Investigation on characteristics of corn stover and sorghum stalk processed by ultrasonic vibration-assisted pelleting

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Abstract

Cellulosic ethanol produced from cellulosic biomass is an alternative to petroleum-based liquid transportation fuels. The cost-effectiveness of cellulosic ethanol manufacturing has been hindered by several technical barriers. One such barrier is that low density of biomass causes high costs of biomass transportation, handling, and storage. Another barrier is low sugar yield in enzymatic hydrolysis, making enzymatic hydrolysis an expensive and slow step. Ultrasonic vibration-assisted (UV-A) pelleting of cellulosic biomass can increase its density and reduce the costs of biomass transportation and handling. In addition, sugar yield of biomass pellets processed by UV-A pelleting was higher than that of particles (unpelleted biomass) with diluted acid pretreatment. The reason that UV-A pelleting could increase sugar yield of biomass is still unclear. The objective of this study was to investigate reasons that UV-A pelleting combined with diluted acid pretreatment could increase sugar yield of biomass. High sugar yield is preferred to achieve high ethanol yield. Effects of UV-A pelleting on biomass characteristics (such as chemical composition, crystallinity index, thermal properties, and morphological structure) were investigated. The results showed there was no significant difference in chemical composition between pellets and particles. However, crystallinity of biomass

increased after UV-A pelleting. In addition, pellets had higher decomposition temperature than particles, indicating that pellets were more thermally stable than particles. Examinations on morphological structure of biomass showed that softened surface regions of biomass were removed and cellulose microfibrils were revealed after UV-A pelleting.

Keywords biomass, ethanol, pelleting, characteristics, ultrasonic, sugar yield

1 Introduction

Cellulosic ethanol produced from cellulosic biomass (herbaceous, woody, and generally inedible portions of plant matter) is an attractive alternative to petroleum-based liquid transportation fuels. Land resources in the U.S. are sufficient to sustain production of enough biomass annually to displace 30% or more of the nation's current petroleum consumption [1]. Furthermore, cellulosic ethanol has great environmental advantages over grain-based ethanol [2,3].

Cost-effective manufacturing of cellulosic ethanol has been facing several technical barriers. One barrier is related to low density of raw cellulosic biomass (ranging from 24 to 266 kg/m³ [4]), causing high costs in biomass transportation and storage. Another barrier is low sugar yield in enzymatic hydrolysis, which leads to low biomass-to-ethanol conversion rate and high costs in converting biomass into ethanol.

Pelleting (agglomeration of small particles into larger particles by means of mechanical or thermal processing [5]) can significantly increase density of cellulosic biomass. The density of biomass pellets could reach 1200 kg/m³ [6]. In turn, costs for transporting and storing of pelleted cellulosic biomass are less than 1/2 and 1/10 of those of raw cellulosic biomass [7,8]. In addition, pellets with uniform size and shape are easier for handling with existing equipment. A variety of traditional pelleting methods have been reported in the literature, including ring-die pelleting [9-11], flat-die pelleting [9,11], screw extrusion [12], and piston press [13]. For these pelleting methods, cellulosic biomass usually needs to be preheated (by high-temperature steam or heated dies) and binders are often needed [4]. By contrast,

ultrasonic vibration-assisted (UV-A) pelleting does not require preheated biomass and binders. However, UV-A pelleting can produce pellets whose density and durability are comparable to those produced by traditional pelleting methods [6].

Pelleting of biomass has also been considered as an effective pretreatment method to increase biomass sugar yield in enzymatic hydrolysis. Theerarattananoon et al. [14] reported that sugar yield of biomass (big bluestem, corn stover, sorghum stalk, and wheat straw) processed by ring-die pelleting was 3-11% higher than that of unpelleted biomass. Lamsal et al. [15] reported that sugar yield of wheat bran processed by screw extrusion was about 30% higher than that of unpelleted wheat bran. A similar trend was reported by Yoo et al. [16,17] in screw extruding of soybean hulls. Our previous studies showed that UV-A pelleting of biomass was beneficial for increasing sugar yield of biomass in enzymatic hydrolysis. Zhang et al. [18] reported that, with dilute acid pretreatment, switchgrass processed by UV-A pelleting had 20% higher sugar yield than unpelleted switchgrass, while the difference became 75% without pretreatment. Zhang et al. [19] reported that biomass (corn stover and sorghum stalk) processed by UV-A pelleting had higher sugar yield than particles (unpelleted biomass) under dilute acid pretreatment. However, the reason that UV-A pelleting increases sugar yield of biomass is still unclear.

