



Mild alkaline presoaking and organosolv pretreatment of corn stover and their impacts on corn stover composition, structure, and digestibility



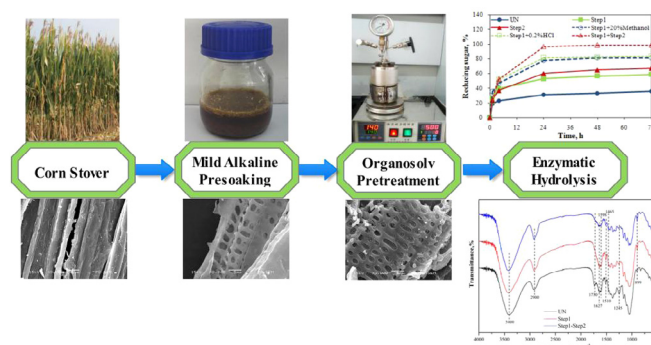
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HIGHLIGHTS

- Mild alkaline presoaking and organosolv pretreatment of CS were evaluated.
- The maximum total sugar yield achieved was 98.6% with a moderate enzyme loading.
- Large amounts of lignin and hemicelluloses were removed after pretreatment.
- The SSA and PV significantly enlarged after pretreatment.
- The CrI of the pretreated residue increased but the cellulose was highly digestible.

GRAPHICAL ABSTRACT



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ABSTRACT

An efficient strategy was developed in current work for biochemical conversion of carbohydrates of corn stover into monosaccharides. Corn stover was first presoaked in mild alkaline solution (1% Na₂S) under 40 °C for 4 h, after which about 35.3% of the lignin was successfully removed while the specific surface area was notably enlarged. Then the presoaked solids were subjected to organosolv pretreatment that employed 20% methanol with an addition of 0.2% HCl as catalyst at 160 °C for 20 min, and the maximum total sugar yield of the pretreated corn stover achieved was 98.6%. The intact structure of corn stover was disrupted by this two-step process, which resulted in a porous but crystalline structure of the regenerated solids that were mainly composed of cellulose. The enlarged specific surface area and increased accessibility made the regenerated solids highly digestible by a moderate enzyme loading.

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1. Introduction

Production of biofuels and value-added bio-based chemicals from lignocellulosic biomass has become a substitute in pursuit of renewable surrogate to fossil sources. Lignocellulosic biomass is an abundant, low-cost, and promising source that could be converted to fermentable sugars through biochemical or thermochemical process (Kim et al., 2015). However, the challenge associated

with this process is significantly greater than the first generation biofuels due to the complex association of cellulose-lignin-hemicelluloses in native lignocellulosic biomass, making it difficult to break down and offering limited accessibility to enzymes and microorganisms (Auxenfans et al., 2014; Perez-Pimienta et al., 2013). In this context, an adequate pretreatment step is essential to mitigate the complexity of biomass structure and to facilitate the accessibility of enzymes to cellulose surface (Kumar and Wyman, 2009; Toquero and Bolado, 2014). Existing efforts are devoted to development of a technically and economically feasible pretreatment method that fulfill this objective, and a variety of

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chemical, physical, physicochemical, and biological pretreatment methods were therefore established and intensively studied. Each method has different impacts on the composition and structure characteristics of the lignocellulosic material, and possesses pervasive impacts on all the other steps of the biomass conversion process, in terms of enzymatic hydrolysis, fermentation, product separation, and waste water treatment (Yang and Wyman, 2008).

Among existing pretreatment techniques, alkaline pretreatments under high severity conditions are more effective for lignin and hemicelluloses removal, while minor cellulose solubilization occurs concomitantly. In comparison, alkaline presoaking processes, such as aqueous ammonia or dilute NaOH presoaking, are usually applied under milder pretreatment conditions, thus preserve larger portion of carbohydrate, especially hemicelluloses (Gupta and Lee, 2010). However, these alkaline presoaking pretreatments have been proven to be only effective in treatment of low lignin content feedstock and require high recovery cost. Recently, alkalic salts has been employed to increase the efficiency of alkaline pretreatments (Kim et al., 2014), with the advantages of less corrosion and recyclable. Compared to other pretreatment methods, alkali salt pretreatment shows obvious saponification of uronic bonds which link lignin to hemicelluloses (Reilly et al., 2015), partial removal of hemicelluloses (including acetyl groups and uronic acids), and swelling of cellulose structure, resulting in a substantial increase of the fiber surface area (Asgher et al., 2013; Carvalho et al., 2016; Mendes et al., 2015). However, an effective alkalic salt pretreatment usually requires a pretreatment temperature higher than 100 °C, besides a high alkali concentration ($\geq 4\%$) and a corrosion-resistant reactor (Geng et al., 2014; Gu et al., 2012; Kim et al., 2014). Apply of alkali salts in presoaking process under mild conditions has yet been reported.

