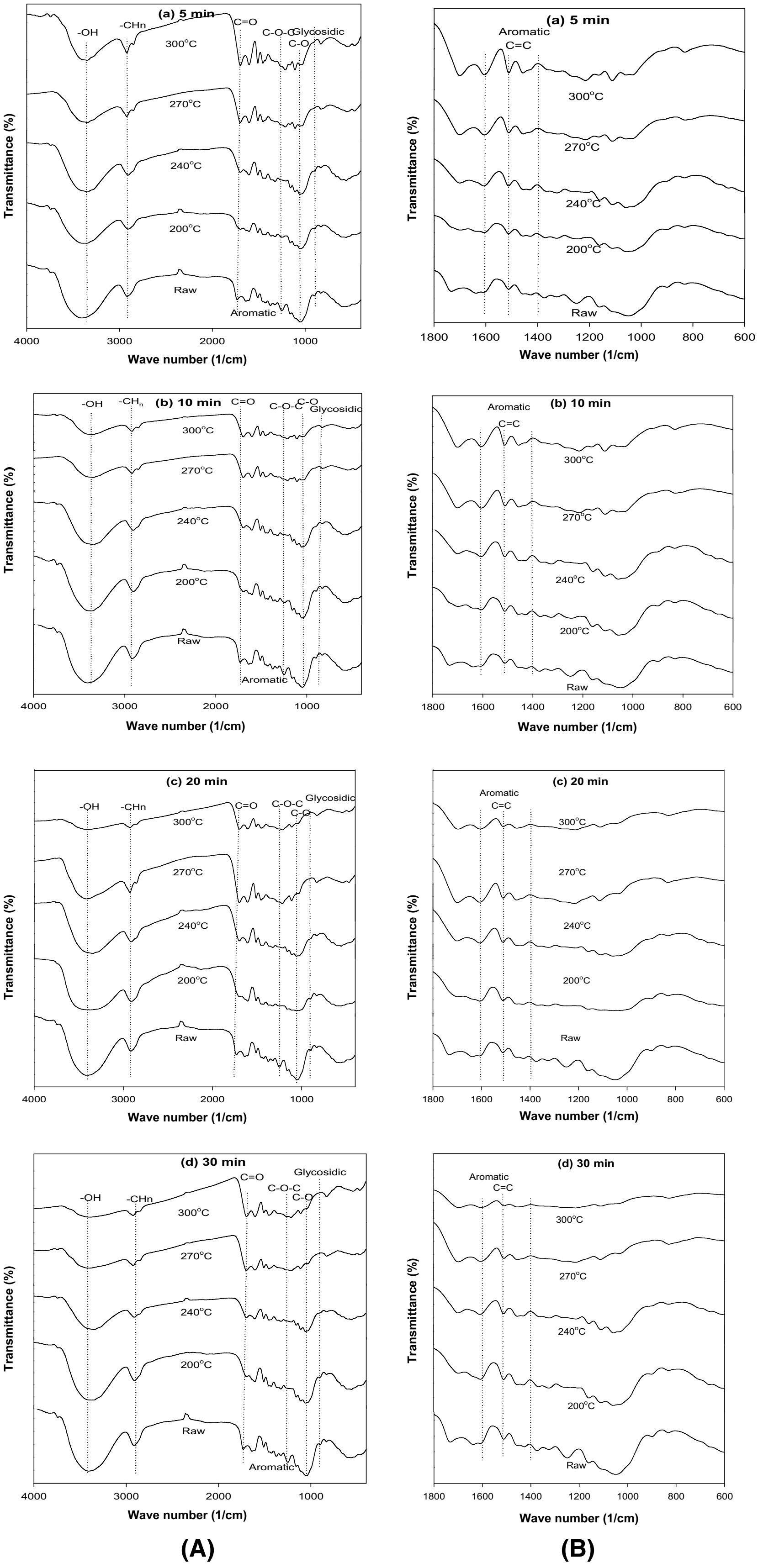

Fig. 6 FTIR spectra of raw and treated sugarcane bagasse in various conditions. **[A]** Complete spectra in various conditions. **[B]** Excerpt of spectra. (*a* 5 min, *b* 10 min, *c* 20 min, *d* 30 min)