In this study, effects of UV-A pelleting on characteristics (such as crystallinity index, chemical structure, and thermal properties) of corn stover and sorghum stalk were investigated to explain the mechanism which UV-A pelleting increases sugar yield of biomass. A variety of measurement methods were used to determine the characteristics, such as X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), thermo-gravimetric analysis (TGA), and solid-state cross polarization/magic angle spinning (CP/MAS) ^{13}C nuclear magnetic resonance (NMR) spectroscopy. Morphological structure of biomass was also observed using scanning electron microscope (SEM).

2 Materials and methods

2.1 Materials

Corn stover and sorghum stalk used in this study were harvested at the Kansas State Agronomy Farm in November, 2010. After harvesting, they were chopped to approximately 180-230 mm using a large tub grinder (Haybuster H-1150 series, DuraTech Industries International Inc., Jamestown, ND, USA). Chopped biomass was then transported to a lab located at Kansas State University in sealed paper bags. Figure 1 shows the experimental procedure. The chopped biomass was milled into particles using a cutting mill (model SM 2000, Retsch, Inc., Haan, Germany) with a sieve whose mesh size was 1 mm. The milled biomass was referred to as biomass particles which were separated into two portions. One portion of biomass was processed by UV-A pelleting. Both particles and pellets were then pretreated by diluted acid solution. Enzymatic hydrolysis was performed on biomass sample. Moisture content (MC) of biomass particles was measured and adjusted to 10% by following an NREL laboratory analytical procedure before pretreatment [20]. Biomass with 10% MC would produce pellets with high density and durability in previous experiment.

2.2 Experimental setup for UV-A pelleting

UV-A pelleting was conducted on a modified ultrasonic machine (model AP-1000, Sonic-Mill, Albuquerque, NM, USA). The schematic illustration of the experimental setup for UV-A pelleting is shown in Fig. 2. The machine was composed of two systems: an ultrasonic vibration generation system, and a pneumatic loading system.

The ultrasonic-vibration generation system was consisted of three major parts: a power supply, a converter, and a pelleting tool. The power supply converted 60 Hz electrical supply into 20 kHz electrical power. The high-frequency electrical power was applied to the piezoelectric converter and converted into high-frequency mechanical motion. The mechanical motion was amplified by the coupler and

transmitted to the titanium pelleting tool which vibrated at the frequency of 20 kHz. The pelleting tool was connected to the converter and used to compress biomass particles into pellets. Ultrasonic power (percentage of power from power supply) can be adjusted from 0-100% and controls amplitude of the pelleting tool vibration. The higher the ultrasonic power, the larger the tool vibration amplitude.

The pneumatic loading system was consisted of three major parts: an air compressor, a pressure regulator, and a pneumatic cylinder. The air compressor (1.2 kw, 125 liters, Sears, Roebuck and Co., Hoffman Estates, IL, USA) produced compressed air which was fed into the pneumatic cylinder (ARO Equipment Corporation, Bryan, OH, USA). The air pressure in the pneumatic cylinder was controlled by the pressure regulator and referred to as pelleting pressure. The pneumatic cylinder was driven by the compressed air and pushed the pelleting against biomass in a three-piece aluminum mold.

The mold was used to held biomass particles and clamped by a fixture on to the machine. The top two parts of the mold formed a central cylindrical cavity and the bottom part served as a base. The diameter of the mold cavity (18.6 mm) was slightly larger than that of the tip of the pelleting tool (17.4 mm).

There are five steps to make a pellet in this study: (1) assemble the mold and put 1 g of biomass particles in the central cavity of the mold, (2) adjust pelleting pressure to 50 psi and feed the pelleting tool down to compress particles, (3) turn on ultrasonic power at 50% and count 3 min using a stop watch, (4) turn off ultrasonic power and lift up the pellet tool, and (5) disassemble the mold and take out the pellet. Since there is no mass loss in the pelleting process, same amount of the initial particles for both particles and pellets.

2.3 Pretreatment

Pretreatment was carried out on a pressure reactor (Parr Instrument Company, Moline, IL, USA) with a 600 mL reaction vessel. A mixture of 20 g biomass (particles or pellets) and 200 mL 2% (w/v) diluted sulfuric acid (solid content about 10%) were loaded into the reaction vessel at room temperature. The pellets were totally dissolved

in diluted sulfuric acid before heating. The biomass slurry was treated at 140 °C for 30 min. Meanwhile, two four-blade impellers were used to stir the slurry to ensure that temperature was evenly distributed in pretreatment. Pretreated biomass was washed with distilled water and centrifuged three times (at 8000 rpm for 20 min) to remove dissolved sugars and sulfuric acid. Washed biomass samples were weighed and split into two portions. The MC of pretreated biomass ranged from 84.5% to 89 % after pretreatment for different samples. The rest portion was used for moisture content measurement and chemical compositional analysis.

