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Combined dilute hydrochloric acid and alkaline wet oxidation pretreatment to improve sugar recovery of corn stover

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ABSTRACT

Two-stage dilute hydrochloric acid (DA)/aqueous ammonia wet oxidation (AWO) pretreatment was used to recover the sugars of corn stover. The morphology characterizations of samples were detected by SEM, BET and SXT. The results showed that DA-AWO process demonstrated a positive effect on sugar recovery compared to AWO-DA. 82.8% of xylan was recovered in the first stage of DA-AWO process at 120 °C for 40 min with 1 wt% HCl. The second stage was performed under relative mild reaction conditions (130 °C, 12.6 wt% ammonium hydroxide, 3.0 MPa O_2, 40 min), and 86.1% lignin could be removed. 71.5% of glucan was achieved with a low enzyme dosage (3 FPU·g^{-1}) in the following enzymatic hydrolysis. DA-AWO pretreatment was effective due to its sufficient hydrolysis of hemicellulose in the first stage and remarkably removal of the lignin in the second stage, resulting in high sugar recovery with a low enzyme dosage.

1. Introduction

Lignocellulose, consisting of cellulose, hemicellulose and lignin, has gained considerable interests of scientists due to its renewable, being friendly to environment, low cost and availability (Corma et al., 2007; Nigam and Singh, 2011; Savaliya et al., 2018). Conversion of polysaccharides in lignocellulosic biomass into high-value products is deemed as a potential alternative way to produce them by fossil-based materials (Shi et al., 2013; Lin et al., 2017). To achieve this goal, it is necessary to fractionate out cellulose and hemicellulose from lignocellulosic feedstocks. However, the natural recalcitrance of biomass protects it from the biological or non-biological destruction (Rabemanolontsoa and Saka, 2016; Shirkavand et al., 2016). Therefore, a pretreatment step is necessary. Various pretreatment methods have been developed during the last decades. These methods include (i) physical means, i.e., milling and extrusion; (ii) chemical procedures i.e., alkaline, acid and ionic liquids; (iii) biological pretreatments using microorganisms; (iv) physical-chemical means i.e., steam explosion, wet oxidation (Alvira et al., 2010; Kim et al., 2016b; Rabemanolontsoa and Saka, 2016; Sun et al., 2016).

Due to the different composition and hydrolysis conditions for polysaccharides and lignin, it is hard to largely remove lignin without the risk of polysaccharides loss or low enzymatic hydrolysis efficiency only using single pretreatment method (Jonsson and Martin, 2016; Kim, 2018). Thus, a two-stage pretreatment has been investigated in order to maximize sugar recovery (Cayetano and Kim, 2018; Li et al., 2016b; Rigual et al., 2018). Dilute hydrochloric acid followed by lime (Zu et al., 2014), Dilute hydrochloric acid followed by wet milling (Liu et al., 2016) were used to pretreat corn stover, which could increase sugar recovery with a relative high enzyme input. During the two-stage pretreatment, dilute acids such as hydrochloric acid, sulfuric acid are frequently used to fractionate hemicellulose (Qin et al., 2012). The hemicelluloses can be easily and nearly acid-hydrolyzed into monosaccharides, which improves porosity of biomass and increases the accessibility of cellulases to celluloses (Weiss et al., 2010; Zhai et al., 2018; Zu et al., 2014). In addition, when dilute hydrochloric acid as opposed to dilute sulfuric acid was used for hydrolysis, pretreatment temperature was relatively low, thus less byproducts were generated and more sugars could be recovered. (Liu et al., 2016).

The removal of lignin is the other important stage during the two-stage pretreatment process since it plays a central role to improve the hydrolysis efficiency of cellulases. Wet oxidation (air, oxygen or

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peroxide) is an available thermal oxidation method for removing lignin from lignocellulosic materials (Arvaniti et al., 2012; Srinivas et al., 2016; Kolaczkowski et al., 1999). It has been reported that the combination of bases with WO (alkaline wet oxidation) could readily enhance the delignification of biomass, thus facilitating enzymatic hydrolysis of cellulose. Chang et al (2001) used $Ca(OH)_2$ to treat poplar wood at 150 °C, 1.4 MPa O_2 for 6 h, resulting in 78% lignin removal. Klinke et al (2002) used Na_2CO_3 to treat wheat straw at 195 °C, 1.2 MPa O_2 for 10 min, and 62% lignin was removed. It also has been proved that alkaline wet oxidation can reduce the formation of inhibitor (Martín et al., 2008). However, the alkalis such as Na_2CO_3, $Ca(OH)_2$ are hard to be recovered. Its rigorous reaction conditions (especially high temperature) may render a series of issues including unfavorable sugars loss, high energy consumption and safety problems (Arvaniti et al., 2012; Baroutian et al., 2013; Martin et al., 2007), and thus lead to detrimental effects on its industrial application.

