Plagiarism Checker X - Report

Originality Assessment

Overall Similarity: **27%**

Date: Sep 2, 2021

Statistics: 1835 words Plagiarized / 6748 Total words

Remarks: Moderate similarity detected, you better improve the document (if required).

Vol.:(0123456789) 1 3 Waste Biomass Valor (2017) 8:1941–1951 DOI 10.1007/s12649-017-9898-9

ORIGINAL PAPER

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

Dewi Agustina Iryani1,2 · Satoshi Kumagai3 · Moriyasu Nonaka4 · Keiko Sasaki4 · Tsuyoshi Hirajima4

bagasse could be a solution to reduce environmental pollution caused by the combustion of wet stockpiled sugar cane bagasse in the sugar industry. The treated sugarcane bagasse reduces energy loss, smoke and water vapor during the combustion process.

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

Abstract Hydrothermal carbonization of sugarcane bagasse using hot-compressed-water was investigated for the treatment of solid material to understand the occur ring decomposition reactions. The experiments were per formed 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

* Dewi Agustina Iryani dewi.agustina@eng.unila.ac.id

1 Department of Chemical Engineering, University of Lampung, Bandar Lampung 35145, Indonesia

2 Research and Development Center for Tropical Biomass, University of Lampung, Bandar Lampung 35145, Indonesia

3 Research and Education Center of Carbon Resources, Kyushu University, Fukuoka 819-0395, Japan

4 Department of Earth and Resources Engineering, Kyushu University, Fukuoka 819-0395,

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 sugar cane 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 sugar cane 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 car bonization 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 follow ing 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. N2 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. (1) Yield of solid product (wt%) = mass of solid product (g) mass of raw material (g) × 100%Author's personal copy 1943 Waste Biomass Valor (2017) 8:1941–1951 1 3 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% H2SO4 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 HClO4 used as the mobile phase, delivered at a flow rate of 0.7 ml/min. Cellulose and hemicellulose were deter mined by the following correlations [21]: 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 char acterized by several methods. A Yanaco CHN Corder MT-5 (2) Cellulose (wt %) = glucose (wt %) × 0.9 (3) Hemicellulose (wt %) = (xylose + arabinose) (wt %) × 0.88 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]: 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]: 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. (4) HHV (MJ kg-1) = 0.3383C + 1.442 (H − O∕8) (5) Energy density ratio = HHV of solid product HHV of raw material (6) Energy yield(wt %) = Yield of solid product (wt %) × energy density ratio (7) Recovery ratio = (chemical component in treated material) (chemical component in raw) × yield of solid product Table 1   Chemical components of sugarcane bagasse d.b. dry basis 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 Table 2   Ultimate, proximate and heating values of sugarcane bagasse d.a.f dry ash free basis, diff. difference, VM volatile matter, FC fixed carbon, GCV gross caloric value 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

1944

1 3 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. 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 Table 3 Thermogravimetric program for proximate analysis Step Heating rate (°C/min) Temperature indicated (°C) Period (min) Atmosphere 1 0 20 15 N2 2 30 107 10 N2 3 80 900 10 N2 4 0 900 15 O2 Volatile Matter F ixed Carbon 0 20 40 60 80 100 0 20 40 60 80 100 10 1 0 2 0 3 0 FC(%wtd.a.f) VM(wt%d.a.f) (a) (d) (c) (b) 200°C 0 20 40 60 80 100 0 20 40 60 80 100 0 1 0 2 0 3 0 FC(%wtd.a.f) VM(wt%d.a.f) 240°C 0 20 40 60 80 100 0 20 40 60 80 100 0 1 0 2 0 3 0 FC(wt%d.a.f) VM(wt%d.a.f) Time (min) 270°C 0 20 40 60 80 100 0 20 40 60 80 100 0 1 0 2 0 3 0 FC(wt%d.a.f) VM(wt%d.a.f) Time (min) 300°C 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]. 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 Table 4   Elemental composition of solid residue after treatments

Treatment conditions Ultimate analysis (wt%, d.a.f.)