2.4 Enzymatic hydrolysis

Enzymatic hydrolysis was conducted in a 1.36% (w/v) sodium acetate buffer solution with the addition of 0.02% (w/v) sodium azide to prevent the microbial growth during hydrolysis. The pH value of the solution was adjusted to 4.8. Biomass of 5 g dry weight was mixed with 100 mL buffer solution in 125 mL flasks in a 50 °C water bath shaker (Model C76, New Brunswick Scientific, Edison, NJ, USA) agitating at 180 rpm for 72 h. The enzyme loading (Accellerase 1500TM, Genencor Inc., Rochester, NY, USA) was 1 mL/g cellulose. This enzyme complex contains multiple enzyme activities, including exoglucanase, endoglucanase (2200-2800 CMC U/g), hemicellulose, and b-glucosidase (525-778 pNPGU/g). The endoglucanase activity is standardized on the basis of its activity on carboxymethylcellulose (CMC). Beta-glucosidase activity is standardized on the basis of activity on pNP-glucoside. The enzyme loading was about 2700-3500 FPU/g of cellulose. The hydrolysis slurry was sampled every 24 h by withdrawing 1 mL of slurry from each flask into vials. The vials were placed in boiling water for 15 min to deactivate the enzyme. Then samples were centrifuged at 13500 rpm for 15 min. 0.1 mL supernatant was withdrawn and mixed with 0.9 mL distilled water in 1.5 mL vials. The supernatant was then filtered into 1.5 mL autosampler vials through 0.2 µm hydrophilic PTFE syringe filters (Millipore, Billerica, MA). Filtered samples were stored at 0°C until HPLC analysis.

In this study, sugar yield means the percentage of cellulose enzymatically converted to glucose in hydrolysis. It was calculated by the following formula:

$$\text{Sugar yield} = \frac{c \times V}{1.11 \times m} \times 100\% \quad (1)$$

where c is the concentration (g/L) of glucose in the vials and determined by HPLC analysis, V is the total volume (L) of the slurry in the flasks, m is the weight of cellulose before enzymatic hydrolysis (g), and the number 1.11 is the cellulose-to-glucose conversion factor.

2.5 Analytical methods

Moisture content (MC) of particles and pellets was measured by following a NREL laboratory analytical procedure [20]. The biomass was dried in an oven with the temperature of 105 °C for 24 h to determine the MC in the material. MC of biomass represents the amount of moisture (water) contained in a certain amount of biomass and can be calculated by Equation (2):

$$MC = \frac{m_1 - m_2}{m_1} \times 100\% \quad (2)$$

where m_1 is the initial biomass weight (g), m_2 is the biomass weight after heating.

Composition of biomass before and after pretreatment was determined by following NREL laboratory analytical procedures [21,22]. The experiment for each sample was replicated twice. The composition of biomass was reported as percentages of glucan (cellulose), xylan (major hemicellulose constituent), and lignin including acid-insoluble (AIL) and acid-soluble lignin (ASL). Glucose, xylose, mannose, and arabinose were determined via an HPLC instrument (Shi-madzu, Kyoto, Japan) equipped with an RCM monosaccharide column (300 x 7.8 mm; Phenomenex, Torrence, CA, USA), and a refractive index detector (RID-10A, Shimadzu, Kyoto, Japan). The mobile phase was 0.6 mL/min of double-distilled water, and oven temperature was 80 °C.

2.6 XRD analysis

Crystallinity index (CrI) of the biomass samples before and after pretreatment was analyzed by wide-angle X-ray diffraction (XRD) with a desktop X-ray diffractometer (Rigaku Instrument Co., Woodlands, TX, USA). Samples were irradiated with Cu K α ($\lambda=1.5$ Å) rays at 15 KV and grade range was between 10° to 30° with a step size of 0.02° at room temperature. The scan speed was set at 2°/min. The presence of crystallinity in a sample can be detected by absorption peaks. The CrI was calculated using the method reported by Segal et al. [23] in Equation (3):

$$CrI = \frac{I_{002} - I_{amorphous}}{I_{002}} \times 100 \quad (3)$$

where I_{002} is the intensity of crystallinity portion of biomass at 22.5° and $I_{amorphous}$ is the intensity of the background scatter (amorphous region) at 18.7°.

2.7 FTIR analysis

FTIR was used to investigate the structure of constituents and chemical changes in cellulosic biomass. FTIR analyses were performed using a PerkinElmer Spectrum 400 FT-IR spectrometer (PerkinElmer Inc., Waltham, MA, USA). All spectra were recorded in the absorbance mode in the wave number range of 400-4000 cm^{-1} with a detection resolution of 4 cm^{-1} in the transmission mode and 16 scans per sample. About 5 mg of dried sample was used in each test.