A two-step pretreatment combining dilute hydrochloric acid (DA) with alkaline wet oxidation was developed in this research. In alkaline wet oxidation stage, the combination of aqueous ammonia and wet oxidation (AWO) was adopted. The reason for choice of aqueous ammonia is that it can depolymerize lignin, selectively break lignin-hemicellulose bonds (Wyman et al., 2005). In addition, the insertion of ammonia molecules into corn stover would increase accesses for cellulases to cellulose (Gao et al., 2012). Aqueous ammonia is inexpensive and can be recycled in industrial applications. Cl^- left in wastewater was not friendly to environment if discharged directly. But during the two-step pretreatment, the wastewater containing Cl^- produced from DA process could be used to neutralize the alkaline wastewater from AWO process. Therefore, the pretreatment method combining DA with AWO had less harm to the environment. Corn stover, produced in large quantities every year in China, could be used as the feedstocks. It was reported that the sequence of the conversion of hemicellulose and lignin removal had a remarkable impact on the cellulase hydrolysis (Kim et al., 2016a; Li et al., 2016a; Park et al., 2017). The effects of precedence order of DA and AWO (DA-AWO or AWO-DA) on sugars recovery were investigated. As a comparison, DA and AWO treatment were also conducted. The structure changes of corn stover before and after pretreatment were characterized by scanning electron microscopy (SEM), Brunauer-Emmet-Teller (BET) and soft X-ray tomography (SXT) to evaluate the impacts of two-step pretreatment on corn stover.

2. Methods

2.1. Materials

Corn stover was harvested from the north of Anhui province in China. The corn stover was dried and grinded by a cutting mill (FW 177, Aisite Co.,Ltd., Tianjin, China) to pass through a 40-mesh screen. The corn stover was stored in a drying vessel at room temperature before use. Oxygen (purity of 99%) was purchased from Nanjing Shangyuan industrial gas coMPany. Enzymes were donated by Novozymes (China) Investment Co., Ltd. All chemicals were bought from Sinopharm Group Chemical Reagent Co., Ltd. (Shanghai, China) and used as received without further purification.

2.2. DA pretreatment

The reaction conditions of DA stage used in this study were the optimal conditions which were obtained in our previous study (Zu et al., 2014). The corn stover was pretreated using 1 wt% HCl at 120 °C for 40 min with a solid-to-liquid ration of 1:10 (g/mL) in 70 mL batch reactor with mechanical stirring. After the pretreatment, the reactor was moved away from the heating jacket and cooled down to room temperature with cold water. Then the reaction mixture was separated by filtration. The liquor was collected, and the solid remains were washed with deionized water to remove the residual acid. All the experiments were performed at least in duplicate.

2.3. AWO pretreatment

The corn stover was pretreated using the combination of aqueous ammonia and oxygen. The effects of different ammonium hydroxide concentrations (6.2, 12.6, 16.0, 19.4, 22.9, 26.5 wt%), reaction temperatures (100, 110, 120, 130, 140, 150 °C), reaction times (20, 30, 40, 50, 60 min) and oxygen pressures (1.0, 2.0, 2.5, 3.0, 3.5, 4.0 MPa) on the glucan yield from enzymatic hydrolysis were investigated. Reaching the desired temperature of experiments need 12 min. The reaction time was counted when the desired temperature was reached. The pretreatment was terminated immediately in cold water. After the pretreatment, the residues were separated by filtration, washed by deionized water until the filtrate reached the native pH. All the experiments were performed at least in duplicate.

2.4. Combined of DA with AWO pretreatment

Corn stover was pretreated by two-stage processes (DA and AWO). The precedence order of DA and AWO (DA-AWO or AWO-DA) was investigated. In the first stage, the raw material was pretreated by DA or AWO process in 70 mL batch reactor with a stirrer. After the first stage pretreatment, the reactor was cooled down using cooling water. The solid residues was collected by filtration, washed by deionized water until reached the native pH and used as the feedstock for the following stage. In the second stage, the opposite AWO or DA process was conducted. The reaction conditions used in the second stage was similar to that corresponding single process. After two-stage pretreatment, the solid was also washed by deionized water until the filtrate reached the native pH and used as the feedstock for the enzymatic hydrolysis. All the experiments were performed at least in duplicate.

2.5. Enzymatic hydrolysis

All the untreated and pretreated samples were attempted to produce glucan by enzymatic hydrolysis. The enzymatic hydrolysis was conducted according to the method described by An et al (An et al., 2017). The cellulases were loaded at 3 FPU·g^{-1} glucan and supplemented with 20 CBU of β-glucosidase. 0.03 g/mL sodium azide was added as an antibiotic to inhibit microbial infection during the enzymatic hydrolysis. The hydrolysis process proceeded for 72 h. After enzymatic hydrolysis, the hydrolysate and residues were separated by centrifugation. The hydrolysate was collected to determine glucan yield by high performance liquid chromatography (HPLC) (An et al., 2017). Each sample was carried out at least in duplicate.

2.6. Chemical composition and structural analysis

The chemical composition of untreated and pretreated samples were analyzed using the methods mentioned in our previous work (Liu et al., 2016). The changes of morphology were imaged by scanning electron microscopy (SEM, SIRION200, USA). The specific surface area (SSA) and total pore volume (PV) of the samples were determined by performing N_2 absorption/desorption experiments on a Micromeritic TristarII3020 M (USA) analyzer.

Soft X-ray tomography (SXT), usually used in medical and biology, was introduced to examine the porosity of samples. SXT was performed at the beamline BL07W in the National Synchrotron Radiation Laboratory in Hefei, China. The data of samples were reconstructed using Mimics 16.0. The samples need preliminary treatment before the SXT analysis. Firstly, they were embedded by LR White resin (Chundawat et al., 2011). Then the embedded samples were sectioned to 500 nm using a Diatome diamond knife on a Leica EM UTC ultramicrotome (Leica, Wetzlar, Germany), and finally sectioned samples were collected using Formvar coated copper slot grids (SPI supplies,