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Short Communication

Lower pressure heating steam is practical for the distributed dry dilute sulfuric acid pretreatment

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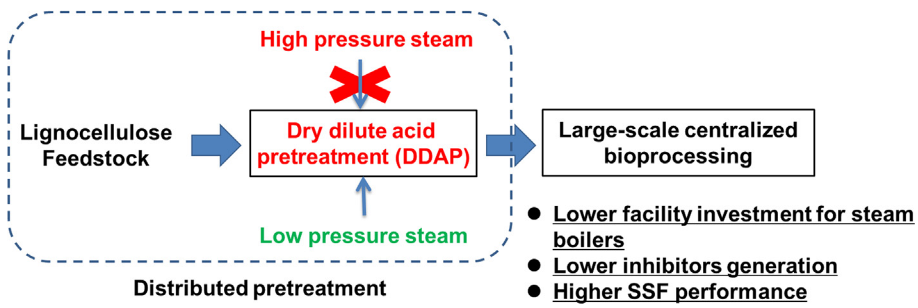
HIGHLIGHTS

- Lower pressure heating steam was practical for dry dilute acid pretreatment.
- Lower inhibitors generated in pretreatment using lower pressure heating steam.
- High SSF performance was obtained for corn stover pretreated by lower pressure steam.
- Lower pressure heating steam caused shorter mixing time during pretreatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Most studies paid more attention to the pretreatment temperature and the resulted pretreatment efficiency, while ignored the heating media and their scalability to an industry scale. This study aimed to use a relative low pressure heating steam easily provided by steam boiler to meet the requirement of distributed dry dilute acid pretreatment. The results showed that the physical properties of the pretreated corn stover were maintained stable using the steam pressure varying from 1.5, 1.7, 1.9 to 2.1 MPa. Enzymatic hydrolysis and high solids loading simultaneous saccharification and fermentation (SSF) results were also satisfying. CFD simulation indicated that the high injection velocity of the low pressure steam resulted in a high steam holdup and made the mixing time of steam and solid corn stover during pretreatment much shorter in comparison with the higher pressure steam. This study provides a design basis for the boiler requirement in distributed pretreatment concept.

1. Introduction

Pretreatment is a prerequisite step to destroy the lignocellulose structures and enhance cellulose hydrolysis efficiency for ensuring extensive lignocellulose biorefining for biofuels and biochemicals production (Yang and Wyman, 2008). A number of pretreatment methods including dilute acid, steam explosion, ammonia fiber expansion, alkaline treatment, and ionic liquid have been developed (Tucker et al., 2003; Brownell et al., 1986; Teymouri et al., 2005; Chang et al., 1998; Lee et al., 2009), and almost all of these pretreatments have a temperature effect, namely the relatively higher temperature used, the more effective pretreatment performance obtained (Mosier et al., 2005).

Most studies only paid their attentions to the pretreatment temperature and the resulted pretreatment efficiency, while ignored the heating media and their scalability to an industry scale. The oil or sand bath or the electrical heating coils are widely used to heat the pretreatment reaction in bench-scale experiments (Wyman et al., 2009), but hot steam is the preferred option in

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industry. In a bench-scale process development unit for ethanol production from lignocellulose proposed by Palmqvist et al., the saturated steam with high pressure of 3.0 MPa and 235 °C was used for heating the pretreatment (Palmqvist et al., 1996). In National Renewable Energy Laboratory (NREL)'s design report, the superheated steam with 1.3 MPa and 268 °C for heating the pretreatment reaction was supplied by the unit "combustor, boiler, and turbogenerator" (Humbird et al., 2011). As for the newly proposed distributed pretreatment concept, which can ensure a secure and reliable feedstock supply, to build a steam boiler with 3.0 MPa pressure is a great challenge for both manufacturing and its made material (Eranki et al., 2011; Zhang et al., 2016). The thermal plant could supply superheated steam to meet the requirement in pretreatment unit, but it is more practical for the centralized bioprocessing plant with respect to the high investment, other than the small decentralized pretreatment centers. Therefore, it is better to employ a low pressure heating steam or look for a suitable and easy-scalable heating method for pretreatment.

The main objective of this study was to explore the effect of different heating steam pressure supplied by boilers on dilute sulfuric acid pretreatment and the following bioprocessing steps. The changes of physical properties, compositions, enzymatic hydrolysis and ethanol fermentability of the corn stover pretreated using the heating steam pressure varying from 1.5, 1.7, 1.9 to 2.1 MPa were tested. Then a simplified CFD model was established to simulate the steam holdup during dry dilute acid pretreatment in the helical ribbon pretreatment reactor to explain the heating steam pressure effect. This study provided a design basis for the boiler requirement in the distributed bioprocessing concept.

2. Materials and methods

2.1. Raw materials

Corn stover was obtained from Dancheng County, Henan Province, China, in fall 2013. Corn stover was water-washed to remove the field dirts, air-dried, and milled using a beater pulverizer to pass through the 10-mm diameter apertures. The milled corn stover was sealed in plastic bags and stored at room temperature until used.