2.8 Thermogravimetric analysis (TGA)

TGA was performed to measure the thermal properties of biomass samples (particles and pellets) before and after pretreatment. It was carried out on a Pyris 1 Thermogravimetric Analyzer (The PerkinElmer Co., Norwalk, CT, USA). Dynamic thermogravimetric scans were conducted in a temperature range from 30 to 600°C at a heating rate of 20 °C/min. In each test, biomass sample of 5-6 mg was used.

2.9 Solid-State ^{13}C NMR spectroscopy

Solid-State ^{13}C NMR spectroscopy was used to determine the changes in chemical structure of biomass. Solid state NMR spectra were acquired on a Bruker Avance III 400 spectrometer (Bruker Biospin, Billerica, MA, USA) operating at 400.1

MHz for ^1H and 100.6 MHz for ^{13}C . A 7 mm spin module in a 4 module multiple sample solids (MSS) probe (Revolution NMR, Ft. Collins, CO) was used. Spectrometer setup used 3-methylglutaric acid (MGA) as a secondary external chemical shift reference via the methyl peak at 18.84 ppm relative to TMS. Each sample was packed into a 7 mm zirconia (ZrIO_2) rotor (Revolution NMR, Ft. Collins, CO, USA). Cross polarization was used for all measurements with a contact time of 1 min. The spectral width was 40 kHz and the acquisition time was 30 min. Proton decoupling was performed with SPINAL-64 and a proton decoupling field of 64 kHz.

2.10 SEM analysis

SEM was used to observe the changes in morphology of biomass. An EVO MA10 SEM (Carl Zeiss Microscopy, Thornwood, NY, USA) was operated at 5 kV was used to image the samples. Before observation, the samples were sputter-coated with a thin layer of gold to make the fibers conductive. The samples were mounted on conductive adhesive carbon tapes.

3 Results and discussion

3.1 Results on Sugar yield and compositional analysis

Although partial results have been published in previous paper [19], results were summarized for readers. Figure 3 shows the sugar yield results of particles and pellets in enzymatic hydrolysis. It can be seen that pellets had 13 % higher sugar yield than particles after 72 h hydrolysis. This result is consistent with our previous study with switchgrass [18]. This implies that UV-A pelleting might be considered as a pretreatment method to increase sugar yield in enzymatic hydrolysis.

Table 1 shows the chemical compositions of various types of biomass samples. It can be seen that, without pretreatment, there was no significant difference between particles and pellets, indicating that UV-A pelleting at above experimental condition (50 psi, 50% ultrasonic power, and 3 min) did not alter the chemical composition of biomass. After pretreatment, the percentage of xylan was significantly reduced from 24% to 2%, indicating that most hemicellulose was removed during

acid pretreatment. Glucan content increased from 40% to 52% and lignin content increased from 16% to 33%. Glucan content in pellets was slightly but not significantly (at the significance level of 0.05) higher than that in biomass particles.

3.2 Results on FTIR analysis

In FTIR analysis, the major structural components in cellulosic biomass (cellulose, hemicellulose, and lignin) are identified by absorption bands. Table 2 summarizes the assignments of FTIR absorption bands reported in the literature. The FTIR spectra of various biomass samples obtained in this study are shown in Figs. 4-6.

FTIR spectra of pure hemicellulose, particles, and pellets are shown in Fig. 4. The hemicellulose-related absorption bands can be identified from the characteristic peaks with wave numbers of 900, 991, 1043, 1164, and 1260 cm^{-1} [24,29,31]. The location of these peaks is consistent with the observations of Chen et al. [24] and Ren et al. [31]. Before pretreatment, the five peaks could be observed in both biomass particles and pellets. There was no significant difference in the pattern of FTIR spectra of hemicellulose between particles and pellets, implying that UV-A pelleting did not alter hemicellulose content in biomass. This is consistent with the results of compositional analysis in Table 1. However, after pretreatment, the peaks at 1043 and 1260 cm^{-1} were obviously reduced, indicating a significant reduction in hemicellulose content in the pretreated biomass [24].

FTIR spectra of pure cellulose, particles, and pellets are shown in Fig. 5. The cellulose-related absorption bands can be identified from the characteristic peaks with wave numbers of 900, 1033, 1060, 1106, 1164, and 1370 cm^{-1} [24,25,29]. The location of these peaks is similar to those obtained by Chen et al. [24], Liu et al. [32], and Adapa et al. [29]. Before pretreatment, the peaks at 1033, 1060, 1106, and 1370 cm^{-1} are not clear for both particles and pellets. But there is no clear difference in the spectra between particles and pellets, implying that UV-A pelleting did not change cellulose content in biomass. After pretreatment, the aforementioned peaks are notable for both particles and pellets. This indicates that removal of hemicellulose

during pretreatment could expose the cellulose in the biomass [24]. This result is also consistent with the compositional data in Table 1.

