Structural and Thermal Stability Changes of Rice Straw Fibers during Anaerobic Digestion

Tengfei Xia,[a,b] Enhui Sun,[a] Wanying Tang,[b] Hongying Huang,[a,]* Guofeng Wu,[a] and Xiaochen Jin [a,b]

Rice straw fibers are potential raw materials that can be used to produce biogas and reinforcing fibers for composites. In order to ascertain the effects of anaerobic digestion on the structural properties of the fibers, the structure of fibrous residuals with different digestion time, including 0, 10, 20, and 30 days, were investigated. The normalized biogas production volume was 224 mL/g volatile solid of substrate, of which the methane content was about 50%. Fiber detergent analyses of the straw before and after 10 days digestion indicated that the cellulose levels increased from 34.3% to 41.3%, and cellulose crystallinity index ranged from 44.9% to 49.9%, respectively. After the rice straw had been digested for 30 days, the cellulose and hemicelluloses of the rice straw were partially degraded; the crystallinity index of the cellulose decreased from 44.9% to 40.1% based on XRD analyses, and the amount of hydroxyl groups were observed to decrease based on FT-IR analyses. Consequently, the polarity and hygroscopicity of the rice straw fibers were speculated to be lowered based on these observed changes. Furthermore, the relative amount of lignin in the straw residuals increased as digestion time increased, which increased the thermal stability of the resulting fibers. As a result of anaerobic digestion, the properties of the rice straw fibers for their use in plastic composites were enhanced.

Keywords: Rice straw fibers; Anaerobic digestion; Structural changes; Thermal stability

*Contact information: a: Circular Agriculture Research Center, Jiangsu Academy of Agricultural Science, Nanjing, 210014, P. R. China; b: Institute of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, 210094, P. R. China; *Corresponding author: sfmicrolab@163.com*

INTRODUCTION

The development and utilization of renewable energy and natural resources has become a crucial research subject due to the limited fossil fuel reserves around the world. Biomass energy sources represent an important portion of renewable energy resources that can be used as substitutes for fossil fuels; these new resources are being studied to be applied in daily life (Sambusiti *et al.* 2013; Yao *et al.* 2013). At present, agriculture residues, including wheat and rice straw, corn stalks, and vegetable residuals, are important sources of biomass materials, and they are being used for ethanol fermentation. Other applications of residuals include anaerobic digestion of straw to produce biogas (Ahn *et al.* 2010; Singh *et al.* 2012), as well as the use of plant fibers to reinforce plastic composites, which were then used for building materials and automotive parts.

Rice straw is an important and an abundant agriculture residue in China, where it is second only to wheat straw. The annual amount of rice straw produced in China was about 220 million tons (the data from Chinese Statistical Yearbook of 2017). Currently, anaerobic digestion of rice straw is being used for biogas production. During anaerobic digestion, constituents of rice straw, mainly cellulose and hemicelluloses, are degraded by anaerobic microbes to produce biogas (Teghammar *et al.* 2012). The undigested residuals from anaerobic fermentation can be used as organic fertilizer for agriculture (Chen *et al.* 2013). Rice straw fibers are composed of cellulose, hemicelluloses, and lignin (Sambusiti *et al*. 2013). Cellulose is a monosaccharide polymer composed of glucose, and is the main constituent of straw fibers before and after anaerobic digestion to produce biogas. Cellulose polymer chains form hydrogen bonds among themselves to form crystalline cellulose, which contributes considerably to the mechanical strength properties of the fibers (Dobreva *et al*. 2010). On the other hand, there are some cellulose polymer chains that are not closely associated with one another *via* hydrogen bonding; these loosely associated monosaccharide polymer chains are referred to as amorphous cellulose (Thygesen *et al*. 2005). Hemicelluloses are composed of different saccharide units, including glucose, mannose, and xylose, as well as some arabinose, fructose, *etc*. The fibrils and microfibers of cellulose, with some hemicelluloses, are hydrogen-bonded to one another to constitute a web framework for the fiber skeleton to sustain the plant cell. In addition, lignin is an amorphous polymer composed of phenylpropane units, namely syringyl, guaiacyl, and *p*-coumaryl alcohol (Xiao *et al*. 2001). Lignin's structure contains non-phenolics, phenolics, aliphatic hydroxyls, and conjugated double bonds; these structural groups react easily with many reagents, which allow lignin in rice straw to be chemically modified. Furthermore, lignin is a suitable reinforcing polymeric material due to its higher strength, stiffness, and rheological properties when compared to cellulose (Lu *et al*. 2013). In fact, lignin is one of the plant's defensive mechanisms to protect the cells from microbial attack; it is almost non-degradable under anaerobic conditions (Rui *et al*. 2010; Mussoline *et al*. 2013; Thomsen *et al*. 2014). The carbohydrate constituents of straw fibers contain many polar hydroxyl groups that make the lignocellulosic fibers hygroscopic and hydrophilic. As a result, rice straw fibers are generally incompatible when incorporated into a hydrophobic polymer matrix to form a fiber-reinforced composite material (Khandanlou *et al*. 2014). Hence, when rice straw fibers are used in composites, the lignocellulosic fibers need to be chemically modified to improve their compatibility with the plastic composite matrix (Pandey *et al.* 2010).