Temperature (oC)	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

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) (O/C) atomic ratio 0.2 0 .4 0.6 0 .8 1.0 (H/C)atomicratio 0.0 0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 Wood Cellulose Lignin An thracite Bituminous Lignite Sub-bituminous Raw 1,a 1,b 1,c 2,a 1,d 1,e 2,b 3,a 2,c 2,d 3,b 2,e 3,c 4,a 4,b 3,d 4,c 3,e 4,d 4,e Dehydration Demethanation Decarbox ylation

1 3 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 stock piled 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. 3 Distributions of a higher heating value, b energy density ratio, c yield of solid products, and d energy yield undergoing hydrohermal carbonization 200 °C 240 °C 270°C 300 °C 10 20 30 0 5 10 15 20 25 30 HigherheatingValue (MJ/kg) Time (min) (a) Higher Heatin g V alue 0.5 1 1.5 2 0 5 10 15 20 25 30 Ratioofenergydensification Time (min) Energy density ratio 20 40 60 80 100 0 5 10 15 20 25 30 Yield(wt%) Time (min) (c) Yield of solid product 40 60 80 100 0 5 10 15 20 25 30 Yield(wt%) Time (min) (d) Energy yield (b) Author's personal copy 1947 Waste Biomass Valor (2017) 8:1941–1951 1 3 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 hydrother mal 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, repolymerization 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. 4 Recovery ratio of each component in solid product in various conditions Cellulose Hemicellulose Acid insoluble residue] 0 50 100 150 200 0 5 10 15 20 25 30 (a) 200°C 0 5 10 15 20 25 30 (b) 240°C 0 50 100 150 200 0 5 10 15 20 25 30 (c) 270 °C 0 5 10 15 20 25 30 (d) 300° C Recoverycomponentinsolid (product(wt%) Time (min)Author's personal copy 1948 Waste Biomass Valor (2017) 8:1941–19511 3 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 (r2) 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 CHn 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 defor mation 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 0 0.2 0.4 0.6 0.8 1 1.2 0 0 .2 0.4 0 .6 0.8 11.2 Ratio of acid insoluble lignin (wt% d.b) Ratio of fixed carbon (wt% d.a.f) 3 min 5 min 10 min 20 min 30 min 25°C 200°C 240°C 270°C 300°C Fig. 5 Correlation between fixed carbon values and acid insoluble residue contentAuthor's personal copy 1949 Waste Biomass Valor (2017) 8:1941–1951 1 3 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) Wave number (1/cm) 1000 2000 3000 4000 Transmittance (%) Raw 200oC 240oC 270oC 300oC (a) 5 min -OH -CHn C=O C-O-C C-O Glycosidic Aromatic Wave number (1/cm) 600 800 1000 1200 1400 1600 1800 Transmittance (%) Raw 200oC 240oC 270oC 300oC (a) 5 min C=C Aromatic Wave number (1/cm) 1000 2000 3000 4000 Transmittance (%) (b) 10 min Raw 200oC 240oC 270oC 300oC -OH -CHn C=O C-O-C C-O Glycosidic Aromatic Wave number (1/cm) 600 800 1000 1200 1400 1600 1800 Transmittance (%) (b) 10 min Raw 200oC 240oC 270oC 300oC C=C Aromatic (c) 20 min Raw 200oC 240oC 270oC 300oC Wave number (1/cm) 1000 2000 3000 4000 Transmittance (%) -OH -CHn C=O C-O-C C-O Glycosidic (c) 20 min Raw 200oC 240oC 270oC 300oC Wave number (1/cm) 600 800 1000 1200 1400 1600 1800 Transmittance (%) C=C Aromatic Wave number (1/cm) 1000 2000 3000 4000 Transmittance (%) Raw 200oC 240oC 270oC 300oC Aromatic -OH -CHn C=O C-O-C C-O Glycosidic (d) 30 min (d) 30 min

11 3 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 oxy gen 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.

References

1. Rogalinski, T., Ingram, T., Brunner, G.: Hydrolysis of lignocellulosic biomass in water under elevated temperatures and pressures. The J. Supercrit. Fluids. 47, 54–63 (2008)

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

Author's personal copy 1951 Waste Biomass Valor (2017) 8:1941–1951 1 3

2. Rodrigues, R.C.L.B., Felipe, M.D.G.A., Silva, J.B.A., Vitolo, M.: Response surface methodology for xylitol production from sugarcane bagasse hemicellulosic hydrolyzate using controlled vacuum evaporation process variables. Process Biochem. 38, 1231–1237 (2003)

3. Lavarack, B.P., Griffin, G.J., Rodman, D.: The acid hydrolysis of sugarcane bagasse hemicellulose to produce xylose, arabinose, glucose and other products. Biomass Bioenergy. 23, 367–380 (2002)

4. Garcia-Pèrez, M., Chaala, A., Yang, J., Roy, C.: Co-pyrolysis of sugarcane bagasse with petroleum residue. Part I: thermogravimetric analysis. Fuel 80(9), 1245–1258 (2001)

5. Tsai, W.T., Lee, M.K., Chang, Y.M.: Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. Anal. Appl. Pyrolysis 76 230–237 (2006)

6. Boussarsar, H., Roge, B., Mathlouthi, M.: Optimization of sugarcane bagasse conversion by hydrothermal treatment for the recovery of xylose. Bioresour. Technol. 100, 6537–6542 (2009)

