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Research Paper

Comparing the hydrolysis and biogas production performance of alkali and acid pretreatments of rice straw using two-stage anaerobic fermentation

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ARTICLE INFO

Article history:
Received 23 August 2014
Received in revised form
1 February 2015
Accepted 16 February 2015
Published online 4 March 2015

Keywords:
Rice straw
Pretreatment
Hydrolysate
Anaerobic fermentation
Two-stage

To enhance rice straw degradation and improve biogas production in a two-stage anaerobic system, rice straw was treated with either dilute alkali or acid. Firstly, the effects of NaOH or HCl concentration, temperature and time on glucose conversion, degradation of cellulose and hemi-cellulose were investigated. It was found that glucose conversion rate and the organic matter content were greater with alkali rather than acid pretreatment. Suitable conditions for hydrolysis using NaOH pretreatment were 2% (w/w), 60 h and 60 °C. With these conditions the glucose conversion rate was 55.5%. Secondly, the hydrolysate was used as substrate for batch anaerobic fermentation tests at different organic loadings. The maximum methane yield of hydrolysate from NaOH pretreatment was 193.2 ml g^{-1} [COD]. For the HCl pretreatment, the maximum methane production rate was 287.0 ml g^{-1} [COD] which was 43.89% higher than with NaOH. Although the NaOH solution was more efficient in improving rice straw hydrolysis, the hydrolysate from the HCl pretreatment had greater methane production at a similar organic loading.

1. Introduction

Research into renewable energy has received more attention in recent years to help solve energy supply and global warming problems (Kemppainen et al., 2012; Oleskowicz-Popiel et al., 2012; Talebnia, Karakashev, & Angelidaki, 2010). Biogas is one of the most popular forms of renewable energy able to be produced from organic wastes. To ensure adequate sources of feedstock for biogas production, lignocellulosic materials such as manure fibre and crop residues have widely been studied to enhance digestibility and improve the productivity of anaerobic digestion (AD) (Hendriks & Zeeman, 2009; Yu et al., 2014).

Rice straw is one of the most abundant, low-cost and renewable lignocellulosic materials in the world. The lignocellulose in rice straw contains about 32–47% cellulose, 19–27% hemicellulose and 5–24% lignin (Zhao et al., 2010). Cellulose is a crystalline material while hemicellulose is amorphous (Guerra-Rodríguez, Portilla-Rivera, Jarquín-

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http://dx.doi.org/10.1016/j.biosystemseng.2015.02.007

Enríquez, Ramírez, & Vázquez, 2012). Several researchers reported that crystalline structure of cellulose limits the utilisation of lignocellulose (Sun et al., 2007). Therefore, pretreatment of lignocellulose is an important step in breaking down the chemical structure of the straw and enhancing the conversion efficiency of cellulose and hemicellulose to increase sugars. Various pretreatment methods have been investigated, such as using ammonia, alkali, acid, and steam explosion (Bauer et al., 2014; McIntosh & Vancov, 2011; Nguyen et al., 2010; Satari Baboukani, Vossoughi, & Alemzadeh, 2012; Zhao, Wang, Zhu, Ragauskas, & Deng, 2008). The hydrolysate obtained following the pretreatment of lignocellulosic materials contains abundant reducing sugars. These reducing sugars are easily degraded and utilised in anaerobic fermentation.