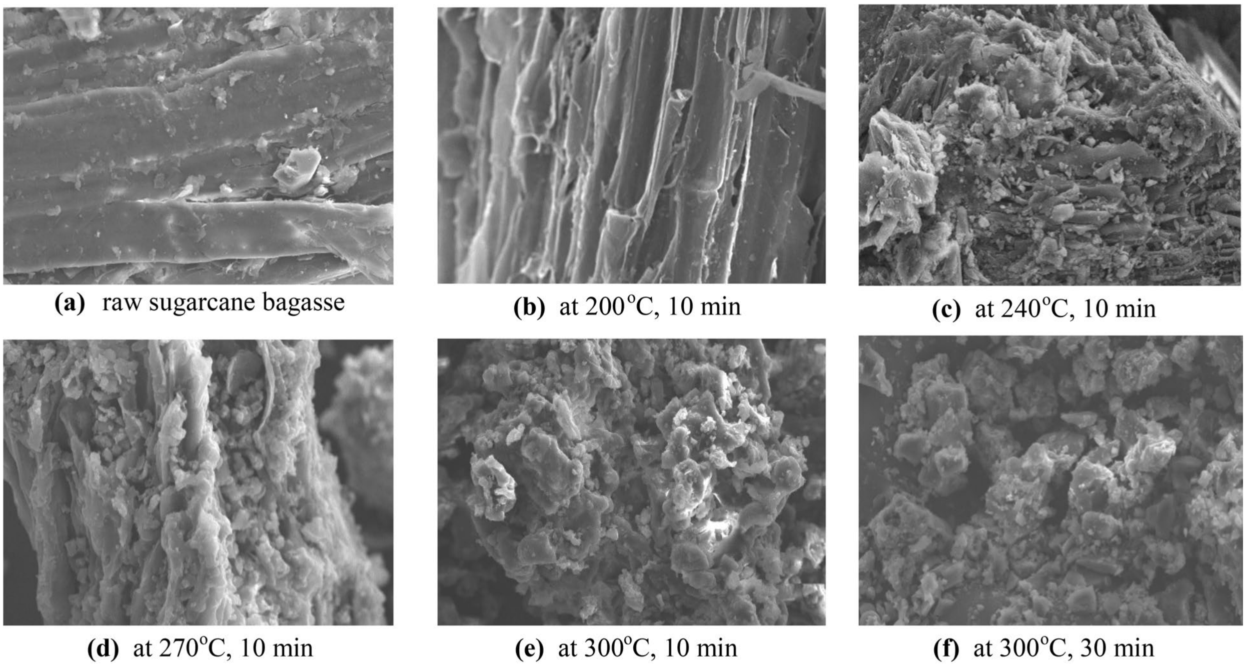

Fig. 7 SEM images of raw and HCW-treated sugarcane bagasse in various conditions

the fibrous matrix polymer network. The treatment successfully removes hemicellulose and cellulose, and under harsh conditions, re-localization of lignin occurs on the material surface.

Conclusions

The physicochemical characteristics of treated solid products from hydrothermal carbonization treatment varied depending on temperature and treatment time of the treatment. Chemical composition analysis showed that the treated solid product differed significantly from the initial raw material composition. During treatment, the cellulose and hemicellulose content gradually decreased. Hemicellulose starts to degrade at 200 °C (3 min) and is completely degraded and undetected at 200 °C (10 min). Cellulose starts to decompose at 240 °C (5 min) and completely degrades at 300 °C. At temperatures above 240 °C, the composition of the solid product was dominated by an acid insoluble solid residue. Increased content of the acid insoluble is mainly caused by hydrochar or products from re-polymerization or condensation reactions of the saccharide decomposition products. The reaction process leads to an increase in the fixed carbon and a decrease in the volatile matter content of the solid product.

As well as the hydrolysis reaction, simultaneous reactions such as dehydration, carboxylation, condensation and aromatization reactions were also observed, allowing for rapid conversion of sugarcane bagasse into a carbonaceous product. The dehydration reaction significantly decreased the oxygen content and slightly decreased the hydrogen content of the treated material. Because of decreased amounts of oxygen and hydrogen, the carbon content increased, subsequently increasing the caloric value and energy density.

Optimum conditions were found at 300 °C for the production of a solid product with high caloric value and fixed carbon content. This product had a composition comparable with typical solid fuels such as lignite (or low rank-coal). These results indicate that hydrothermal carbonization could be a solution to reduce environmental pollution caused by the combustion of wet stockpiled sugarcane bagasse in the sugar industry. The treated sugarcane bagasse reduces energy loss, smoke and water vapor during the combustion process and also produces valuable chemical compounds such as furans and organic acids.

Acknowledgements The authors are grateful for the financial support of The Global COE Program (Novel Carbon Resources Sciences, Kyushu University) and Grant-in-Aid for Scientific Research Nos. 21246135 and 24246149, and the Japan Science and Technology Agency (JST).

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