BIOMASS AND BIOENERGY 71 (2014) 106–112

Available online at www.sciencedirect.com

ScienceDirect

http://www.elsevier.com/locate/biombioe

Physicochemical changes of rice straw after lime pretreatment and mesophilic dry digestion

Yue-gan Liang [a], Beijiu Cheng [b], You-bin Si [a], De-ju Cao [a], Er Nie [c], Jie Tang [a], Xiao-hong Liu [a], Zheng Zheng [c,*], Xing-zhang Luo [c,*]

[a] School of Resources and Environment, Anhui Agricultural University, Hefei 230036, PR China
[b] Key Laboratory of Crop Biology of Anhui Province, Anhui Agricultural University, Hefei 230036, PR China
[c] Department of Environmental Science and Engineering, Fudan University, Shanghai 200433, PR China

ARTICLE INFO

Article history:
Received 4 November 2011
Received in revised form
1 March 2013
Accepted 24 October 2014
Available online 14 November 2014

Keywords:
Rice straw
Lime pretreatment
Dry anaerobic digestion
Mass transfer
Crystallinity index
Thermal property

ABSTRACT

A better understanding of the physicochemical properties of the material, its changes and the effects of anaerobic digestion, will help to improve methane production efficiency. The physicochemical changes of rice straw after solid-state lime pretreatment and dry digestion were investigated. Those changes were revealed by the composition of the substrate before any treatment, from samples of the material during the process and by the final product. Such compositions were studied with X-ray, Fourier transform infrared spectroscopy and thermogravimetric analyzes. The obtained results showed that low mass transfer limited the lignin modification and polysaccharide decomposition, resulted in a low biogas yield; and that after pretreatment and 60 days of mesophilic dry digestion, the concentration of cellulose decreased (23.4%) as well as hemicellulose (13.1%). In the opposite case, the concentration of lignin increased (59%) as well as ash (108%). The crystallinity index increased by 5.4% after pretreatment and decreased by 4.8% after digestion. The FTIR spectrogram of the raw sample included a peak reflecting absorption of ester linkages. This peak was absent from FTIR spectra of pretreated and digested samples, indicating that such linkages are broken during pretreatment and then digested by the microorganisms during the anaerobic fermentation. Furthermore, lime pretreatment and dry digestion significantly changed the decomposed profiles and rate, the distribution of pyrolysis product. The obtained data showed that polysaccharides and lignin were decomposed during pretreatment and digestion phases, leading to changes in structural and thermal properties.

1. Introduction

Rice (*Oryza sativa* L.) is one of the main esculent cereals in China and its annual production accounts for about 30% of the total word's yield [1]. Its major by-product is rice straw. At present, large quantities of rice straw are burned in open fields in China, which not only wastes a renewable resource, but also causes serious environmental pollution [1–3]. Anaerobic digestion of rice straw is an alternative method that may produce a clean fuel for energy generation.

The process of dry anaerobic digestion (dry digestion) has attracted substantial interest because of its low construction and operation costs [4]. The leaching bed reactor (LBR) system

* Corresponding authors. Tel./fax: +86 21 65643342.
E-mail addresses: ygliang@ahau.edu.cn (Y.-g. Liang), zzhenghj@fudan.edu.cn (Z. Zheng), lxz@fudan.edu.cn (X.-z. Luo).
http://dx.doi.org/10.1016/j.biombioe.2014.10.020
0961-9534/

has shown some promise as a method for dry digestion of organic wastes [5], and it has been used widely for anaerobic digestion of various organic matters, including municipal solid waste [5], manure [6] and agricultural residues [2,7–10]. In those studies, the performance of dry digestion of various biomasses was investigated; however, few studies have focused on the changes in physicochemical characteristics of digested matter. A better understanding of the physicochemical properties of the material, its changes and the effects of anaerobic digestion on such properties, will help to improve methane production efficiency, because the information on the physicochemical changes is useful for optimizing the pretreatment parameters (pretreatment time, loading mass, etc) and anaerobic digestion parameters (moisture content, temperature, etc).

The lignocellulosic structure of rice straw is resistant to biodegradation or enzymatic hydrolysis [11]. Lime pretreatment markedly improves lignocellulosic biodegradation [12]. In this study, lime pretreatment of rice straw in solid-state conditions was selected, to avoid wastewater production and treatment [13].

