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Screw extrude steam explosion: A promising pretreatment of corn stover to enhance enzymatic hydrolysis

Jingwen Chen [a,b], Wengui Zhang [a,b], Hongman Zhang [c], Qiuxiang Zhang [d], He Huang [a,b,*]

[a] State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing 210009, China
[b] College of Life Science and Pharmaceutical Engineering, Nanjing University of Technology, Nanjing 210009, China
[c] Department of Applied Chemistry, College of Science, Nanjing University of Technology, Nanjing 210009, China
[d] Electrical and Mechanical Engineering College – Safety Engineering, Beijing University of Chemical Technology, Beijing 100029, China

HIGHLIGHTS

- Screw extruder and steam explosion are combined.
- Pins on the screw help to scratch material to get better effect upon explosion.
- The pins cut material to save an operating step.
- Effect of pretreatment is analyzed and compared with SE with a serial of methods.

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ABSTRACT

A screw extrude steam explosion (SESE) apparatus was designed and introduced to pretreat corn stover continuously for its following enzymatic hydrolysis. SESE parameters temperature (100, 120, 150 °C) and residence time (1, 2, 3 min) were investigated. The enzymatic hydrolysis of corn stover pretreated by SESE and steam explosion (SE) process was carried out and analyzed systematically. A serial of analysis methods were established, and the corn stover before/after the pretreatment were characterized by scanning electron microscope (SEM), X-ray Diffraction (XRD) and Thermal Gravity/Derivative Thermal Gravity Analysis (TG/DTG). After treated by SESE pretreatment at the optimum condition (150 °C, 2 min), the pretreated corn stover exhibited highest enzymatic hydrolysis yield (89%), and rare fermentation inhibitors formed. Characterization results indicated that the highest yield could be attributed to the effective removal of lignin/hemicellulose and destruction of cellulose structure by SESE pretreatment.

1. Introduction

Lignocellulosic ethanol, normally fermented from agriculture and forestry waste material, is one of the most promising alternative fuel because of the vast non-foodstuff source material adopted and low greenhouse gas emissions compared to fossil fuels (Farrell et al., 2006). Among all the lignocellulosic materials, corn stover is of particular interest, because it's bountiful reserved and cheapness. Corn stover used as raw material also meets the demand of problematic solid wastes disposal. However, the lignocellulosic matrix structure in corn stover forms nature recalcitrance to enzymatic hydrolysis. Therefore, to enhance the accessibility of the enzyme, pretreatment to stover is considered to be a necessary process to break the lignin seal and disrupt the crystalline structure of cellulose (Grous et al., 1986). The major processes of lignocellulosic ethanol production contain pretreatment, enzymatic hydrolysis, ethanol fermentation and product concentration (Wyman, 1999). An effective pretreatment is characterized by several criteria. Namely, it should preserve the pentose (hemicellulose) and hexose (cellulose) fractions, and limit formation of fermentation inhibitors, and minimize energy demands and cost (Nathan et al., 2005).

Pretreatments, such as dilute acid, lime, and ammonia treating process are potential cost-effective methods, but the adding of chemicals caused series of cost and environment problems (Weiss et al., 2010; Li et al., 2012). Meanwhile, steam explosion (SE) shows ability to induce auto hydrolysis and defiberation without adding chemicals (Martín-Sampedro et al., 2012). It has been applied commercially to hydrolyze hemicellulose for manufacture ethanol and

* Corresponding author at: College of Life Science and Pharmaceutical Engineering, Nanjing University of Technology, Nanjing 210009, China. Tel./fax: +86 25 83172094.
E-mail address: biotech@njut.edu.cn (H. Huang).

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other bio-products. In steam explosion, biomass is exposed to highly pressurized steam followed by rapid reduction in pressure. The treatment results in substantial destruction of the lignocellulose structure, hydrolysis of the hemicellulosic fraction, depolymerization of the lignin components and defibration of cellulose (Moniruzzaman, 1996). Therefore, the accessibility of the cellulose components to enzyme is greatly improved. Compared with other existing pretreatment methods, the advantages of steam explosion include a significantly lower environmental impact, lower capital investment and less hazardous process chemicals (Öhgren et al., 2007).

However, SE is considered as a high energy consuming batch process with high operating temperature (>200 °C) and high pressure (as listed in Table 1). After the SE pretreatment, high enzymatic hydrolysis yield is obtained (>88.6%), but various fermentation inhibitors also generate at a high temperature and pressure. The inhibitors are mainly composed of formic acid, acetic acid, furfural, 5-HMF et al., which exert obvious inhibitions to the following ethanol fermentation (Sun and Cheng, 2002). Therefore, many researchers aimed at the detoxification of the hydrolysate resulting from steam explosion (Zhang et al., 2012; Yu et al., 2011). There are also some researchers pointed out that the ability of SE pretreatment is only physical effect (Brownell et al., 1986; Biermann et al., 1984) instead of chemical alternations to the micro structure of the raw material. Furthermore, in SE process, the raw materials need to be cut up previously (Chang et al., 2012).

