Industrial Crops & Products 121 (2018) 73–79

Contents lists available at ScienceDirect

Industrial Crops & Products

journal homepage: www.elsevier.com/locate/indcrop

The characteristic changes of rice straw fibers in anaerobic digestion and its effect on rice straw-reinforced composites

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A R T I C L E I N F O

Keywords:
Rice straw fiber
Anaerobic digestion
Characteristic changes
Rice straw
Reinforced composites

A B S T R A C T

Rice straw (RS) was utilized to produce biogas, and its biogas residues (BR) were studied on different degradation time. When rice straw was digested, much biogas was produced with average 50% methane. In anaerobic condition, non-fiber contents were mainly digested in the initial 10 days. Meanwhile, the surface of rice straw fibers became rough and its onset decomposition temperature also rose from 170 °C to 210 °C. Cellulose and hemicellulose were digested from 10 days to 30 days, and it determined that the cellulose crystallinity declined from 44.9% to 40.1% and hydroxyl groups was also seen to decrease, which conduces to the reduction of polarity and hydroscopicity. However, lignin was hardly digested in the whole anaerobic process. Inevitably, lignin was accumulated to contribute to the thermal stability and mechanical properties of rice straw fibers. Furthermore, rice straw/low-density polyethylene (RS/LDPE) and biogas residues/low-density polyethylene (BR/LDPE) composites were prepared. Compared with RS/LDPE composites, BR/LDPE composites showed obviously better tensile and flexural properties. Consequently, biogas residues of rice straw have better chemical and physical properties than the undigested rice straw.

1. Instruction

With the constant reduction of the oil fuel all over the world, the development and utilization of renewable energy and resource had become crucial research subject. Biomass energy sources as the important portion of renewable energy, especially plant energy, are the available substitutes of fossil energy, which are being widely researched and applied to science and technology as well as daily life (Yao et al., 2013; Sambusiti et al., 2013). At present, agriculture residues, including wheat straw, rice straw, corn straw and vegetable straw, are important source of biomass materials that are not only utilized to produce energy, for example, ethanol fermentation with rice straw and anaerobic digestion to produce biogas (Singh and Bishnoi, 2012; Ahn et al., 2010), but also as important raw materials to reinforce plant fiber composites for architecture infrastructure and automobile (Pandey et al., 2010).

Rice straw is a kind important and abundant agriculture residue in China, only secondly to wheat straw and corn stalk. The annual amount of rice straw in China ranges between 180 and 270 million tons (Lu et al., 2010). Now, rice straw anaerobic digestion is actively applied to the biogas production. In the anaerobic condition, part components of rice straw, mainly containing cellulose and hemicelluloses, were degraded to produce biogas by anaerobic microorganism (Teghammar et al., 2012). The difficult-degraded components as biogas residues were used as fertilizer (Chen et al., 2013). Rice straw fibers are mainly composed of cellulose, hemicelluloses and lignin (Sambusiti et al., 2013). Cellulose consisting of many glucose molecular polymers is the main component of straw fibers and biogas residues, and some cellulose are linked by hydrogen bond to form crystalline cellulose that plays an important part in the mechanical property of fibers (Dobreva et al., 2010). On the contrary, some cellulose can't agglomerate into fiber crystal and are referred to as amorphous celluloses (Thygesen et al., 2005). Hemicellulose is composed of different monosaccharides, including glucose, mannose, xylose and some arabinose, fructose and so on. The microfibers of hemicellulose and cellulose combined by hydrogen bond constitute web framework as fiber skeleton to sustain plant cell. In addition, lignin is a special non-polysaccharides component composed of aromatic alcohols and its ramifications such as syringyl alcohol, guaiacyl alcohol, and p-coumaryl alcohol (Xiao et al., 2001). Lignin structure contains aromatic group, phenolic hydroxyl group, alcoholic hydroxyl group and conjugated double bond, so lignin is easier to react with many chemical reagents, which declared that high lignin content is beneficial for modifying rice straw fibers by chemical methods. Furthermore, lignin is appropriate as a reinforce

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https://doi.org/10.1016/j.indcrop.2018.04.004
Received 27 August 2017; Accepted 1 April 2018

material on account of its better strength, stiffness and rheological property than cellulose (Lu et al., 2013). In fact, lignin is one of the plants defensive mechanisms against microbial attack and is almost undegradable at anaerobic conditions (Thomsen et al., 2014; Mussoline et al., 2013; Zhao et al., 2010). Based on the components and structure of straw fibers, lignocellulosic fibers containing many —OH groups have strong polarity and hydrophilia attributed to lots of hydroxyl of polysaccharide. As a result, rice straw fibers as reinforce materials are generally incompatible with the hydrophobic polymer matrix (Khandanlou et al., 2014). Therefore, when rice straw fibers are applied to composites, it is inevitable to preprocess and modify these straw fibers (Pandey et al., 2010).

