



Stepwise pretreatment of aqueous ammonia and ethylenediamine improve enzymatic hydrolysis of corn stover

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ABSTRACT

It is a trade-off between sugar loss in pretreatment and sugar release in hydrolysis for most pretreatment. Here, a stepwise mild pretreatments of aqueous ammonia pretreatment and ethylenediamine was developed to reduce the sugar loss during pretreatment process and improve the sugar release in enzymatic hydrolysis of corn stover. Among four parameters of stepwise pretreatment (NH₃ loading, aqueous ammonia pretreatment time, ethylenediamine loading and ethylenediamine pretreatment time), aqueous ammonia pretreatment time and ethylenediamine loading played the key roles in the improving enzymatic hydrolysis. More than 95% glucan and 85% xylan were reserved in the pretreated solid after stepwise pretreatment. The glucan and xylan conversion reached 94.18% and 72.81%, respectively, with a low enzyme loading of 10 mg cellulase/g glucan. The characterization of the pretreated solid suggested that in stepwise pretreatment process, aqueous ammonia pretreatment increased the specific surface area of pretreated solid by 26.4%, while ethylenediamine pretreatment resulted in the collapse of the biomass porous structure and hence reduced the specific surface area. Crystalline index of the biomass increased after aqueous ammonia pretreatment, while the crystalline index was decreased from 53.22% to 32.13% after ethylenediamine pretreatment. Results implied that aqueous ammonia pretreatment enhanced productive enzyme adsorption on biomass mainly by increasing specific surface area, while ethylenediamine pretreatment improved productive enzyme adsorption by the coalescence and re-localization of lignin to expose more accessible surface. As a result, these interactive effects provided by the stepwise pretreatment improved the accessibility of the pretreated corn stover to enzymes and thus increased sugar release significantly.

1. Background

Lignocellulosic biomass, such as forest, agricultural, and agroindustrial residues, are widely available at relatively low cost. They are the most important resources as the feedstocks for biorefineries to produce biofuels and chemicals, which substitute for the role of petrochemistry in modern society (Silveira et al., 2015). Lignocellulosic biomass mainly consists of cellulose (30–50%), hemicelluloses (10–25%) and lignin (10–30%) (Li et al., 2010; Zhu et al., 2015). Generally, carbohydrates from lignocellulosic biomass can be

fractionated and hydrolyzed into fermentable sugars (mainly glucose and xylose) and then to a wide variety of biofuels and other chemicals (Bozell and Petersen, 2010; Zhu et al., 2016).

Because of the intimate connection among these three highly polymerized components in the plant cell wall, pretreatment is considered as the first prerequisite for the efficient deconstruction and further utilization of lignocellulosic biomass (Galbe et al., 2012; Silveira et al., 2015). An ideal pretreatment approach must efficiently disrupt the rigid structure of biomass, reduce the generation of inhibitory compounds for enzymes and fermentation strains and prevent

Abbreviations: SP, stepwise pretreatment; AP, aqueous ammonia pretreatment; EDA, ethylenediamine; EP, ethylenediamine pretreatment; SSA, specific surface area; CrI, crystalline index; CS, corn stover; LAP, laboratory analytical procedure; AIL, acid insoluble lignin; SEM, scanning electron micrograph; TEM, transmission electron microscope; BSA, bovine serum albumin; FTIR, Fourier transform infrared; XRD, X-ray diffraction; CBM, cellulose-binding domain; GFP, green fluorescent protein; AFI, adsorption fluorescence intensity; CC, cell corners; CL, cell lumen; S, secondary wall layers

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Table 1
Sugar recovery analysis of the untreated and pretreated corn stover.

	NH ₃ loading (g/g)	AP time ^a (h)	EDA ^b loading (mL/g)	EP time ^c (min)	Glucan recovery (%)	Xylan recovery (%)	AIL ^d recovery (%)
1	–	–	–	–	100.00	100.00	100.00
2	2	48	–	–	106.67 ± 1.07	105.79 ± 0.85	86.93 ± 0.04
3	–	–	0.6	20	96.95 ± 0.30	83.01 ± 0.10	79.23 ± 0.14
4	0.75	48	0.6	20	104.77 ± 1.21	85.60 ± 0.86	83.42 ± 0.21
5	1.25	48	0.6	20	104.09 ± 0.54	84.46 ± 0.37	83.31 ± 0.46
6	2	48	0.6	20	103.85 ± 0.83	84.53 ± 0.41	79.64 ± 1.13
7	2.5	48	0.6	20	105.84 ± 0.07	84.61 ± 0.10	83.12 ± 0.23
8	2	8	0.6	20	104.00 ± 0.38	100.26 ± 0.07	87.49 ± 1.76
9	2	12	0.6	20	102.82 ± 0.51	84.59 ± 0.41	86.10 ± 1.33
10	2	24	0.6	20	101.78 ± 0.62	84.65 ± 1.37	85.38 ± 0.23
11	2	48	0.6	40	96.65 ± 0.64	95.83 ± 0.39	71.22 ± 0.23
12	2	48	0.6	60	96.77 ± 1.44	100.34 ± 0.37	67.09 ± 1.15
13	2	48	0.6	120	99.12 ± 0.47	100.03 ± 0.53	67.13 ± 0.23
14	2	48	0.4	120	99.55 ± 0.27	99.02 ± 0.20	71.32 ± 0.49
15	2	48	0.2	120	101.98 ± 0.20	99.76 ± 2.07	82.01 ± 0.71
16	2	48	0.1	120	101.66 ± 0.93	100.72 ± 0.37	89.44 ± 1.33

^a AP, aqueous ammonia pretreatment and temperature of the pretreatment is 60 °C.

