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Pretreatment of corn stover with diluted acetic acid for enhancement of acidogenic fermentation

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HIGHLIGHTS

- Diluted acetic acid pretreatment of corn stover was optimized by RSM.
- 2.712 g/L furfural cannot inhibit acidogenic fermentation.
- pH 5 can improve butyric acid fermentation and avoid propionic acid fermentation.

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ABSTRACT

A Box-Behnken design of response surface method was used to optimize acetic acid-catalyzed hydrothermal pretreatment of corn stover, in respect to acid concentration (0.05–0.25%), treatment time (5–15 min) and reaction temperature (180–210 °C). Acidogenic fermentations with different initial pH and hydrolyzates were also measured to evaluate the optimal pretreatment conditions for maximizing acid production. The results showed that pretreatment with 0.25% acetic acid at 191 °C for 7.74 min was found to be the most optimal condition for pretreatment of corn stover under which the production of acids can reach the highest level. Acidogenic fermentation with the hydrolyzate of pretreatment at the optimal condition at the initial pH = 5 was shown to be butyric acid type fermentation, producing 21.84 g acetic acid, 7.246 g propionic acid, 9.170 butyric acid and 1.035 g isovaleric acid from 100 g of corn stover in 900 g of water containing 2.25 g acetic acid.

1. Introduction

Agricultural residues are the most abundant renewable resources on the Earth. With the sharp increase of the world's demand for energy and traditional energy shortages, seeking sustainable renewable biomass energy has been the concern of researchers in the world. Conversion of crop residues into biogas through various technologies is one of the most effective and cheapest methods to reduce environmental pollution and develop new energy resources (Hsu et al., 2010; Lu et al., 2009; Wu et al., 2010). However, the main component of crop residues such as corn stover is lignocellulose, which is characterized by compact structure, chemical stability, and can hardly be degraded by most of the microorganisms under normal fermentation. Therefore, to achieve efficient use of crop residues, pretreatment is the key point.

The diluted acid is the most extensively studied and the most effective lignocellulose pretreatment catalyst (Qin et al., 2012; Zhang et al., 2011b). Inorganic acids such as sulfuric acid and nitric acid are extensively studied in diluted acid methods (Lu et al., 2009; Shen and Wyman, 2011; Zhang et al., 2011a). Although, inorganic acid pretreatment is very efficient, it is not suitable for methane production because methane production is inhibited due to the production of H_2S and N_2 from reducing sulphate and nitrate, respectively (Wang et al., 2012; Zhao et al., 2010). Additionally, the use of strong acid would cause serious environmental concerns. On the other hand, xylose or glucose produced in the pretreatment stage degrades with the inorganic acid-catalyzed at a high temperature, reducing the yields of sugar (Chen et al., 2009). In addition, inorganic acids have serious corrosive effect on the pretreatment equipment, thus increasing the cost of investment.

Diluted organic acid pretreatment has received less attention. However, Diluted organic acid pretreatment has some desirable characteristics compared with diluted inorganic acid, including effective hydrolysis, less degradation products and more oligomeric sugars (Kootstra et al., 2009a,b; Qin et al., 2012). Previous

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studies (Garrote et al., 2002; Jin et al., 2005; Xu et al., 2010) showed that acetic acid is generated from the splitting of thermally labile acetyl groups of hemicelluloses and the produced acetic acid can continue to catalyse the hydrolysis of lignocellulosic biomass, such as corn stover. Therefore, the amount of the pre-catalyst can be reduced. At the same time, acetic acid can be used as the substrate in the process of anaerobic fermentation. In this study, diluted acetic acid-catalyzed hydrothermal pretreatment was carried out to pretreat corn stover. A Box-Behnken Design of response surface method (RSM) was used to evaluate the effect of acetic acid concentration, treatment time and reaction temperature.

So far, relatively little is known about the effects of thermal acid pretreatments on the efficiency of anaerobic digestion, especially to the acid producing fermentation. Anaerobic acidogenic fermentation can be divided into three types: Propionic acid-type fermentation, Butyric acid-type fermentation and Ethanol-type fermentation depending on the end product composition of acidogenic fermentation, of which Butyric acid-type and Ethanol-type fermentation is proved to be favorable to the subsequent biogas production (Song et al., 2011; Wang et al., 2006). In this study, two types of hydrolyzates from pretreatments were fermented to produce volatile fatty acids (VFAs) and the acid production capacity of sugar and furfural in the hydrolyzate to the anaerobic fermentation was investigated.

