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Short Communication

A two-stage pretreatment process using dilute hydrochloric acid followed by Fenton oxidation to improve sugar recovery from corn stover

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HIGHLIGHTS

- Dilute hydrochloric acid followed by Fenton oxidation is an effective pretreatment process.
- Fenton oxidation pretreatment has significant effect on lignin removal under mild conditions.
- Fenton oxidation pretreatment can decrease enzyme dosage with high sugar recovery.

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ABSTRACT

A two-stage pretreatment process is proposed in this research in order to improve sugar recovery from corn stover. In the proposed process, corn stover is hydrolyzed by dilute hydrochloric acid to recover xylose, which is followed by a Fenton reagent oxidation to remove lignin. 0.7 wt% dilute hydrochloric acid is applied in the first stage pretreatment at 120 °C for 40 min, resulting in 81.0% xylose removal. Fenton reagent oxidation (1 g/L $FeSO_4·7H_2O$ and 30 g/L H_2O_2) is performed at room temperature (about 20 °C) for 12 has a second stage which resulted in 32.9% lignin removal. The glucose yield in the subsequent enzymatic hydrolysis was 71.3% with a very low cellulase dosage (3 FPU/g). This two-stage pretreatment is effective due to the hydrolysis of hemicelluloses in the first stage and the removal of lignin in the second stage, resulting in a very high sugar recovery with a low enzyme loading.

1. Introduction

Faced with the adverse environmental impacts such as CO_2 emission and acid rain caused by the combustion of fossil resources, there is more focus on the development of alternative resources (Kuang et al., 2016). Lignocellulosic biomasses have enormous potential to replace a portion of fossil fuels, due to its abundance, low cost, and not being in competition with food. (Alonso et al., 2013).

Lignocelluloses consist of three main polymeric components, namely, cellulose, hemicelluloses and lignin (Ravindran and Jaiswal, 2016). Cellulose and hemicelluloses can be hydrolyzed into monomer sugars (Shen et al., 2016). However, cellulose, hemicelluloses and lignin form a complex cross-linked structure. The recalcitrant structure of lignocelluloses protects the carbohydrates from degradation by enzymes (Sanderson, 2011). Thus, pretreatment methods are used in lignocelluloses hydrolysis in an attempt to break the complex structure (Wi et al., 2015). A multitude of pretreatment methods have been investigated in the past (Ravindran and Jaiswal, 2016; Shirkavand et al., 2016): methods such as physical procedures (milling (Schneider et al., 2016), ultrasonic (Liyakathali et al., 2016)), chemical processes (acid (Zhang et al., 2016), alkaline, ionic liquid (Sathitsuksanoh et al., 2013)) and physico-chemical means (steam explosion (Huang et al., 2015), wet oxidation) have shown good results.

Although the pretreatment methods mentioned above are shown to be effective on lignocellulosic biomass degradation, it still has been difficult to maximize the utilization of materials through one-stage pretreatment on account of different structural features between cellulose, hemicelluloses and lignin (Ravindran and Jaiswal, 2016). Consequently, a two-stage pretreatment method have been suggested so as to maximize sugar recovery from hydrolysis (Jeong and Lee, 2016; Liu et al., 2016; Zu et al.,

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2014). During the process, hemicelluloses and cellulose were hydrolyzed in different stages, resulting in a higher sugar recovery with a decrease of the enzyme dosage.

During two-stage pretreatment, dilute acid is frequently applied in the first stage to hydrolyze hemicelluloses from lignocellulosic materials. (Liu et al., 2016; Zu et al., 2014). After pretreatment, hemicelluloses are hydrolyzed, and accessibility of enzymes to cellulose was improved. However, the dilute acid pretreatment is not conducive to the removal of lignin (Sun et al., 2016), affecting enzymatic hydrolysis negatively (Ravindran and Jaiswal, 2016). Thus, a subsequent delignification process is desired to further destroy the lignocellulosic structure.

Oxidation pretreatments are used because of their specific effect on lignin removal. Among the oxidizing agents, hydrogen peroxide has been used frequently. Although hydrogen peroxide is an excellent oxidant, its reaction kinetics are slow at low concentrations. However, the addition of Fe^{2+} ions increases the oxidative strength of the peroxide: the Fe^{2+} ions act as a catalyst to decompose hydrogen peroxide into two different kinds of oxygen radicals (HO**.** and HOO**.**).

The hydroxyl radicals generated from the Fenton reagent plays an effective role in lignin degradation. Thus, Fenton reagent has been used to deal with wastewater for many years. In the recent years, Fenton oxidation was applied to pretreatment of lignocelluloses to improve enzymatic hydrolysis (He et al., 2015; Jeong and Lee, 2016). This pretreatment method showed positive results; however, there are still some shortcomings of this approach such as the consumption of large amounts of cellulase (30 FPU/g by He et al. (2015)) or reagents input (0.95 g/L of $FeSO_4$ and 29.8 g/L of H_2O_2 by Jeong and Lee (2016)) which had detrimental effects on industrial applications.