X-ray and Fourier transform infrared (FTIR) spectroscopy analyses are useful techniques for studying structural changes and matter decomposition of lignocelluloses after pretreatment and wet digestion [14–16]. Composition decomposition and structure changes may affect the thermal properties of biomass, such as the decomposition profile and rate. The aim of thermal analysis was to investigate the effect of pretreatment and digestion on pyrolysis characteristics so as to offer basic information for the utilization of pretreated and digested biomass for producing fuel gas. Thermal properties of various biomasses have been assessed by thermogravimetric (TG) analysis [17–19]. In a summary, to study the physicochemical changes of rice straw after lime pretreatment and microbiological modification, the raw material as well as the treated biomass were evaluated at their composition, crystallinity, functional groups and thermal properties using different tests like X-ray, FTIR, and TG.

2. Materials and methods

2.1. Leaching bed reactor (LBR)

The polymethyl methacrylate LBR was 590 mm high, and had an inner diameter of 140 mm and a working volume of 6.0 L. There existed three areas from top to bottom for LBR: a distribution section, a reaction section and a leaching liquor storage section. An electrically powered rotary distributor was placed at the top of the LBR in order to homogenously distribute the recycled leachate over the bed. A PMMA mesh with a pore size of 1.5 mm was placed at the bottom of the reaction section to prevent digested biomass dropping into the leachate. Leachate was collected at the liquor storing section of the reactor bottom and the volume of liquor storing section was 0.76 L with 50 mm height. A more detailed description of the LBR components is provided elsewhere [20]. The reactor temperature was set at 35 ± 1 °C for economical feasibility and controlled by circulating hot water through a water jacket.

2.2. Rice straw, anaerobic seed cultures, and sample preparation

The straw of hybrid Indica rice (Shanyou 4th) was harvested and collected from a farm in Feidong County, Anhui Province, China, in September 2009. Later on, the straw was chopped into 4–5 cm lengths with paper shears after air-drying, and then placed into a sealed bag and stored in the dark at ambient temperature for less than a month. The initial content of cellulose was 35.6%, hemicellulose 22.0% and lignin 5.7%, in addition the masses concentration of the main elements were carbon (C) 38.1%, hydrogen (H) 5.6%, nitrogen (N) 1.4%, and oxygen (O) 54.9%. The total solids (TS) content of rice straw was 92.6% and volatile solids (VS) content was 82.9% of the TS.

The anaerobic culture was obtained from previous digestion liquor [14]. The culture was filtered through a screen with a mesh size of 2-mm and then concentrated by settling before being used as the inoculum. The TS content of the inoculum was 8.5% and VS content was 56% of the TS.

Raw and treated rice samples were prepared according to the National Renewable Energy Laboratory standard procedure [21]. Raw rice straw was dried at 45 °C for 48 h and a low dry temperature was selected for reducing volatile matter loss, and cooled in a dessicator to room temperature, and then placed into a sealed bag and stored in the dark at ambient temperature until analysis. Pretreated or digested biomass was first washed clean with tap water, and then dried and stored for analysis in the same way as the raw straw. Finally, the rice straw was ground and passed through a 100-mesh screen to prepare the sample for elemental, X-ray, FTIR and thermal analyses.

2.3. Solid-state lime pretreatment

In this study, the pretreatment and dry digestion methods followed the operational methods [22]. Rice straw was subjected to a 5 day solid-state lime pretreatment before dry digestion. First, two portions (each 350 g) of air-dried rice straw were respectively placed into two plastic buckets, and then 17.7 g $Ca(OH)_2$, 350 mL distilled water and 175 mL seed culture were added into each bucket. The mixtures were uniformly mixed, and the buckets covered with plastic films, closed with plastic rings, and kept in the laboratory at the ambient temperature (20 ± 3 °C) for 5 days.

2.4. Dry anaerobic digestion

At the end of pretreatment, 525 mL seed culture, 175 mL distilled water, and 7.0 g NH_4HCO_3 were added into each bucket and thoroughly mixed. Then, the mixtures were subjected to 60 days of dry digestion at 35 ± 1 °C. The solid loading rate of LBR (58.8 g rice straw/L working volume) was chosen according to the results from a two-phase digestion of rice straw [2].

Two identical LBRs were used in this study. The changes in the physicochemical characteristics of rice straw were investigated in the first LBR (LBR1), whereas the characteristics of biogas production were explored in the second LBR (LBR2). To investigate the profile in physicochemical change during dry digestion, one portion of mixed straw was first