2. Methods

2.1. Experimental design and set up

Design-Expert 7.0.1.0 software (Stat-Ease, Inc., MN, USA) was used for the experimental design, model fitting and statistical data analysis. In order to reduce the number of experiments needed, a Box-Behnken Design was applied. The conditions of experiments included acetic acid concentration (0.05–0.25%), treatment time (5–15 min) and reaction temperature (180–210 °C). Experimental data for each response factor were expressed in mathematical models. Table 1 shows ws the levels of variables chosen for the design.

2.2. Preparation and analysis of corn stover

Corn stovers were harvested at a local farm and leaves were discarded. Stovers were cut to 1–3 cm small pieces and dried at 60 °C in a fan-assisted oven, milled into fine particles and screened into fractions (10–20 mesh) in preparation for pretreatment. Chemical composition of corn stover was analyzed in triplicates using a two-step acid hydrolysis method proposed by the National Renewable Energies Laboratory in Colorado, USA (NREL, 2008). Monomeric sugars in liquor were determined by high performance liquid chromatography (HPLC, LabAlliance, USA) using a column (BioRad Aminex HPX-87H, 300 × 7.8 mm) at 65 °C and 5 mM H_2SO_4 as mobile phase at a flow rate of 0.6 mL/min. A refractive index detector was used for sugars and acetic acid analysis and a UV detector was used for furfural (Zhang et al., 2011b).

Table 1
Levels of variables chosen for the design.

Trial	Factors		
	Acetic acid concentration (%(w/w))	Treatment time (min)	Reaction temperature (°C)
1	0.05	10	180
2	0.15	15	180
3	0.15	5	180
4	0.25	10	180
c × 3[a]	0.15	10	195
5	0.05	15	195
6	0.05	5	195
7	0.25	15	195
8	0.25	5	195
9	0.05	10	210
10	0.25	10	210
11	0.15	15	210
12	0.15	5	210

[a] c × 3 Represents the central point of the experiments, and it was replicated three times.

2.3. Acetic acid-catalyzed hydrothermal pretreatment

Pretreatment was performed in a laboratory scale stainless steel cylindrical reactor with a total volume of 200 mL. A salt bath with a liquid mixture of $NaNO_2$ and KNO_3 in a proportion 1:1 was used to give the desired temperature, as described in previous investigation (Lu et al., 2009). Heating time from room temperature to 180 °C required about 17 min, while one more minute was required to heat the reactor to 195 °C or 210 °C. When the desired temperature inside the reactor was reached, the treatment time was started to be counted. After the target treatment time was reached, the reactor was taken out from the salt bath and sunk into a water bath to cool it down to 50 °C for about 4 min. The liquor/solid ratio was 9 g liquor/g solid corn stover in all experiments with a total weight of 80 g.

2.4. Anaerobic acidogenic fermentation

Pretreatment experimental conditions were optimized with Design-Expert 7.0.1.0 software. Corn stover was pretreated under optimized conditions. Two kinds of specific hydrolysates under optimized experimental conditions were selected for fermentation. The first kind of hydrolysate (hydrolysate A) is obtained when chemical oxygen demand (COD) and total sugar reached the maximum at the same time. The second (hydrolysate B) is obtained when COD and furfural reached the maximum at the same time. The two kinds of optimized pretreatment conditions were shown in Table 2. Standard methods (China EPA, 2002) were used to determine COD.

Biological acidification fermentation took place in six anaerobic flasks (numbered 1#–6#) and these six flasks were placed in water bath shaker at 37 ± 1 °C. The volume of each flask was 1000 mL and the working volume was 800 mL. Seeding sludge was from a local anaerobic fermentation tank utilizing food waste. When the acidification fermentation began ($t = 0$), sludge concentration in the flask was 4000 mg MLVSS/L and organic load was 1.0 g COD/g MLVSS (Lin and cheng, 2006; Lin et al., 2008). The mixed liquor volatile suspended solids (MLVSS) were those solids lost on ignition also according to the Standard Methods (China EPA, 2002), and it is an approximation of the amount of biomass present in the mixed liquor. Hydrolysate A was added into flasks 1# and 2# with pH = 7 and pH = 5 respectively. Hydrolysate B was added into flasks 3# and 4# with pH = 7 and pH = 5 respectively. Distilled water was added into flasks 5# and 6# with pH = 7 and PH = 5 respectively as blank test.

At the specified time 5 mL sample was used to measure pH with a digital pH-meter (pHS-3C, China). Volatile fatty acids (VFAs) were afterwards determined by high performance liquid chromatography (HPLC, LabAlliance, USA) with a refractive index detector by using a column (BioRad Aminex HPX-87H, 300 × 7.8 mm) at 65 °C and 5 mM H_2SO_4 as mobile phase at a flow rate of 0.6 mL/min. The retention times of VFAs including Acetic acid, propionic acid, butyric acid and isovaleric acid were 13.218 min, 15.474 min, 19.043 min and 21.966 min, respectively.