Organosolv pretreatment is another promising technology that has attracted considerable attention in past decades (Obama et al., 2012; Zhang et al., 2016a,b). Compared with other pretreatments, organosolv pretreatment has some particular advantages: (1) the high-quality lignin isolated from organosolv pretreatment can be used for the synthesis of several co-products (Hage et al., 2011; Pan et al., 2006) and (2) the organic solvents are easy to recover by distillation and can be recycled (Zhang et al., 2016a). Most of the organic solvents reported are bulk commodity chemicals, such as ethanol, methanol, acetone, glycerol, or solvents that used for biphasic fraction systems, such as methyl isobutyl ketone (MIBK) and tetrahydrofuran (THF). These solvents are cost effective compared to other cellulose dissolving solvents, such as ionic liquids. However, the non-catalyst organosolv pretreatment process usually requires high reaction temperature (160–220 °C) and high organic solvent concentration ($\geq 60\%$) (Chen et al., 2015; Novo et al., 2011) in order to achieve self-acidification by the cleavage of α -aryl ether and arylglycerol- β -aryl ether bonds (Zhang et al., 2016a). Using of dilute acid as catalyst can reduce the high reaction temperature which was considered as a necessity for the organosolv pretreatment, and facilitates the decomposition of hemicellulose that leads to efficient enzymatic hydrolysis (Sookyeong et al., 2016).

In order to achieve a high sugar recovery from lignocelluloses and reduce the formation of inhibitory compounds, lots of pretreatment methods that combine two-stage pretreatment have been explored (Liu et al., 2016; Min et al., 2015). In present work, dilute alkali salt solution was chose to presoak the lignocellulosic biomass before organosolv pretreatment to disrupt the cross-linked bonds between lignin and carbohydrates, partially remove lignin, and to make cellulose swollen. Afterwards, methanol pretreatment with the addition of very dilute hydrochloride acid was applied to the presoaked solid residue to dissolve lignin, hydrolyze hemicelluloses, and make the cellulose residue highly digestible. The pretreated solid residues were characterized by Bru-

nauer–Emmett–Teller method (BET), Scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) in order to elucidate the impacts of different pretreatment processes on composition, structure, and surface characteristics of corn stover.

2. Materials and methods

2.1. Materials

Corn stover (CS) was obtained from nearby farm in the city of Changzhou, Jiangsu, China. After CS was milled to a size smaller than 3 mm, it was washed with deionized water and dried at 85 °C until constant weight. The dry CS was stored in sealed plastic sample bags at -20 °C for future use. Accellerase 1500 (96 FPU/mL) was generously provided by Genencor (Wuxi, Jiangsu Province, China), while Novozyme 188 (066K0676603 \pm 5 CBU/mL, 68 \pm 5 mg protein/mL) was purchased from Sigma (St. Louis, MO, USA) for β -glucosidase supplementation. Sodium sulfide (Na_2S) (purity $\geq 98.0\%$) and methanol (purity $\geq 99.5\%$) were purchased from Changzhou Runyou Commercial and Trading Co. Ltd. (Changzhou, China). All other chemicals used were from commercial source and of reagent grade.

2.2. Pretreatment

2.2.1. Presoaking of CS by Na_2S solution

The CS was presoaked in Na_2S solution under different conditions that optimized by orthogonal experimental design. The impacts of crucial variables including Na_2S concentration of 0.5–1% (w/w), reaction temperature of 30–50 °C, presoaking residence time of 3–5 h, and solid-to-liquid ratio of 1:10 to 1:20 (g:L) were investigated. After presoaking, the CS solid was filtrated and washed several times by distilled water until neutral. The collected solids were used for organosolv pretreatment in the second step or subjected to enzymatic hydrolysis and other analyses.

2.2.2. Organosolv pretreatment of CS

The presoaked solid residue from the first step was then pretreated by organic solvent with addition of extremely dilute acid. The impacts of different types of organic solvent, such as methanol, ethanol, ethylene glycol, glycerol, acetone, and toluene were evaluated in this study. Dilute acid, including hydrochloric acid, sulfuric acid, phosphoric acid, acetic acid, oxalic acid, maleic acid, citric acid, and formic acid were also screened. The organosolv pretreatment was conducted in a high-temperature and high-pressure stainless steel reactor with a total volume of 100 mL (Zhenjiang Dantu Universal Electrical Equipment, China). The influences of operating parameters, such as organic solvent concentration (0–50 w/v%), acid concentration (0–0.25 w/v%), pretreatment temperature (120–170 °C), and residence time (10–60 min) were evaluated. After pretreatment, the reactor was quenched in an iced water bath and then the solid residue was separated and washed until neutral.

2.3. Compositional analysis

The chemical compositions of CS were determined using a two-step acid hydrolysis of standard protocol by National Renewable Energy Laboratory (Sluiter et al., 2011). Monomer sugars were quantified by HPLC (high performance liquid chromatography) method as described below. The carbohydrates and lignin contents in raw corn stover determined were 37.1% of cellulose, 20.9% of hemicellulose, 13.5% of lignin, and 1.3% of ash.

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