Many pretreatment methods have been utilized when pre-treating rice straw, including chemical and physical methods. The most common chemical methods include alkali pretreatment (Jayamani *et al*. 2016; Tayfun *et al.* 2016) and coupling agent pretreatment (Shih *et al.* 2012). Physical methods include heat treating (Chen *et al.* 2015), mechanical-high pressure steam treating (Chen *et al.* 2011), and electron radiating (Ismail *et al.* 2012). Chemical methods produce reagent wastes that can lead to environmental emissions, while physical methods are expensive.

Biological pretreatment methods utilize microbial agents, such as bacteria, fungi and enzymes, to modify straw fibers. Little research has been published on biological pretreatment methods to modify straw fibers. Several investigators utilized fungi to degrade wheat straw. Mechanical strength and thermal properties of wheat straw was effectively improved with such pretreatments (Panthapulakkal and Sain 2006; Sain and Panthapulakkal 2006). An anaerobic digestion process has been studied as a possible method to modify straw fibers, as well as producing a biogas by-product. Anaerobic digestion of straw fibers is an important way to transform agriculture residues into biomass energy using anaerobic bacteria (Sieling *et al.* 2013); a simplified overview of the mechanism of anaerobic digestion was presented in Fig. 1 (Glissmann and Conrad 2000; Chandra *et al*. 2012).

In the initial stage of anaerobic digestion, the fiber structure of the rice straw is degraded and hydrolyzed by anaerobic microbes, which converts hemicelluloses and cellulose into acetic acid, volatile fatty acids (VFA), hydrogen, and carbon dioxide. Then hydrogen-producing acetogenic bacteria hydrolyze VFA into acetic acid, hydrogen, and carbon dioxide (Lei *et al.* 2010). Finally, methanogenic bacteria convert acetic acid, hydrogen and carbon dioxide into methane. The cell wall and cellulose, which compose the structure of the straw fibers, are gradually degraded with the extension of fermentation time (Appels *et al.* 2008; Yang 2014). Based on the above description of anaerobic digestion, anaerobic digestion is a complex biological process. However, there has been relatively little research on the structure of residue from anaerobic digestion of rice straw. There is a need to know more about the structure of rice straw with different digestion time. Therefore, the goal of this investigation was to ascertain the effect of anaerobic digestion on rice straw and analyze the structural and componential change of rice straw at different stages of anaerobic digestion. Furthermore, the variation of conditions during anaerobic digestion is expected to contribute to the determination of appropriate digestion time. A hypothetical mechanism for this pretreatment method is proposed in this work to improve the constituents and physical structure of rice straw fibers based on the experimental data.

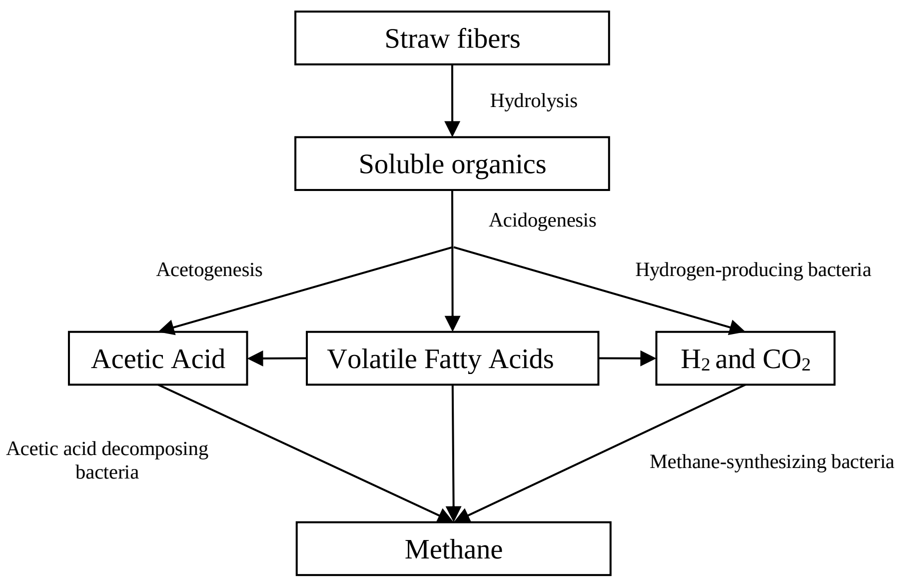

Fig. 1. The simplified description of anaerobic digestion of straw fibers

EXPERIMENTAL

Materials

Rice straw was obtained from a farm at the Jiangsu Academy of Agricultural Sciences (Nanjing, China). The straw was reduced in size into 0.3 mm to 0.9 mm particles using a grinder. Then the rice straw powder was dried at 105 °C in a ventilated oven to a moisture content of 3%. Waste activated sludge was obtained from a pig farm in