FTIR spectra of pure lignin, particles, and pellets are shown in Fig. 6. The lignin-related bands can be identified from the characteristic peaks with wave numbers of 1033, 1270, 1425, 1462, 1509, and 1599 cm^{-1} [25,27,29]. The location of these peaks is similar to those obtained by Chen et al. [24], Apada et al. [29], Xiao et al. [27], and Sun et al. [28]. The six peaks were clearly observed for both pretreated and unpretreated biomass samples, revealing that lignin content is not affected by dilute acid pretreatment. The peaks around 1599, 1509, 1462, and 1425 cm^{-1} were enhanced after pretreatment, indicating that pretreated samples have higher lignin content [24,27].

3.3 Results on biomass crystallinity index

Cellulose exists within a matrix of hemicellulose and lignin which block access of enzyme to the cellulose. Cellulose consists of crystalline regions (with highly ordered molecule arrangement) and amorphous regions (with less ordered molecule arrangement) [33]. Crystallinity index (CrI) is defined as the percentage of the amount (weight) of crystalline material in biomass [23,34]. CrI has been correlated with the accessibility of cellulose to cellulase enzyme and considered as an influencing factor to sugar yield in enzymatic hydrolysis.

The XRD patterns of corn stover particles and pellets before and after pretreatment are shown in Fig. 7. A major diffraction peak of cellulose crystallographic plane can be identified in the range of 22-23° [24,27]. Before pretreatment, the crystalline structure (around peak 22.5°) is not obvious due to the coverage of cellulose by hemicellulose and lignin [24]. After pretreatment, the peak around 22.5° is significantly increased, indicating that the crystalline cellulose of pretreated corn stover is clearly exhibited due to the removal of hemicellulose (amorphous region of biomass) and disruption of hydrogen bonding of cellulose chain by pretreatment [34,35]. The increased percentage of crystalline portion in biomass resulted in a higher CrI.

Figure 8 shows the effects of UV-A pelleting on the CrI of corn stover and sorghum stalk. It can be seen that pellets had higher CrIs than particles whether pretreatment was applied or not. Similar results were reported by other researchers with ring-die pelleting [36] and screw extrusion [16]. More crystalline portion in biomass was exposed during thermal-mechanical interaction in pelleting process [16,36]. Mikushina et al. reported that intensive mechanical action on cellulosic biomass can cause destruction of macromolecular chains, leads to mutual displacement of separate structural elements [37]. Displacement of structural elements of polymeric chains is first of all accompanied by distortion of initial packing of the chains and loss of ordering [38]. Mikushina et al. reported surface area and CrI of wood increased after mechanical treatment (vibratory centrifugal and planetary mill) [37]. Yoshida et al. reported delignification sample or break-in of lignin showed a higher degree of crystallinity [39]. More crystalline portion exposed in biomass increased surface area, making enzyme more accessible. Pelleting may be considered a delignification process and mechanical treatment. Thus, pelleted biomass has higher sugar yield than biomass particles. However, some researchers believed that lower CrI increases initial hydrolysis rate of cellulose and hemicellulose, making more enzyme accessible for hydrolysis [40]. Besides, diluted acid pretreatments increase CrI because the solubilization of lignin and hemicellulose (both are amorphous components), resulting in an increased percentage of crystalline regions [41].

3.4 Results on thermogravimetric analysis

Results on TGA and derivative thermogravimetric (DTG) analysis for corn stover and sorghum stalk are displayed in Figs. 9 and 10. It can be seen from Figs. 9 (a) and 10 (a) that weight loss of samples that occurred at 30-280°C was less than 10% of the total sample weight. As heating temperature increased from 280 to 400 °C, the samples had a remarkable weight loss of up to 70%. The remains of the samples were ashes. There was no evident difference in TGA results between

particles and pellets after pretreatment. However, before pretreatment, there was obvious difference between them especially for corn stover.

The DTG (first derivative) profiles for the rate of weight loss of samples are displayed in Figs. 9 (b) and 10 (b). The DTG curves of untreated biomass exhibit three peaks. The first peak appeared at the temperature around 30-85°C. It represented elimination of absorbed or combined water in the sample [42]. The second peak appeared at 222-228 °C, which was attributed to decomposition of hemicellulose [43]. The third peak appeared at 319-351 °C, which was attributed to decomposition of cellulose [24]. Lignin decomposed over 200-500 °C and decomposition of lignin did not form a peak because the various oxygen functional groups generated during lignin decomposition had different thermal stabilities [44]. For pretreatment biomass, only two peaks were observed. The peak at 222-228 °C disappeared, indicating that hemicellulose was removed during pretreatment.