7. Sasaki, M., Adschiri, T., Arai, K.: Fractionation of sugarcane bagasse by hydrothermal treatment. Bioresour. Technol. 86, 301–304 (2003)

8. Pandey, A., Carlos, R.S., Nigam, P., Soccol, V.T.: Biotechnological potential of agro-industrial residues. I: Sugarcane bagasse. Bioresour. Technol. 74, 69–80. (2000)

9. Hirajima, T., Kobayashi, H., Yukawa, K., Tsunekawa, K., Fukushima, M., Sasaki, K., Osato, K., Sutou, Y.: Fundamental study on the production of woody biomass fuel using hydrothermal treatment. J. MMIJ. 119(3), 118–124 (2003)

10. Inoue, S., Hanaoka, T., Minowa, T.: Hot compressed water treatment for production of charcoal from wood. J. Chem. Eng. Jpn. 35, 1020–1023 (2002)

11. Yuliansyah, A.T., Hirajima,

T., Kumagai, S., Sasaki, K.: Production of solid from agricultural waste of the palm oil industry by hydrothermal treatment. Waste Biomass Valor J. 1, 395–405 (2010) 12. Kruse, A., Dinjus, E.: Hot compressed water as reaction medium and reactant. I. Properties and synthesis reaction. J. Supercrit. Fluids 39, 363–380 (2007) 13. Kumagai, S., Hirajima, T., Nonaka, M., Hayashi, N.: Hydrothermal carbonization behavior of moso-bamboo (Phyllostachys heterocycla) in hot-compressed water. The wood carbonization research. Society. 8(2), 53–60 (2012) 14. Allen, S.G., Kam, L.C., Zenmann, A.J., Antal, M.J.: Fractionation of sugarcane with hot, compressed, liquid water. Ind. Eng. 35, 2709–2715 (1996) 15. Cardona, C.A., Quintero, J.A., Paz, I.C.: Production of bioethanol from sugarcane bagasse: status and perspectives. Bioresour. Technol. 101, 4754–4766 (2010) 16. Ju, Y.H., Huynh, L.H., Kasim, N.S., Guo, T.J., Wang, J.H., Fazari, A.E.: Analysis of soluble and insoluble fractions of alkali and subcritical water treated sugarcane bagasse. Carbohydr. Polym. 83, 591–599 (2010) 17. Laser, M., Schulman, D., Allen, S.G., Lichwa, J., Antal, M.J., Lynd, L.R.: A comparison of liquid hot water and steam pretreatment of sugarcane bagasse for bioconversion to ethanol. Bioresour. Technol. 81, 33–44 (2002) 18. Chen, W.H., Ye, S.C., Sheen, H.K.: Hydrothermal carbonization of sugarcane bagasse via torrefaction in association with microwave heating. Bioresour. Technol. 118, 195–203. (2012) 19. Iryani, D.A., Kumagai, S., Nonaka, M., Nagashima, Y., Sasaki, K., Hirajima, T.: The hot compressed water treatment of solid waste material from the sugar industry for valuable chemical production, Int. J. Green Energy 11, 577–588 (2014) 20. Iryani, D.A., Kumagai, S., Nonaka, M., Sasaki, K., Hirajima, T.: Hydrothermal carbonization kinetics of sugarcane bagasse treated by hot compressed water under variabel temperature conditions. ARPN J. Eng. Appl. Sci. 11(7), 4833–4839 (2016) 21. Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Crocker, D.: Determination of structural carbohydrates and lignin in biomass, in: The US National Renewable Energy Laboratory Technical Report, US National Renewable Energy Laboratory. (2005) 22. Selvig, W.A., Gibson, F.H.: Chemistry of Coal Utilization, p. 132. John Wiley and Sons, New York (1945) 23. Yan, W., Acharjee, T.C., Coronella, C.J., Vasquez, V.R.: Thermal pretreatment of lignocellulosic biomass. Environ. Prog. Sustain.