Jin Tan of the Jiangsu Province of China; the sludge had a total solid (TS) content of 3.5%. Before the sludge was utilized, it was cultivated by the addition of a 25 wt. % sucrose solution for 2 days to activate the microbes in the sludge. The sucrose was decomposed to produce biogas in the sludge when the methane content of biogas was over 50%, which was the theoretical amount to assess the appropriate sludge activity. The cultivated sludge was then considered ready for experimental use.

Anaerobic Fermentation of Rice Straw

To a 5 L fermentation cylinder, 330 g rice straw powder (about 8 wt.%), 1670 mL water (42 wt. %), and 2000 mL activated sludge that contained approximately 6.2wt.% dry basis (50 wt. %) were added The contents were stirred to mix them uniformly. This was done in triplicate, and the fermentation reactors were labeled as C1, C2, and C3, respectively. The fermentation reactor lid was tightly sealed, and the generated biogas was captured and its volume measured using gas and water bottles. Anaerobic digestion was performed at 37 °C for 30 days, and the methane content in the biogas was measured using a gas chromatography instrument (model GC-9890A, Renhua; Nanjing, China). The total volume of biogas generated each day was measured by water displacement. Concurrently, a portion of the slurry in the fermentation reactor was taken every ten days, and the suspended solids were separated from the liquor. The solids were washed 6 to 8 times with clean water with a 0.3 mm filter until the filtrate was clean. Next, the recovered solid residues were dried at 80 °C for 24 h. Finally, the dried solids were broken-up so that they would pass through a 0.9 mm sieve.

Determination of Lignocellulosic Constituents

The amount of cellulose, hemicelluloses, lignin, and ash in the rice straw fibers were ascertained by the fiber detergent analysis method developed by Van Soest (1965) to analyze forage fiber. Three replicates were performed on each analyzed sample, and the reported values were the averages of the replicates.

The laboratory reagents used were as follows:

1. Neutral detergent: Into a 1000 mL beaker was added 18.6 g disodium ethylenediaminetetraacetic acid (EDTA), 6.8 g sodium tetraborate decahydrate, 30 g sodium lauryl sulfate, and 10 mL 2-ethoxyethanol. A small amount of distilled water was then added to dissolve these reagents. Into a second beaker was added 11.50 g disodium hydrogen phosphate dodecahydrate with some distilled water; the contents of the beaker were then heated to dissolve the reagent. Once all components in both beakers had been dissolved, the solution of the second beaker was poured into and mixed in the first beaker. Finally, the mixed solution was added to a 1000 mL volumetric flask and diluted to the mark with distilled water. The resulting solution pH should be about 6.9 to 7.1.
2. Acid detergent: Add 20 g cetyltrimethyl ammonium bromide (CTAB) to 1000 mL 1N sulfuric acid at room temperature. Mix until CTAB is dissolved.
3. 72 wt. % Sulfuric acid
4. Ethanol
5. *n*-Octanol

The analytical procedure for quantifying the various constituents was described as follows:

Neutral-detergent fiber (NDF): The mass of a 250 mL beaker (denoted as m_0) was determined. Then 1 g of the dried power sample (denoted as m_1) and 100 mL neutral detergent solution were added to the beaker. Then a few drops of *n*-octanol were added to inhibit foaming during boiling. The solution was heated until boiling; a slow boil was maintained under reflux for 80 min. When the time ended, the boiled sample was filtered through a fritted glass crucible (Gooch-type) and the solids were washed in the fritted crucible with distilled water. The crucible with its solids was dried to constant weight at 105 °C; the mass of the hot crucible with dried solids was determined (denoted as m_2). The amount of NDF (as a percentage) was calculated as:

$$\text{NDF} = ((m_2 - m_0)/m_1) \times 100\% \quad (1)$$

Acid-detergent fiber (ADF): Acid detergent solution was added to the recovered neutral-detergent residues from the above procedure. The NDF process was repeated except that acid detergent solution was used in place of neutral detergent solution. The mass of the oven-dried crucible with ADF residuals was determined (denoted as m_3). The amount of ADF (as a percentage) was calculated as:

$$\text{ADF} = ((m_3 - m_0)/m_1) \times 100\% \quad (2)$$

The amount of hemicelluloses in the powdered sample was computed as:

$$\%\ \text{Hemicellulose content} = \text{NDF} – \text{ADF} =((m_2 – m_3)/m_1) \times 100\% \quad (3)$$