3.5 Solid-State ¹³C NMR Analysis

Similar to FTIR analysis, the solid-state ¹³C NMR analysis is a qualitative technique that has been used to determine the chemical structure and composition of biomass samples. Figures. 11 and 12 show the ¹³C NMR spectra of biomass particles and pellets before and after pretreatment. Table 3 summarized chemical shift assignments of the biomass spectra which were reported in the literature [27,45-47].

Signals appeared in the region of 50-105 ppm were assigned to various cellulosic carbons [27]. The sharp signals at 65.5, 89.2-93, and 105.4 ppm were assigned to C-6, C-4, and C-1 carbons of crystalline cellulose, respectively. The shape signals at 63 and 84 ppm were assigned to C-6, and C-4 carbons of amorphous cellulose, respectively. The signals at 72.9-75.2 ppm were assigned to C-2, C-3, and C-5 carbons of cellulose. Base on Figs. 11, a comparison between samples 1 (corn stover particles) and 3 (corn stover pellets) reveals that there was no significant difference in the aforementioned cellulose-related signals. This indicates that UV-A pelleting does not have strong effects on either amorphous or crystalline cellulose. The same tend was found for sorghum stalk (Fig. 12). However, signals at 56, 63, 75,

and 89 ppm for both corn stover and sorghum stalk increased after pretreatment, indicating that pretreatment altered the cellulose structure of biomass.

Signals at 23-25 and 172 ppm were assigned to methyl and carboxylic groups of the acetyl function of hemicellulose [27]. For both corn stover and sorghum stalk, there was no apparent difference in the intensity of these two signals between particles and pellets (e.g., by comparing samples 1 and 3 in Figs. 11), indicating that UV-A pelleting did not remove hemicellulose. This result is consistent with the composition data in Table 1. By comparing samples 1 and 3 with samples 2 and 4 in Figs 11 and 12, it can be seen that the intensity of the two signals disappeared after pretreatment. This evidently confirmed the removal of hemicellulose during pretreatment. The results were consistent with the compositional analysis data in Table 1 and FTIR spectra in Fig 4.

Signals for aromatic carbons of lignin in the ^{13}C NMR spectra were shown in a region of 110-155 ppm [27]. Guaiacyl (G) and Syringyl (S) are main components in lignin. Base on Table 3, G was identified by signals at 153 (C-4, G etherified), 147-148 (C-3, G etherified), 136-137 (C-1, G etherified), 133-134 (C-1, G nonetherified), 122-123 (C-6, G), 115-117 (C5, G), and 113.8 ppm (C-2, G) [27,28,40]. S was assigned by signals at 153-154 (C-3/C-5, S etherified), 147-148 (C-3/C-5, S nonetherified), 136-137 (C-1/C-4, S etherified), and 133-134 ppm (C-1/C-4, S nonetherified) [27,45,46]. Besides G and S, the signal at 56 ppm was assigned to methoxyl carbons in lignin [47]. The intensity of signals at 56, 147, and 153 ppm increased after pretreatment, as can be seen by comparing samples 2 and 4 in Figs. 11 and 12. It indicates that lignin content in biomass increased after pretreatment. However, there was no significant difference in intensities of lignin signals before and after UV-A pelleting.

3.6 Morphological structure analysis

In the SEM image of corn stover particles before pretreatment (Fig. 13(a)), samples exhibited regular and compact surface structure. After pelleting, softened surface region of biomass was removed, revealing cellulose microfibrils with 2.3-3.4

μm in width, as shown in Fig. 13(b). Ultrasound is a pressure wave which could propagate through a medium with a vast amount of energy dissipation [48]. Acoustic cavitation is defined as ultrasound produces pressure waves which propagate through water, generating gas and vapor bubbles that grow and collapse violently at high velocity [49]. Acoustic cavitation occurs more readily at a frequency of 20–40 kHz [50]. Bubble implosion and fragmentation produce micro-regions of extreme conditions with estimated temperatures up to 1000 °C and pressures up to 100 MPa [51]. Cavitation could induce many physical–chemical effects on biomass disintegration and cell walls of biomass [48, 51–54]. Chu et al. [53] investigated ultrasonic pre-treatment on anaerobic digestion of flocculated activated biosolids. They reported that ultrasonic energy could disrupt floc structure or cell walls of biosolids and release a large proportion of organics from the sludge particles. Similar results were reported by Zhang et al. [51]. Bussemaker and Zhang reported that Ultrasound produces chemical-physical effects which are both found to augment the pretreatment of lignocellulose via delignification and surface erosion [54]. Ultrasonic-vibration assisted pelleting is a new pretreatment that pressure wave propagates through biomass with certain moisture content. The high frequency vibration may have the effects on water molecules inside the biomass. It is reported that high ultrasonic power resulted in high temperature over 130 °C within 1 min because mechanical energy was transferred to heat energy [55]. The high temperature even caused charring of biomass [56]. Thus, morphological structure of the biomass was changed due to shear strength and high temperature caused by high frequency vibration during pelleting. Mechanical disintegration of biomass can greatly transform insoluble organics into a soluble form in hydrolysis [53]. So the digestion efficiency of pellets in enzymatic hydrolysis was improved.