^b EDA, ethylenediamine.

^c EP, ethylenediamine pretreatment and temperature of the pretreatment is 100 °C.

^d AIL stands for acid insoluble lignin.

fermentable sugar losses. In addition, it should be dry-to-dry process to achieve subsequent high solid loading fermentation and facilitate lignin recovery for value-added products (Qin et al., 2013, 2015; Zhu et al., 2015).

Various pretreatment technologies, such as acidic, alkaline pretreatment and steam explosion, have been developed to deconstruct lignocellulosic biomass. Acidic pretreatment is usually conducted either at high holding temperature (> 180 °C) for short residence time or low holding temperature (< 120 °C) for long residence time, which would lead to the degradation of hemicelluloses and the generation of degraded products (Kumar and Sharma, 2017; Sassner et al., 2008). Whereas, ambient conditions are always applied in alkaline pretreatment. It increases enzyme accessibility mainly by solubilizing hemicellulose, modifying and removing the lignin fraction, and swelling and decrystallizing cellulose (Bali et al., 2015). Ammonia pretreatment is widely used to reduce biomass recalcitrance (Kim et al., 2008). In addition, ethylenediamine (EDA) pretreatment is another potential method applied to deconstruct biomass and release the fermentable sugars. It can be conducted with an extremely high solid loading at ambient pressure. By transforming cellulose allomorph and modifying lignin fraction, it significantly improves the enzymatic hydrolysis of lignocellulosic biomass (Qin et al., 2015). However, these single pretreatments have their respective disadvantages, such as the loss of sugars, the generation of degradation products, long time of reaction, high requirement for corrosion resistance of reaction equipment and environmental pollution (Mosier et al., 2005). Therefore, many researchers have focused on the combination of different pretreatment technologies to avoid their disadvantages. Previous study showed that glucose yield of poplar (*Populus alba*) co-treated with *Lenzites betulina* C5617 and liquid hot water treatment resulted in a 2.66-fold increase than that of sole liquid hot water, and an increase (2.25-fold) of glucose yield was observed by the combination of *Trametes ochracea* C6888 with liquid hot water (Wang et al., 2012). After alkaline pretreatment, the soluble protein and soluble carbohydrate concentration of ultrasonic pretreated biosludge increased from 0.00 to 0.83 g/L and from 0.07 to 0.47 g/L, respectively (Li et al., 2015). The reducing sugar and glucose yield of rice (*Populus alba*) straw co-treated with bacterium *Sphingobacterium* sp. LD-1 and NaOH/Urea showed 1.396-fold and 1.372-fold increase than that of sole NaOH/Urea treatment (Dai et al., 2015). These combined pretreatment methods maximize the advantages of each single pretreatment and thus significantly improve the efficiency of enzymatic hydrolysis.

Severe pretreatment sets high standards for reaction equipment and

always results in sugar loss, while mild pretreatment is always less efficient to reduce biomass recalcitrance. Therefore, to efficiently reduce sugar loss and deconstruct the biomass, a novel stepwise pretreatment of AP and EP was developed in this study. The four parameters of stepwise pretreatment (NH₃ loading, AP time, EDA loading and EP time) was evaluated in pretreatment of corn stover. The enzymatic hydrolysis performance was used as the key metric for assessing the pretreatment efficiency. Various characterization methods were employed to reveal the modification of corn stover structure by stepwise pretreatment. In addition, the complicated relationship between the two mild pretreatments in stepwise pretreatment was finally elucidated.

2. Materials and methods

2.1. Materials

Corn (*Zea mays* L.) stover (CS) used in the present study was collected from the suburbs of Tianjin, China. It was naturally dried and then chopped to about 2 mm. The prepared corn stover contains 5.45% moisture. It consists of 31.70% glucan, 17.10% xylan, and 17.43% acid insoluble lignin (AIL) based on the dry weight. It was stored in sealed sacks at room temperature for further use.

2.2. Pretreatment

During aqueous ammonia pretreatment, the prepared corn stover was first mixed with aqueous ammonia (25%, w/v) in screw-capped laboratory bottles (pyrex bottles). The bottles were placed in the electric oven with no agitation. During EP, the ammonia pretreated corn stover was mixed with designated volumes of EDA in 500 mL glass tumbler. Aluminum foil was used to prevent EDA volatilization. Then the glass tumbler was put into electric oven with no agitation. After designated pretreatment time, the aluminum foil was taken off to accelerate EDA volatilization (Qin et al., 2015). Pretreatment temperature for ammonia pretreatment and EDA pretreatment was 60 °C and 100 °C, respectively. The parameters of pretreatment including NH₃ loading, residence time, and EDA loading were investigated as shown in Table 1. The following extensive washing process will not be necessary afterward the pretreatment.

2.3. Enzymatic hydrolysis

Enzymatic hydrolysis of pretreated corn stover was conducted at 3%

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