Acid-detergent lignin (ADL): The ADF solids obtained from the previous step in the fritted crucible was treated with 25 mL 72 wt. % sulfuric acid at room temperature for 2 h. Afterwards, the insolubilized solid in the fritted crucible was washed to neutral pH by boiling water; then the crucible was dried at 105 °C and the mass was determined (denoted as m_4). Finally, the crucible was heated to 550 °C for 6 h in a muffle furnace, and then cooled to room temperature in a desiccator. The mass of the crucible with ash after muffle furnace treatment was determined (denoted as m_5). The remaining constituents of the powder sample were calculated from the mass measurements using the equations:

$$\%\ \text{Cellulose content} = ((m_3 – m_4)/m_1) \times 100\% \quad (4)$$

$$\%\ \text{Acid-detergent lignin content} = ((m_4 – m_5)/m_1) \times 100\% \quad (5)$$

$$\%\ \text{Inorganic ash content} = ((m_5 – m_0)/m_1) \times 100\% \quad (6)$$

Gas Chromatography

The methane content of biogas was detected by gas chromatography equipped with a TCD thermal conductivity detector and TCD-01 column (4mm×1m, SHIMADZU, Japan). The temperatures of the detector, column and injector were set at 100 °C, 150 °C, and 130 °C, respectively. The flow rate of the hydrogen as carrier gas was 50 mL/min, and the sample volume was 0.5 mL.

Fourier Transform-Infrared (FT-IR) Spectroscopy Analysis

A FT-IR spectrometer (Nicolet iS 10 model, Thermo Scientific; Waltham, MA, USA) was used to characterize the changes to the physical structure and to the constituents of rice straw fibers during anaerobic fermentation. The sample was incorporated with KBr and pressed into a disc. The spectra of the disk were recorded from 4000 to 400 cm^{-1} wavenumbers.

Characterization of Surface Morphology

A scanning electron microscope (SEM) (EVO-LS10 model, Carl Zeiss; Jena, Germany) was used to characterize the microscopic morphologies of the various samples. Samples were observed using a 10 kV acceleration voltage, and 1000x magnification images were obtained. The structure and surface interfaces of the rice straw fibers were evaluated directly from the SEM images.

X-Ray Diffraction (XRD) Analysis

Samples were analyzed by an X-ray diffractometer (model D2 PHASER, Brüker AXS; Karlsruhe, Germany) using Cu Kα radiation (λ =1.54 Å). The diffraction scans were recorded from 5° to 40° range in 0.02° increments. The crystallinity index (% *CrI*) of the cellulose in the various rice straw fiber samples was determined according to the following equation (Zhao *et al.* 2011):

$$\% \, CrI = (I_{002} - I_{am})/I_{200} \times 100\% \tag{7}$$

where I_{002} is the maximum diffraction intensity of the [002] crystalline lattice planes at 2θ of 22° to 23°, and I_{am} is diffraction intensity of the amorphous cellulose, which is taken at a 2θ between 18° and 19°, which is where there is minimum diffraction interference from the crystalline cellulose structures.

Thermal Characterization

Thermogravimetric analysis was the primary method used to characterize the stability of a material. Based on the thermogravimetric curve obtained from this analytical technique, the thermal properties of rice straw fibers could be quantified. Thermo-gravimetric and differential thermal analysis (TG/DTA) of the fibers was obtained using an EXTSTAR series TG/DTA 7200 instrument from SII NanoTechnology Inc. (Japan). The sample temperature was increased from 35 °C to 650 °C at a rate of 10 °C/min with the TG/DTA instrument.

RESULTS AND DISCUSSION

Biogas Production of Rice Straw

Rice straw was decomposed during anaerobic digestion to produce various monosaccharides and volatile fatty acids, and these were further converted into methane, hydrogen, and carbon dioxide gas, along with a little nitrogen gas, to form biogas. Hence, biogas production was an important index to evaluate the anaerobic conditions during digestion. Figure 2 plotted the biogas production and the level of methane for the three fermentation reactors. During anaerobic fermentation, the methane content of the biogas gradually increased from the 3rd to the 13th day, and it peaked at 66% on the 10th to the 13th day. From the 14th to the 20th day, the methane content decreased linearly, but it increased again after the 20th day. Finally, the trend became steady at 50% methane content. Likewise, the biogas production had some similarities to methane level trends, but the maximal production (5700 mL/d) was reached earlier from the 9th to the 12th day, which meant that the rice straw was being digested very quickly during this period. Additionally, the total biogas production and the normalized biogas production for 30 days were determined and the data were listed in Table 1. The average total biogas production from rice straw from the fermentation reactors was 71,800 mL, of which the methane content was about 50%. This observation indicated that the rice straw was primarily digested under anaerobic conditions.