2.2. Strains and enzymes

Saccharomyces cerevisiae DQ1 (CGMCC 2528, China General Microbial Collection Center, Beijing, China) was used for ethanol fermentation. *Amorphotheca resinae* ZN1 (CGMCC 7452, China General Microbial Collection Center, Beijing, China) was used for biodetoxification of dry dilute sulfuric acid pretreated corn stover (He et al., 2016).

The cellulase enzyme Youtell #6 was purchased from Hunan Youtell Biochemical Co., Yueyang, Hunan, China. The filter paper activity of Youtell #6 was 135 FPU/g determined using the NREL protocol LAP-006 (Adney and Baker, 1996), the cellobiase activity was 344 CBU/g, and the protein content was 90 mg per gram of cellulase reagent determined by Bradford method.

2.3. Dry dilute sulfuric acid pretreatment and biodetoxification operations

The pretreatment unit consists of a 20 L pretreatment reactor and a 36 kW electric steam generator. A single helical ribbon stirrer was driven by a motor mounted on top of the reactor through an electromagnetic convertor. Four symmetrical distributed nozzles were designed on the distributor to disperse the steam jetted into the reactor (He et al., 2014). The steam generator was manufactured by Shanghai Huazheng Boiler Manufacture Co, Shanghai, China. It was heated by electricity and generated the saturated steam vapor up to 2.5 MPa and 225 °C. Corn stover was pretreated using dry dilute sulfuric acid pretreatment (DDAP) according to He et al. (2014). Briefly, corn stover and dilute sulfuric acid solution were co-currently fed into the 20 L pretreatment reactor at a solid/liquid ratio of 2:1 (w/w) with sulfuric acid of 2.5 g per 100 g solid lignocellulose and helically stirred at 50 rpm. The saturated heating steam was adjusted to 1.5 MPa (198 °C), 1.7 MPa (204 °C), 1.9 MPa (210 °C) and 2.1 MPa (215 °C), respectively, to heat the mixed corn stover and dilute sulfuric acid to 175 °C for 5 min. The ramping time of the pretreatment using different pressure steam was nearly the same due to the marginal difference in the steam temperature (shown in Table 1). The solids content of the pretreated material was about 50% (w/w) with pH 2.0 and no wastewater was generated.

The pretreated corn stover was detoxified via solid state biodetoxification according to He et al. (2016) before it was hydrolyzed and fermented to ethanol. Briefly, the pretreated corn stover was neutralized with the suspended slurry of 20% (w/w) $Ca(OH)_2$ to pH of 5–6, and then inoculated with *A. resinae* ZN1 spores to start the biodetoxification and lasted for 48 h at 28 °C with sterilized aeration at 1.0 vvm. The solids content of biodetoxified corn stover was still around 50% (w/w). Corn stover composition after biodetoxification showed no obvious change compared with the freshly pretreated corn stover.

2.4. Enzymatic hydrolysis and simultaneous saccharification and fermentation tests

Enzymatic hydrolysis assay of the pretreated corn stover feedstock was carried out according to the protocol of NREL LAP-009 (Brown and Torget, 1996). 0.5 g of the pretreated corn stover (dry base) and 10 mL of deionized water were loaded into a 100 mL flask to prepare the slurry in 0.1 M citrate buffer containing 2.5% (w/w) solids and pH was finely adjusted to 4.8 by adding 5 M NaOH solution. 0.08 mL of cycloheximide (10 mg/mL in deionized water) was added to avoid the microbial contamination. 20 FPU/g DM (dry pretreated corn stover matter) of cellulase was added and the hydrolysis lasted for 72 h at 50 °C and 150 rpm in a water-bath shaking incubator.

SSF was carried out in a 5 L helical ribbon stirrer agitated bioreactor as described in Zhang et al. (2010). Briefly, the pretreated and biodetoxified corn stover was loaded into the bioreactor to reach 25% (w/w) solids content. 15 FPU/g DM of cellulase enzyme was added and the prehydrolysis was carried out for 12 h at 50 °C, then the temperature was reduced to 37 °C and seed cultures of *S. cerevisiae* DQ1 were inoculated into the bioreactor at a 10% ratio (v/v) to start the simultaneous saccharification and fermentation step (SSF). Samples were taken periodically for analysis of ethanol and glucose.

2.5. CFD modeling of pretreatment reactor

A commercial grid-generation tool, ICEM CFD 14.0 (Ansys Inc., Canonsburg, PA, USA) was used to generate the 3D grids of the reactor model for running Fluent 14.0 (Ansys Inc.). The Eulerian-Eulerian two-fluid model was used for the two-phase flow calculations (Xiong et al., 2013, 2015; Aramideh et al., 2015). The corn stover was set as continuous phase and water vapor was set as dispersed phase. The drag force and heat transfer between the phases was simulated by the Schiller-Naumann's model and Ranz-Marshall's model, respectively. The sliding mesh method was used to characterize the impeller rotation. In the simulation, corn stover was considered as incompressible and non-Newtonian fluid and