Energy 28, 435–440 (2009) 24. Van Krevelen, D.W.et al.: 1956 cited from Kimura H., Fujii S. Sekitan Kagaku to Kogyo Sankyo Shuppan. Tokyo. (1979) 25. Fuertes, A.B., Arbestain, M.C., Sevilla, M., Maciá-Agulló, J.A., Fiol, S., López, R., Smernik, R.J., Aitkenhead, W.P., Arce, F., Macias, F.: Chemical and structural properties of carbonaceous products obtained by pyrolysis and hydrothermal carbonization of corn stover. Aust. J. Soil Res. 48, 618–626 (2010) 26. Garrote, G., Dominguez, H., Parajo, J.C.: Hydrothermal processing of lignocellulosic material, Holz als Roh-und-Werkstoff. Eur. J. Wood Wood Prod. 57, 191–202 (1999) 27. 26 Carvalheiro, F., Duarte, L.C., Girio, F.M., Francisco, M.G.: Hemicellulose biorefineries: a review on biomass pretreatments. J. Sci. Ind. Res. 67, 849–864 (2008) 28. 16 Yoshida, K., Kusaki, J., Ehara, K., Saka, S.: Characterization of low molecular weight organic acids from beech wood treated in supercritical water. Appl. Biochem. Biotechnol. 121, 795–806 (2005) 29. 25 Sevilla, M., Fuertes, A.B.: Chemical and structural properties of carbonaceous product obtained by hydrothermal carbonization of saccharides. Chem. A Eur. J. 15, 4195–4203 (2009) 30. Cara, C., Romeo, I., Oliva, J.M., Saez, F., Castro, E.: 2 Liquid hot water pretreatment of olive tree pruning residues. Appl. Biochem. Biotechnol. 137–140(1–12), 379–394 (2007) 31. Proniewicz, L.M., Paluszkiewicz, C., Birczynska, A.W., Majcherczyk, H., Baranski, A., Konieczna, A.: FT-IR and FTRaman study of hydrothermally degraded cellulose. J. Mol. Struct. 596, 163–169 (2001) 32. Yang, H., 2 Yan, R., Chen, H., Lee, D.H., Zeng, C.: Characteristic of hemicellulose, cellulose and lignin pyrolysis, Fuel. 86 1781–1788 (2007) 33. Sun, J.X., Sun, X.F., Sun, R.C., Su, Y.Q.: Fractional extraction and structural characterization of sugarcane bagasse hemicelluloses. J Carbohydr. Polym. 256, 195–204 (2004) 34. Xiao, L.P., Sun, Z.J., Shi, Z.J., Xu, F., Sun, R.C.: Impact of hot compressed water pretreatment on the structural changes of woody biomass for bioethanol production. Bioresources 6(2), 1576–1598 (2011) 35. Liu, Z., Quek, A., Hoekman, S. K., Balasubramanian, R.: 11 Production of solid biochar fuel from waste biomass by hydrother mal carbonization. Fuel 103, 943–949 (2013)

Sources

1. http://download.xuebalib.com/4xyuj19xYcQv.pdf
   INTERNET
   5%

2. https://bioresources.cnr.ncsu.edu/resources/impact-of-hot-compressed-water-pretreatment-on-the-structural-changes-of-woody-biomass-for-bioethanol-production/
   INTERNET
   4%

3. https://pubs.rsc.org/en/content/articlehtml/2015/py/c5py00263j
   INTERNET
   3%

4. https://www.academia.edu/9586284/International_Journal_of_Green_Energy_The_Hot_Compressed_Water_Treatment_of_Solid_Waste_Material_from_the_Sugar_Industry_for_Valuable_Chemical_Production_PLEASE_SCROLL_DOWN_FOR_ARTICLE
   INTERNET
   3%

5. https://bioresources.cnr.ncsu.edu/resources/torrefaction-of-rice-husk-using-tg-ftir-and-its-effect-on-the-fuel-characteristics-carbon-and-energy-yields/
   INTERNET
   2%

6. http://core.ac.uk/display/24072071
   INTERNET
   1%

7. https://www.sciencedirect.com/science/article/pii/S1878522013000593
   INTERNET
   1%

8. https://www.hindawi.com/journals/amse/2017/1706893/
   INTERNET
   1%

9. https://iopscience.iop.org/article/10.1088/1755-1315/65/1/012039
   INTERNET
   <1%

10. https://www.scielo.br/j/bjce/a/Tjfm6RtyRkWCXffBrxGx9hy/
    INTERNET
    <1%

11. https://www.sciencedirect.com/science/article/pii/S0016236112006308
    INTERNET
    <1%

12. http://europepmc.org/articles/PMC3664608
    INTERNET
    <1%

13. https://www.sciencedirect.com/topics/biochemistry-genetics-and-molecular-biology/reaction-temperature
    INTERNET
    <1%

14. http://www.scielo.br/scielo.php?script=sci_arttext&pid=S1517-83822016000200489
    INTERNET
    <1%

30   https://www.sciencedirect.com/science/article/pii/S2238785416301831
      INTERNET
      <1%

31   https://www.sciencedirect.com/science/article/pii/S0960852412007250
      INTERNET
      <1%

32   http://www.rsc.org/suppdata/c8/gc/c8gc03617a/c8gc03617a1.pdf
      INTERNET
      <1%