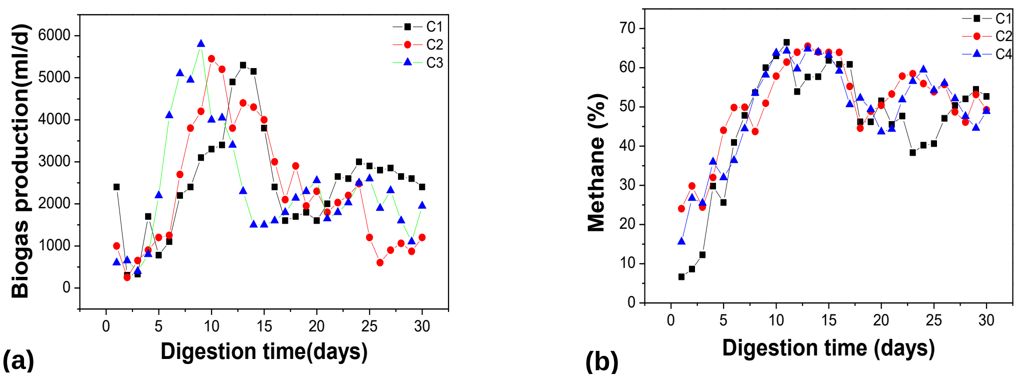

Fig. 2. (a) Methane content in biogas, and b) biogas production rate for each day during anaerobic digestion in the fermentation reactors

Table 1. Total Biogas Production and Methane Yield from the Three Replicates for 30 Days

Reactor	Total Biogas (mL)	Total Methane (mL)	Normalized Biogas (mL/g TS)	Normalized Methane (mL/g TS)
C1	75,710.0	38,180	236.6	119.3
C2	68,790.0	37,874	215.0	118.4
C3	70,900.0	37,021	221.6	115.7

Changes to Rice Straw Fiber Components during Anaerobic Fermentation

With the passing of digestion time, the constituents and the structural features of rice straw fibers were altered. For the purpose of this study, rice straw constituents from different digested times (*i.e.*, 0, 10, 20, and 30 days) were determined by the detergent fiber analysis method developed by Van Soest (1965). Three replicates were performed on each analyzed sample. The average value and errors of original data were analyzed by IBM SPSS 19, and its results obtained from this analysis are listed in Table 2. The conditions of each measurement, including the reaction temperature, time, and reagent dosage, had inevitable slight differences with each other so that the errors of each measurement were different in Table 2. During the first 10 days' digestion, the relative amounts of cellulose, hemicellulose, and lignin increased appreciably (Fig. 3), which implied that organic extractives were preferentially decomposed. During this time period, cellulose and hemicelluloses were hardly digested. Anaerobic digestion from 10 to 20 days obviously resulted in decreases in the relative contents of cellulose and hemicelluloses, where the cellulose was digested faster than hemicelluloses. Meanwhile, cellulose and hemicellulose were fast degraded and transformed into biogas by anaerobic bacteria, which caused the increase of methane content and biogas production based on Fig. 2. From 20 to 30 days, the decomposed rate of the rice straw and the biogas production rate gradually declined. This observation was attributed to the principle that easily digested components, such as hemicelluloses and amorphous celluloses, would be consumed, and that more recalcitrant components to digestions, such as crystalline cellulose and lignin, would remain. The relative levels of lignin and ash increased during digestion, which implied that they were indigestible during fermentation.

Table 2. The Relative Amount of Rice Straw Fiber Components

Digestion Time (days)	Cellulose (%)	Hemicelluloses (%)	Lignin (%)	Ash (%)
0	34.3 ± 0.36	30.2 ± 0.46	5.1 ± 0.10	0.6 ± 0.14
10	41.3 ± 0.49	33.0 ± 0.05	10.0 ± 0.19	2.7 ± 0.63
20	37.6 ± 0.19	30.8 ± 0.26	11.2 ± 0.56	3.8 ± 0.20
30	34.4 ± 0.19	30.0 ± 0.79	13.1 ± 0.59	5.2 ± 0.18

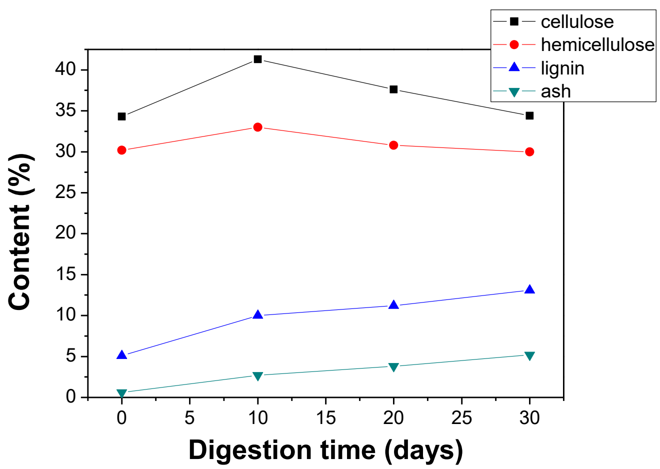

Fig. 3. The change of rice straw components in anaerobic digestion

Lignin is generally reactive towards many different chemical reagents. Hence, high lignin content in the digested rice straw fiber may be beneficial for its further modification by chemical reagents. Furthermore, lignin is an appropriate reinforcing material due to its higher strength, stiffness, and rheological properties than cellulose (Holladay *et al.* 2007). Although untreated and 30-days digested rice straw fibers had almost the same relative levels of cellulose and hemicellulose, the relative levels of lignin appeared to increase.