After pretreatment, microfibrils in corn stover were observed and its surface was clean and smooth, as shown in Fig. 13(c). Although dilute-acid pretreatment disrupted the biomass network and removed hemicellulose, major microfibrillar cellulose structures were still preserved. Surface of cellulose fibers was covered by lignin or lignin carbohydrate complexes [27,57]. Furthermore, annular rings, which

are parts of the biomass internal structure, were revealed in pelleted biomass after pretreatment, as shown in Fig. 13(d).

The SEM images of residues of corn stover after enzymatic hydrolysis were shown in Figs. 13 (e) and 13 (f). Empty holes appeared on the surface of biomass residue (Fig. 13 (e)), indicating that cellulose was digested by enzyme. In addition, cellulose fibrils appeared after enzymatic hydrolysis, as shown in Fig. 13 (f).

Other than removal of soften surface region of biomass, there was no significant difference in the morphological structure between particles and pellets after pretreatment and hydrolysis. Lamsal et al. [15] reported that the increased sugar yield caused by screw extrusion was attributed to continuous removal of soften biomass surface which exposed the interior of biomass to chemical and thermal actions. From the SEM images obtained in this study, removal of soften biomass surface was also found in UV-A pelleting. Therefore, this might be the major reason responsible to the increased sugar yield caused by UV-A pelleting.

4 Conclusions

This paper reports investigations on characteristics of corn stover and sorghum stalk processed by ultrasonic vibration-assisted (UV-A) pelleting. Effects of UV-A pelleting on sugar yield, chemical composition, crystallinity index, chemical structure, and thermal properties of corn stover and sorghum stalk were evaluated. Major conclusions are:

1. UV-A pelleting can increase sugar yield of cellulosic biomass in enzymatic hydrolysis by more than 10%. However, it does not change chemical composition of cellulosic biomass regardless of application of dilute acid pretreatment.
2. Crystallinity index of biomass processed by UV-A pelleting is significantly higher than that of unpelleted biomass. The increased biomass crystallinity index was probably due to the crystallization of amorphous cellulose in biomass and changes in lignin structure when the biomass was subjected to mechanical shear and heat generated in UV-A pelleting. In addition, dilute acid pretreatment significantly increases the crystallinity index of biomass by removing amorphous hemicellulose.

3. Results on FTIR and solid-state ^{13}C NMR analyses indicate that there is no significant difference in biomass structure between particles and pellets. However, dilute acid pretreatment could alter the chemical structure of biomass due to degradation of hemicellulose.
4. The decomposition temperature of pellets is slightly higher than that of particles. In other words, pellets produced by UV-A pelleting are more thermally stable than particles.
5. Morphological structure of biomass is affected by UV-A pelleting. During UV-A pelleting, softened surface region of biomass is removed, revealing cellulose microfibrils. Thus the enzyme can contact with the revealed microfibrils during enzymatic hydrolysis. This could be a reason responsible to increased sugar yield caused by UV-A pelleting.

Acknowledgements

This study is supported by National Science Foundation award CMMI-0970112, U.S. Department of Transportation Sun Grant Program with Project No. DTOS59-07-G-00053, Jiangsu Science Fund award BK20140486, Jiangsu University Fund14KJB480007, China postdoc Fund 2014M560448, CNSF award 51375428, and Jiangsu Science Fund BK20150455. The authors would like to thank Mr. Clycle Treadwell of Sonic-Mill, Inc. for providing the pelleting machine. The authors would like to thank Dr. Barich, an research assistant professor at Kansas University, for his help in using solid state NMR Facilities and providing experimental results. Thanks also go to Leidy Pena Duque, a PhD student in the Department of Biological and Agricultural Engineering at Kansas State University, for her help in determining chemical composition of biomass.

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Table1 Chemical composition of particles and pellets before and after pretreatment