Regarding the pretreatment of rice straw, many pretreatment methods were utilized, including chemical methods, physical methods. Chemical methods such as alkali pre-treated (Tayfun et al., 2016; Jayamani et al., 2016), coupling agent (Shih et al., 2012) dominate in usual methods. Physical methods are involved in heat treating (Chen et al., 2015), mechanical-high pressure steam technique (Chen et al., 2011), and electron radiation (Ismail et al., 2012). However, chemical methods generally cause extra environmental pollution due to waste chemical reagents and physical methods take high expense. For biologic methods, it is regarded as microbial methods modifying straw fiber through culturing bacteria, fungus and enzyme. So far, the research on biological methods to modify straw fibers is only a few numbers. Sain Suhara etc utilized fungus to degrade wheat straw. Mechanical strength and thermal property of wheat straw were effectively improved (Sain and Panthapulakkal 2006). In the article, anaerobic process was studied as a possible method modifying straw fibers, and the characters of biogas residues were systematically investigated by instrumental analysis. Anaerobic digestion of straw fibers is an important way to transform agriculture residues into biomass energy by anaerobic bacteria (Sieling et al., 2013), and its mechanism of anaerobic digestion was simply described by other researchers (Glissmann and Conrad, 2000; Chandra et al., 2012). In the initial stage of anaerobic digestion, straw fiber structure was destroyed and hydrolyzed by anaerobic microorganism in anaerobic condition, so that part of hemicellulose and cellulose were hydrolyzed to produce acetate, volatile fatty acids (VFA), H2 and CO_2, and then hydrogen-producing acetogenic bacteria hydrolyze VFA to acetic acid, hydrogen and carbon dioxide. Finally, methanogenic bacteria convert acetic acid, hydrogen and carbon dioxide into methane. With the extension of fermentation time, the structure of straw particles was gradually destroyed, resulting in the change of cell wall and cellulose structure (Appels et al., 2008; Yang, 2014). According to above theories and researches, this article researches the mechanism of anaerobic digestion as a method to pre-treat rice straw fibers through investigating the change of the component and structure of rice straw fibers in anaerobic process.

2. Materials and methods

2.1. Materials

Rice straw obtained from the farmer of Jiangsu Academy of Agricultural Sciences was grinded into 0.9 mm to 0.3 mm particles by a grinder. Then, the rice straw powder was dried at 105 °C in a ventilative oven, measuring its moisture content for 3%. Waste activated sludge was obtained from a pig farm in Jin Tan of Jiangsu province, and its total solid content (TS) is 3.5%. Before the sludge utilized, it was cultivated through the addition of 25%wt sucrose solution for 2 days for the purpose of activating the microorganism in the sludge. When the CH_4 content of biogas reached over 50%, the sludge was only appropriate to be employed.

2.2. Anaerobic fermentation of rice straw

Rice straw powder about 330 g (8%wt), water 1670 ml (42%wt) and waste activated sludge 2000 ml (50%wt) were added into a 5 L fermentation cylinder, stirring to mix them uniformly, and three repetitions were done, numbered as C_1, C_2, C_3, respectively. Then fermentation cylinders were tightly closed by lids linked with collecting gas bottles and water bottles for measuring biogas. The anaerobic process was done at 37 °C for 30 days, and the CH_4 content and biogas production were observed and recorded through Gas Chromatography analysis (GC-9890A, NanjingRENHUA in China) and the volume of draining water every day during anaerobic process. At the same time, a portion of biogas residues and slurry were taken out every ten days, and the slurry was washed out of the residues with clean water, filtered by a 0.3 mm sifter, repeatedly washed for 6–8 times until the filtrate was clean. Next, the biogas residues of rice straw were dried at 80 °C for 24 h. Finally, the drying residues were rubbed loosely to pass the 0.9 mm sifter.

2.3. Preparation of rice straw fiber-reinforced low-density polyethylene (LDPE) composites

The samples of RS and BR (30 days digestion) at 30 wt% loading were mixed respectively with low-density polyethylene (LDPE 70 wt% loading) at 170 °C. The mixed materials were fabricated by an injection molding, and dumbbell-shaped samples (10 × 3.18 × 3.18 mm) and rectangular samples (80 × 10 × 4 mm) were generated, and every specimen was tested in triplicate.

2.4. Determination of fibers' components

The experiment used Van Soest method (Van Soest, 1965) to ascertaining the contents of cellulose, hemicelluloses, lignin and ash in the rice straw fibers. Three repetitions of every sample were done.

2.5. Fourier transform infrared (FTIR) spectroscopy analysis

FTIR Spectrometer (NicoletS10-Thermo Scientific, American) was used to analyze the molecular level changes of structures and components of rice straw fibers during anaerobic fermentation. Samples were prepared with KBr and pressed into a disc. The observing range was from 4000 to 400 cm^{-1}.

2.6. Characterization of surface morphology

Scanning electron microscope (SEM, EVO-LS10, Carl Zeiss Jena, Germany) was able to observe the microscopic morphology characterization of materials. The samples were observed under 10 kV acceleration voltage and 1000 times images were obtained to straightly reflect the structure and interface condition and evaluate the changes of rice straw fibers.

2.7. X-ray analysis

Samples were analyzed by x-ray diffraction (XRD-D2PHASERX, manufactured by Bruker AXS, Germany) analysis. Anode target is Cu, and the diffraction range is from 5° to 40° by 0.02 step-size and 0.15406 nm wave length. The crystal characterizations of different rice straw fibers were observed and determined through the following Eq. (1) (Zhao et al., 2011).

2.8. Thermal characterization

Thermogravimetry analysis is the main method of measuring the stability of materials. On the basis of thermogravimetry curve, the thermal properties of rice straw fibers can be determined. Thermogravimetry/Differential Thermal Analyzer (EXSTAR series TG/DTA7200, fabricated by SII NanoTechnology Inc.) was used to analyze the fibers. The temperature was lifted from 35 °C to 650 °C, and the