Morphology Characterization

During anaerobic digestion, not only were fiber components changed, but the surface morphologies changed. The visual variations are shown by the SEM images in Fig. 4. The undigested rice straw surfaces were smooth, and the fibril bundles were covered under the epidermis, whereas the epidermis structure was degraded and the fiber surfaces became less smooth after the first 10 days of anaerobic digestion. During this initial period, the cellulose and hemicelluloses were well preserved by the epidermis. This phenomenon seemed consistent with the relative levels of cellulose and hemicelluloses increasing after digesting for 10 days. Afterwards, the lignocellulosic structure was further degraded to expose new fibril bundles for anaerobic digestion, which resulted in deep groves on the fibers' surfaces (Fig. 4(c)). Lots of fibril bundles and microfibers were exposed during this digestion period, and the specific surface area of rice straw particles increased. This allowed for better accessibility of hydrolytic and fermentative bacteria to digest the fiber surfaces. Better fiber surface accessibility to bacteria attack accelerated the digestion of cellulose and hemicelluloses, which caused the biogas production rate to increase to its maximum value. When 30-days-digestion was completed, some fibril bundles and microfibers were completely digested, and fiber surfaces became more rough and irregular.

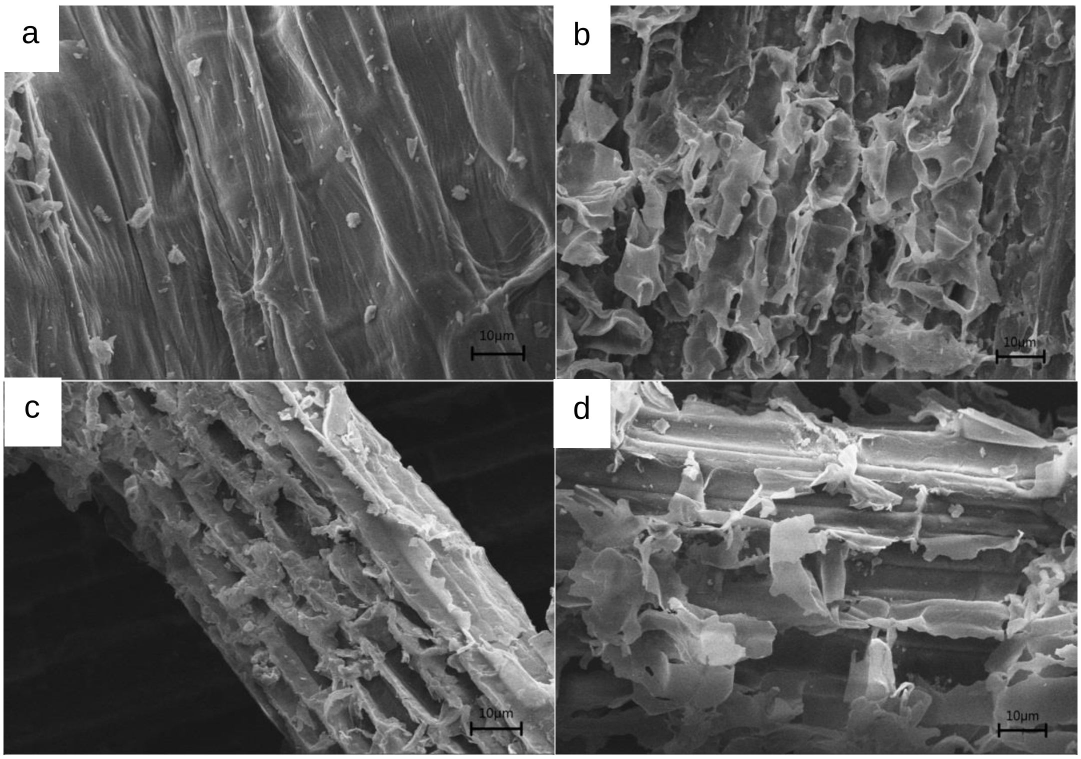

Fig. 4. SEM images of the surfaces of rice straw fibers: (a) untreated; (b) 10 days digestion; (c) 20 days digestion; and (d) 30 days digestion