In order to acquire a high recovery of monosaccharides with a small dosage of Fenton reagents and cellulase, the novel two-stage pretreatment using dilute acid followed by Fenton oxidation pretreatment was investigated. During the first stage, dilute acid is used to hydrolyze hemicelluloses and the amorphous cellulose. After the first-stage pretreatment, the compact structure is broken and a large amount of lignin is exposed. Therefore, a lower amount of Fenton reagent is necessary in the second stage to significantly depolymerize the lignin. Both hemicelluloses and lignin removal during pretreatment will facilitate cellulose hydrolysis with a small dosage of enzymes, producing a high glucose yield. The structural changes before and after pretreatment are characterized by scanning through electron microscopy (SEM), Brunauer-Emmett-Teller (BET) and X-ray diffraction (XRD) in order to evaluate the impacts of this pretreatment on corn stover (CS).

2. Materials and methods

2.1. Materials

Corn stover was collected from the northern part of the Anhui province in China. The composition of the oven-dried biomass was determined in our previous work (Liu et al., 2016). Ferrous sulfate ($FeSO_4{\cdot}7H_2O$) and hydrogen peroxide (H_2O_2) were purchased from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China). Enzymes were donated by Novozymes (China) Investment Co., Ltd. All chemical reagents were used directly without further purification.

2.2. Pretreatment by dilute acid

In a previous study, the optimal reaction condition during dilute acid pretreatment was investigated (Liu et al., 2016). After dilute acid pretreatment, solid residue is oven-dried at 60 °C until constant weight for the second stage of employment.

2.3. Pretreatment by Fenton oxidation

A certain amount of $FeSO_4{\cdot}7H_2O$ and H_2O_2 is mixed with deionized water in a 50 ml volumetric flack with solid residue from the first stage pretreatment. Different compositions of Fenton reagent, liquid-solid ratios, temperature and reaction times have been studied. After pretreatment, the mixture is filtered and the residue taken out and oven-dried to measure moisture content.

2.4. Enzymatic hydrolysis

The wet pretreated sample (0.2 g dry substrate) is put into the sodium acetate buffer at 0.05 M (PH 4.8) in a centrifuge tube and 0.03 g/ml sodium azide is added into the tube so as to inhibit microbial activities. The solid concentration is set at 5%. Enzymes are added into the tube as well. The enzymatic hydrolysis is carried out in a shaking incubator at 50 °C and 120 rpm for 72 h. After enzymatic hydrolysis, the reactant is centrifuged at 8000 r/min for 1 min. Then the hydrolysate is collected to measure the sugar concentration. Each reaction is carried out in duplicate.

2.5. Analysis methods

2.5.1. Sugar determination

The monosaccharides obtained from hydrolysis are determined by high performance liquid chromatography (HPLC). The system is equipped with a HPX-87H column (Bio-Rad, USA) and differential refractive index detector (Waters 2414, USA).

2.5.2. Cellulose, hemicelluloses and lignin determination

Cellulose, hemicelluloses and lignin in the solid residue are analyzed according to the National Renewable Energy Laboratory (NREL) (Sluiter, 2008; Sluiter et al., 2008, 2005; Templeton and Ehrman, 1995).

3. Results and discussion

3.1. Effect of pretreatment methods on sugars recovery

In this study, different combinations of Fenton oxidation and dilute acid pretreatment are used. These combinations for the pretreatment of corn stover include: Fenton oxidation pretreatment (FT), dilute hydrochloric acid pretreatment (DA), Fenton oxidation followed by dilute hydrochloric acid pretreatment (FT-DA) and dilute hydrochloric acid followed by Fenton oxidation pretreatment (DA-FT). The results of the composition of solid residues after pretreatment are shown in Table 1. The glucose yield of raw corn stover after enzymatic hydrolysis was very low (about 21.5%),

Table 1
The composition of solid residue after the different pretreatment processes.[a]

Materials	Solid residue (%)	Glucan (%)	Xylan (%)	Lignin (%)	Others (%)
CS	100	31.6	20.5	22.8	25.1
FT	90.4	30.9	16.6	18.7	24.2
DA	62.5	29.6	3.4	19.2	10.3
FT-DA	60.2	28.2	2.4	17.9	11.7
DA-FT	58.0	25.8	2.0	11.7	18.5

[a] Fenton reagent (1 g/L $FeSO_4{\cdot}7H_2O$ and 30 g/L H_2O_2) pretreatment was carried out at room temperature (about 20 °C) for 12 h. Liquid-solid ratio was 10:1 both in dilute acid pretreatment and Fenton oxidation pretreatment. 3 FPU/g enzyme was adopted during enzymatic hydrolysis.