Acid and alkali hydrolyses are commonly used in pretreatment methods that have been successfully used to treat lignocellulosic materials (Hendriks & Zeeman, 2009; Teramura et al., 2013). Acid pretreatment serves to break down the hemicellulose and make the cellulose more accessible. The xylose is mainly obtained when the hydrolysis of hemicellulose is performed under acid condition. The cellulose in pretreated solid residue can easily be utilised to produce ethanol. Also, many byproducts are generated, such as furfural, hydroxymethylfurfural (HMF) and acetic acid which have been reported as inhibitors for AD (Palmqvist & Hahn-Hägerdal, 2000). To avoid the formation of these inhibitors, moderate temperatures may be used in the acid hydrolysis. Compared with that of acid pretreatment, the reaction pathways of alkali pretreatments are more complex. The delignification reaction is very significant in alkaline hydrolysis, resulting in an increase of internal surface area, a decrease in the degree of polymerisation, a decrease in crystallinity, separation of structural linkages between lignin and carbohydrates, and disruption of the lignin structure (Sun & Cheng, 2002). This peeling reaction produces monomers of hemicellulose that are easily degraded into other inhibitors at high temperature. Sodium hydroxide, ammonia and lime pretreatments have received widespread attention due to their high efficiency. However, many studies treating straw at high temperatures and pressures has lead to inhibition and high energy consumption (McIntosh & Vancov, 2011; Satari Baboukani et al., 2012) moderate pretreatment temperatures still needs further research to improve the economics of alkali pretreatment (Auxenfans et al., 2012; Cabrera et al., 2014; Xu, Cheng, Sharma-Shivappa, & Burns, 2010). Furthermore, comparisons between pretreatments using alkaline and acid giving methane yields and lignocellulose degradation on methane yield and lignocellulose degradation are seldom reported (Zheng, Zhao, Xu, & Li, 2014). The effect of hydrolysate concentration on methane productivity in rice straw has also not been reported.

In this study, alkaline and acid concentration, moderate temperatures and retention time were considered in the pretreatment processes of wheat straw, and their effects on the lignocellulose removal and glucose yield were investigated. The methane productivity from hydrolysate obtained in alkaline pretreatment was compared with that of acid pretreatment. Moreover, the effect of hydrolysate concentration on methane productivity was also tested in batch fermentation experiments.

2. Materials and methods

2.1. Preparation of rice straw

Rice straw was collected from fields in a suburb of Wuhan, China. After collection, the straw was air dried, ground using a grinder and passed through a 2 mm aperture standard screen. The processed straw was then sealed in plastic bags and stored at room temperature for further use and analysis. The characteristics of the rice straw samples were shown in Table 1.

2.2. Alkali pretreatment

Alkali treatment was carried out using a single factor experiment to study the effects of NaOH concentration (0.5%, 1%, 2%, 3%, 4%, w/w), moderate temperatures (15 °C, 30 °C, 45 °C, 60 °C, 75 °C) and retention time (12 h, 24 h, 36 h, 48 h, 60 h) on the degradation of rice straw. While studying the effects of NaOH concentration and retention time, temperature was fixed at 45 °C. While studying the effects of temperature and retention time, NaOH concentration was fixed at 2%. The dry matter of 37.5 g was used in each batch, and fibre concentration was fixed at 7% based on dry matter content. Treated mixture solutions were filtered with filter paper, the contents watered using 1000 ml deionised water, and the wet solid residues prepared analysis of dry matter, fibre composition and structure. A small amount of filtrate was taken for the analysis of glucose and chemical oxygen demand (COD). The remaining filtrates were stored at 4 °C for further use. Each run was duplicated and the average data was reported.

2.3. Acid pretreatment

Similar with alkali treatment, single factor experiment design was used to study the effects of HCl concentration (0.5%, 1.0%, 1.5%, 2.0%, 2.5%, w/w), moderate temperatures (15 °C, 30 °C, 45 °C, 60 °C, 75 °C) and retention time (12 h, 24 h, 36 h, 48 h, 60 h) on the degradation of rice straw. While studying the effects of HCl concentration and retention time, temperature was fixed at 60 °C. While studying the effects of temperature and retention time, HCl concentration was fixed at 1%. The dry matter of 37.5 g was used in each batch, and fibre concentration was fixed at 7% dry matter. Treated mixture solutions were filtered with filter paper and the contents watered using

Table 1 – Characteristics of rice straw.

Parameter	Value
Total solids (TS, %)	93.41%
Volatile solids (VS, %)	88.54%
Neutral detergent fibre (NDF, %)	70.04%
Acid detergent fibre (ADF, %)	40.18%
Cellulose (%)	35.65%
Hemicellulose (%)	29.86%
Lignin (%)	3.88%