Cellulose Crystallinity Structure Analysis

In the structure of rice straw, cellulose crystallinity is a crucial factor that affects the mechanical properties of the fibers. A higher degree of cellulose crystallinity was considered to improve mechanical strength properties of the natural fibers (Thygesen *et al.* 2005; Shah 2013). Hence, the variation of cellulose crystallinity was investigated by XRD (Fig. 5). Crystalline cellulose exhibited distinct XRD peaks of 2θ at 16° and 22°. The 16° diffraction peak corresponds to [110] lattice plane. The diffraction peak of 22° indicates [002] lattice plane (Zhao *et al*. 2011). The peak intensities at [110] and [002] lattice planes were enhanced appreciably after 10 days anaerobic digestion; this observation indicated that the relative levels of crystalline cellulose increased from 44.9% to 49.9% (Table 3). Additionally, just as it was observed from the SEM analysis, cellulose crystallinity was not appreciably affected. From the 10^{th} to 30^{th} day, the XRD the peak intensities decreased, which suggested that the crystalline cellulose was attacked and digested by anaerobic bacteria such that the relative amounts of crystalline cellulose in the undigested and 30-day digested straw decreased.

Table 3. Crystallinity Index of Rice Straw Fibers during Anaerobic Digestion

Digestion Time (days)	Crystallinity Index (%)
0	44.9
10	49.9
20	43.5
30	40.1

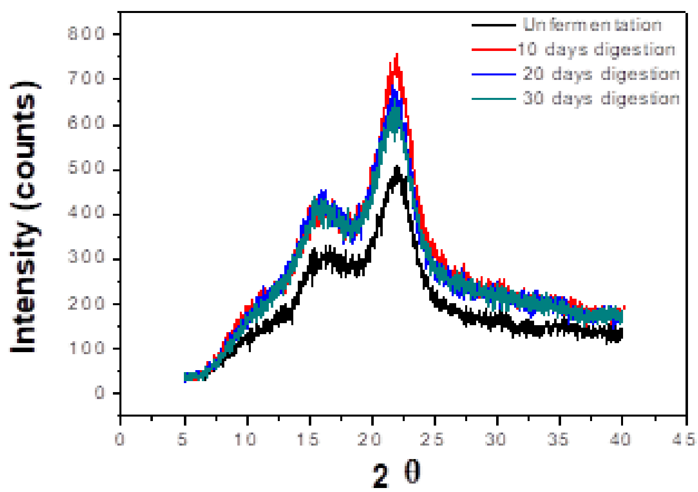

Fig. 5. XRD diffraction patterns of rice straw fibers at different digestion time

Molecular Structure Characterization

The polarity and the hygroscopicity of plant fibers are central problems that prevent them from being used in composite materials; the microstructures of the plant fibers determined these properties (Zhao *et al*. 2011). Hence, FT-IR analysis was used to investigate the molecular structure of the rice straw fibers (Fig. 6). According to the FT-IR spectra, the strong absorption peaks at 3332 cm^{-1} and 2916 cm^{-1} originated from -OH groups and C-H stretching vibration, respectively. Hydroxyl groups were typically found on the cellulose and the hemicelluloses. When the rice straw was digested for 10 days and for 20 days, the -OH absorption peaks were observed to be stronger in the digested versus undigested rice straw, which implied that the relative cellulose and hemicellulose levels increased during digestion. This observation seemed to corroborate the findings presented in Table 2. However, the 30-day digested straw had a weaker -OH absorption peak than the undigested straw. This finding from the FT-IR spectra implied that the polarity and hygroscopicity of the rice straw fibers were appreciably lowered during digestion (Khalil *et al*. 2001; Paul *et al.* 2010).

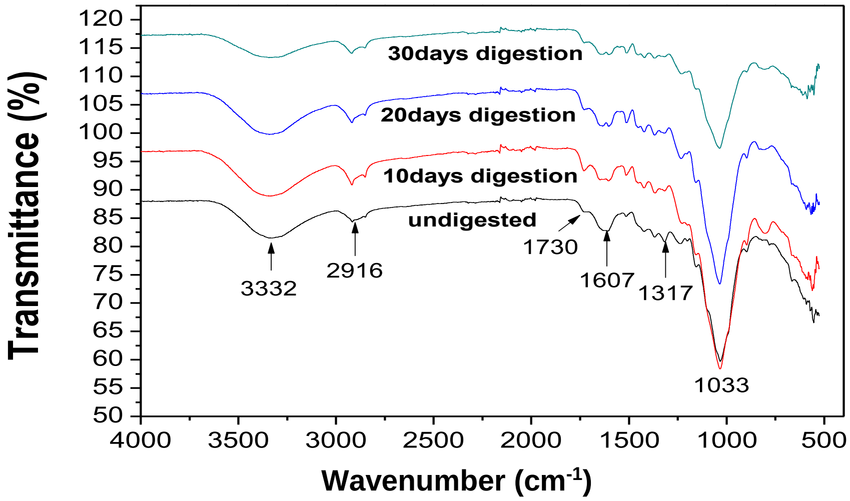

Fig. 6. FI-TR spectra of the undigested rice straw and rice straw digested for 10, 20, and 30 days