In this paper, screw extrude steam explosion (SESE) is designed and introduced to pretreat corn stover (see Electronic Annex Fig. 1). SESE pretreatment is an integration process where the screw extrusion is combined with steam explosion to feed and explode the corn stover continuously. Screw extrusion is widely used in food industry, ceramic fabrication and polymer tube production to twist and transport raw materials (Ribeiro et al., 2006; Chuang and Yeh, 2004). Recently, screw extrusion is applied to pretreat biomass in order to obtain the carbohydrates in the stalks or roots of plants (Chen et al., 2011). Screw extrusion process is optimized or combined with alkali or acid soaking process to get better pretreating effect (Chen et al., 2013; Liu et al., 2013a,b). In this paper, screw extrusion is integrated with steam explosion to pretreat corn stover at a lower temperature compared to the regular steam explosion process. The goal is to minimize the production of fermentation inhibitors while getting a reasonable enzymatic hydrolysis yield.

In screw extrusion, the shearing force and friction among corn stover, the screw and the inter walls of the apparatus provide extra heat to raw material. Therefore, it can reduce the operating temperature in SESE pretreatment compare to the temperature in SE process. Furthermore, the twisting and friction during screw extrusion make the stover soaked by water thoroughly, leading to a better effect upon explosion. Pins planted on the screw help to scratch corn stovers into small pieces. Thereby, during SESE pretreatment, there is no need to cut the raw materials before feeding into the apparatus, where saves certain step compared with traditional SE process.

In this work, corn stover was submitted to SESE at the temperature ranging from 100 °C to 150 °C, without previous cut up. A serial of analysis methods concerning scanning electron microscope (SEM); X-ray Diffraction (XRD); Thermal Gravity/Derivative Thermal Gravity Analysis (TG/DTG) and High-Performance Liquid Chromatography (HPLC) were established to reveal the effects of SESE treatment on corn stover systematically, trying to explain why SESE can achieve a reasonable pretreatment effect at a relatively lower operating temperature.

2. Methods

2.1. Material

Corn stover was gathered from Inner Mongolia, PR China. Raw material was air dried to 8% water content. Corn stover treated by steam explosion was kindly provided by Sinopec Group. Enzymatic hydrolysis was carried out using Glucan cellulase (Sigma–Aldrich Cat. No. C-2730) and β-glucosidase (Sigma–Aldrich Cat. No. G-0395). All standard chemicals, including xylose, glucose, cellobiose, galactose, mannose, arabinose, formic acid, acetic acid, furfural and HMF were purchased from Sigma Chemical Company (Shanghai, PR China).

2.2. SESE pretreatment

The basic structure of the main part of the SESE apparatus can be found in Electronic Annex Fig. 1. The apparatus is divided into three zones: feeding, compression and metering zone. There are several pins fixed around the inner wall, faced to the screw, to cut up and scratch the corn stover. There is a valve at the end of the screw help to hold a specific pressure. A common term used to measure the severity of the steam explosion pretreatment is the 'severity factor', which is determined by the treating temperature and residence time (Overend and Chornet, 1987). A probe stick was set in the entrance of the feed zone to heat and measure the temperature of material. The residence time is controlled through controlling the speed of the screw by a speed transforming gear. The opening of the adjusting device and the pin depth are 45 mm and 20 mm, respectively.

Corn stover was air dried at room temperature to equilibrium moisture content of 8.0% without chipping. Raw materials are heated to determined temperature by electricity in the feed zone and then, together with the hot steam, enter into the compression zone of SESE device, heated and compressed by the energy provided by the friction and compression among the screw, the inter wall of the device and the material. Right after the material is extruded out of the metering zone. Water steam penetrates into the wood fiber cell wall at high pressure, and then condenses into liquid water, wetting cell wall. When the valve at the end of the screw opens, the condensed water in the cell walls evaporates instantaneously due to the suddenly released pressure. And the expansion of the steam acts a shearing force onto the surrounding cell walls, resulting in the rupture of the material. 100 °C, 120 °C and 150 °C temperature and 1 min, 2 min and 3 min residence time were investigated. After the explosion, the material was recovered in a cyclone.

The solid was stored at 4 °C for subsequent characterization and enzymatic hydrolysis. Samples were named as (name of pretreatment)–(treating temperature)–(residence time)–s, where 's' stands

Table 1
Operating conditions of SE pretreatment and its effectiveness.

Additives	Temperature (°C)	Residence time (s)	Pressure (Mpa)	Enzymatic hydrolysis yield	Fermentation inhibitors	References
SO_2	200	600	Not mentioned	89%	Not mentioned	Öhgren et al. (2007)
/	<240	Few	+	Not mentioned	+	Hendriks and Zeeman (2009)
/	Not mentioned	200	2.5	Inhibit	Formic acid Acetic acid Furfural	Chang et al. (2012)
/	200	300	Not mentioned	94.6	Not mentioned	Liu et al. (2013a,b)
/	205	540	1.6	88.6	Not mentioned	Yang et al. (2010)