Type of biomass			Chemical composition (% , dry basis)*					
			Glucan	Xylan	ASL	AIL	Total lignin	Ash
Corn stover	Without pretreatment	Particles	40.9 (0.5)	23.0 (0.5)	1.1 (0.1)	15.5 (0.4)	16.6 (0.5)	2.6 (0.2)
		Pellets	41.6 (0.6)	23.4 (0.2)	1.1 (0.2)	16.1 (0.5)	17.2 (0.5)	2.4 (0.2)
	With pretreatment	Particles	53.1 (0.7)	1.6 (0.2)	0.80 (0.05)	31.8 (1.0)	32.6 (0.9)	5.6 (0.4)
		Pellets	54.4 (0.4)	1.9 (0.4)	0.97 (0.03)	31.3 (0.6)	32.3 (0.5)	6.2 (0.6)
Sorghum stalk	Without pretreatment	Particles	40.5 (0.8)	22.7 (0.8)	0.9 (0.1)	18.1 (0.5)	19.5 (0.6)	2.8 (0.4)
		Pellets	41.1 (0.9)	24.1 (0.6)	0.9 (0.1)	18.3 (0.9)	19.7 (0.7)	2.5 (0.2)
	With pretreatment	Particles	53.4 (0.5)	2.3 (0.1)	0.78 (0.04)	31.1 (0.9)	31.9 (1.0)	3.7 (0.2)
		Pellets	54.3 (0.3)	2.5 (0.3)	1.01 (0.03)	32.2 (0.6)	33.2 (0.6)	3.8 (0.2)

* Expressed as “mean (standard deviation)”

Table 2 Assignment of FTIR absorption bands for biomass

Wavenumber (cm ⁻¹)	Assignment	Reference
1599	Aromatic skeletal vibration plus C=O stretching (related to lignin removal)	[24-27]
1509	C=C stretching from guaiacyl ring of lignin	[25-27]
1462	Aromatic C-H deformation; asymmetric in -CH ₃ and -CH ₂ -	[27]
1425	C-H in-plane deformation with aromatic skeletal stretching	[27,28]
1370	Weak C-O stretching in cellulose	[29]
1270	C-O of guaiacyl ring and C-O stretching	[25,28]
1260	Ester absorbance (related to removal of uronic acid)	[30]
1164	C-O-C asymmetric vibrations at β -glucosidic linkages in cellulose and hemicellulose	[25,27]
1106	Antisymmetric in-phase ring stretch of cellulose	[26]
1060	C-O stretching in cellulose	[25,31]
1043	C-O stretching in C-O-C linkages of hemicellulose	[27,31]
1033	C-O deformation in primary alcohol or C-O, C=C and C-C-O vibration stretching in lignin	[25,29];
1030	C-O stretching in cellulose	[25]
991	β -glucan in hemicellulose	[29]
900	Antisymmetric out-of-plane ring stretch of amorphous cellulose; C-O stretching	[25]

Table 3 Signal assignments for ^{13}C CPMAS spectra of biomass

Chemical Shift (ppm)	Types of carbons
172.5-173.8	Carboxyl groups(COOH) in acetyl groups of hemicellulose
153.1-153.9	S3 (e), S5 (e), G4 (e) in lignin
147.8-148.1	S3 (ne),S5 (ne), G3 in lignin
136.5-137.1	S1 (e), S4 (e), G1 (e) in lignin
133.8-134.1	S1 (ne), S4 (ne), G1 (ne) in lignin
122.1-123.2	G6 in lignin
115.6-116.7	G5 in lignin
113.8	G2 in lignin
105.4	C-1 of cellulose
89.2-93	C-4 of crystalline cellulose
84.2-84.6	C-4 of amorphous cellulose
72.9-75.2	C-2 ,C-3, and C-5 of cellulose
65.5	C-6 of crystalline cellulose
63-63.3	C-6 of amorphous cellulose
56.1-56.7	Methoxyl groups(-OCH ₃) in lignin
23.2-25.2	Methyl (CH ₃) in acetyl groups of hemicellulose

S, syringyl; G, Guaiacyl; ne, nonetherified; e, etherified

Fig.1 Experimental procedure

Fig.2 Experimental setup for UV-A pelleting

Fig. 3 Sugar yield result of particle and pellet for two types of biomass

Fig. 4 FTIR spectra of pure hemicellulose and various biomass samples

Fig. 5 FTIR spectra of pure cellulose and various biomass samples

Fig. 6 FTIR spectra of pure lignin and various biomass samples

Fig. 7 XRD patterns of particles and pellets before and after pretreatment

Fig. 8 Results on CrI values

(a)

(b)

Fig. 9 Distribution of (a) TGA and (b) DTG of corn stover samples

(a)

(b)

Fig. 10 Distribution of (a) TGA and (b) DTG of sorghum stalk samples

Fig. 11 NMR spectra of corn stover (sample 1 – unpretreated particles, sample 2 – pretreated particle, sample 3 – unpretreated pellets, and sample 4 – pretreated pellets)

Fig. 12 NMR spectra of sorghum stalk (sample 1 –unpretreated particles, sample 2 – pretreated particles, sample 3 – unpretreated pellets, and sample 4 – pretreated pellets)

Fig. 13 SEM images of corn stover: (a) outer surface of untreated particles, (b) outer surface of untreated pellets, (c) cellulose bundles of pretreated pellets, (d) annular rings of pretreated pellets, (e) pellets after hydrolysis, and (f) microfibrils of pellet after hydrolysis