The absorption peaks at 1730 cm^{-1} and 1607 cm^{-1} were attributed to stretching vibration of C=O groups from the hemicelluloses and lignin. Surprisingly, these peeks followed the observed trends for the -OH group peeks. The peak of 1317 cm^{-1} was attributed to C-H bonds (bending vibration in plane). The strongest FT-IR peak observed at 1033 cm^{-1} cannot be unambiguously assigned to a specific group; the peak could be attributed to the vibration of different bonds, including C-H and Ar-H bonds (bending vibration in plane), and C-O-C bonds (stretching vibration). The prominence of this peak declined as the digestion time was increased to 30 days. This decrease was ascribed to the decomposition of the cellulose and the hemicelluloses.

Thermal Stability Analysis

As was shown in Fig. 7, the thermogravimetric curves of the undigested and the digested rice straw fibers were obviously different from one another. The onset temperature for thermal decomposition of the undigested rice straw occurred at 170 °C; this onset temperature for the digested rice straw shifted to 210 °C. This observation indicated that the thermal stability of the fibers was greatly enhanced. Most of the labile components, such as pectins and proteins, had been digested by the anaerobic microbes. Additionally, the relative amount of lignin in the digested sample, which was thermally more stable, increased versus the undigested sample. The curves from 180 °C to 380 °C were ascribed to the decomposition of cellulose and the hemicelluloses, and the curves beyond 380 °C were attributed to the decomposition of lignin. More importantly, the thermal decomposition of cellulose and hemicelluloses of the digested rice straw had a higher end temperature, which could be explained by the higher relative levels of lignin. Effectively, anaerobic digestion could be used to improve the thermal stability of rice straw fibers.

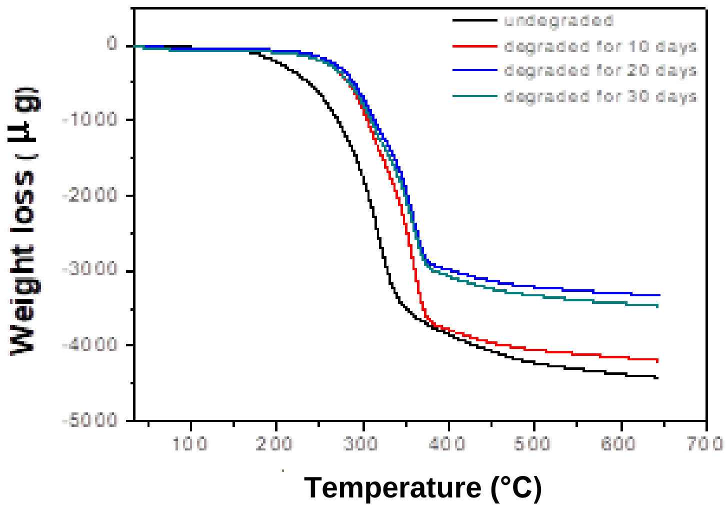

Fig. 7. TG curves of the undigested and digested rice straw

CONCLUSIONS

1. Rice straw was utilized as a substrate to produce biogas and fibers under anaerobic digestion conditions. When rice straw was digested by anaerobic bacteria, appreciable quantities of biogas were produced, which contained approximately 50% methane. The pretreatment process of rice straw produced renewable energy, which was different with fungus pretreated methods (Sain and Panthapulakkal 2006; Panthapulakkal and Sain 2006). When rice straw was digested for 10 days, the relative levels of cellulose and hemicelluloses in the digested fiber residuals increased significantly and the cellulose crystallinity index of rice straw ranged from 44.9% to 49.9%. At the same time, the onset thermal decomposition temperature of the rice straw shifted from 170 °C to 210 °C. These effects were consistent with the effects of the mechanical-high pressure steam treating (Chen *et al.* 2011, 2013).
2. It was determined from XRD analysis that the crystalline cellulose structure was attacked by anaerobic microbes, and the cellulose crystallinity index of the rice straw fibers declined from 44.9% to 40.1%. Cellulose and hemicelluloses were degraded in the time between the 10^{th} and 20^{th} day. The SEM images of the rice straw fibers indicated the surfaces became rougher and more irregular than the undigested fibers. The hydroxyl groups were observed by FT-IR analysis to decrease, which implied the reduction of the polarity and hygroscopicity of the rice straw fibers.
3. The higher relative levels of lignin in the digested straw contributed to the higher thermal stability of the fibers when compared to undigested straw. Consequently, biogas residues of rice straw had better thermal decomposition properties than the undigested straw, and the primary results proved that anaerobic digestion could be not only effectively used for biogas production but also the pretreatment of rice straw for fiber-reinforced composites.

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