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Pretreatment of corn stover for sugar production using dilute hydrochloric acid followed by lime

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HIGHLIGHTS

- High glucose yield is achieved while at relative low enzyme dosage.
- Total sugar yield is high.
- Dilute hydrochloric acid followed by lime is an efficient pretreatment process.

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ABSTRACT

In this study, a two stage process was evaluated to increase the sugar recovery. Firstly, corn stover was treated with diluted hydrochloric acid to maximize the xylose yield, and then the residue was treated with lime to alter the lignin structure and swell the cellulose surface. The optimal condition was 120 °C and 40 min for diluted hydrochloric acid pretreatment followed by lime pretreatment at 60 °C for 12 h with lime loading at 0.1 g/g of substrate. The glucose and xylose yield was 78.0% and 97.0%, respectively, with cellulase dosage at 5 FPU/g of substrate. The total glucose yield increased to 85.9% when the cellulase loading was increased to 10 FPU/g of substrate. This two stage process was effective due to the swelling of the internal surface, an increase in the porosity and a decrease in the degree of polymerization.

1. Introduction

With the increasing fossil fuels prices and negative environmental effects caused by CO_2 emissions from burning fossil fuels, more attention has been paid to increased utilization of lignocellulosic biomass which is a renewable bioresource and mainly composed of cellulose, hemicellulose and lignin. The monosaccharides obtained from the hydrolysis of polysaccharides can be converted to liquid fuels or other high-valued chemicals (Garlock et al., 2011; Sarkar et al., 2012; Shuai et al., 2010). In general, it is difficult for enzymes to degrade the cellulose in the biomass without any pretreatment due to the recalcitrance formed by the rigid cellulose and the cross-linked lignin (da Costa Sousa et al., 2009). The removal of hemicellulose and lignin by pretretament increases the pore size of biomass and expose the cellulose surface, leading to improvement of enzyme accessibility to cellulose for the subsequent enzymatic hydrolysis (Chandra et al., 2007). A large number of pretreatment methods have been studied during the past several decades (Menon and Rao, 2012), such as dilute acid (Chen et al., 2011; Lee et al., 2013), Organosolv (Novo et al., 2011; Obama et al., 2012), steam explosion (Hendriks and Zeeman, 2009), alkaline (McIntosh and Vancov, 2010; Sills and Gossett, 2011), green liquor (Yu et al., 2011), liquid hot water and ammonia pretreatments (Jin et al., 2012; Yu et al., 2010).

Among the various pretreatments, dilute acid and alkaline pretreatments are considered as effective methods and have been extensively studied. Dilute acid, including sulfuric acid, hydrochloric acid and other acids (Qin et al., 2012; Wei et al., 2012), is commonly used to hydrolyze the hemicellulose fraction and increase the porosity of biomass, which will make the cellulose more accessible to enzymes. An advantage of the dilute acid pretreatment processes is that sugars hydrolyzed from hemicelluloses can be recovered. However, lignin is not considerably removed in these acidic processes. Alkalis, including sodium hydroxide and ammonia, are effective for delignification and can increase the cellulose accessibility. Lime pretreatment has also been widely studied because of its own merits of lower chemical cost, safer handling, and easier recovery, as compared to sodium hydroxide and ammonia (Mosier et al., 2005; Wang and Cheng, 2011; Xu et al., 2010). Another attractive feature of lime is the inverse correlation between solubility and temperature, which provides a higher pH

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environment at a lower temperature. Nevertheless, like all alkaline pretreatment processes, hemicelluloses will also be partially solubilized and need further precipitation and utilization (McIntosh and Vancov, 2010). Furthermore, some inhibitory compounds could be generated during the alkaline pretreatments (McIntosh and Vancov, 2010). In order to achieve a higher xylose recovery and make cellulose more accessible to enzymes, some two-stage pretreatments (Huijgen et al., 2012; Kim et al., 2011) have been investigated. The two-stage pretreatment can effectively increase the surface area and porosity, resulting in a more effective enzymatic hydrolysis (Kim et al., 2012). But when alkali is used in the first stage, hemicelluloses will be partially removed in the delignification process, and lead to a relatively low xylose yield in next hydrolysis precess (Kim et al., 2011). Ammonia followed by dilute sulfuric acid (Kim et al., 2011), dilute sulfuric acid followed by sodium hydroxide, and dilute sulfuric acid followed by organosolv delignification were studied (Huijgen et al., 2012; Kim et al., 2012). When dilute sulfuric acid as opposed to dilute hydrochloric acid is used for hydrolysis, relatively high pretreatment temperature is needed (Bustos et al., 2003; Li et al., 2008), and inhibitory products including furfural, HMF and other organic acids are generated at the higher pretreatment temperatures (Lee et al., 2013). Sodium hydroxide is costly while pretreatments employing ammonia/organic solvents require a relatively high-cost recovery process (Menon and Rao, 2012). In the proposed process, a significantly cheaper alkali source is being used, which would make a two stage process more economically viable.

In order to achieve low process energy consumption, low enzyme loading, high sugar yield, and inner recycle of wastewater, a novel two-stage biomass pretreatment method was investigated in this study. Dilute hydrochloric acid hydrolysis was carried out in the first stage to hydrolyze hemicellulose with attempt to maximize xylose yield. The hydrolysate could be further utilized in two different ways. In one way, xylose in hydrolysate could be converted to furfural in diphasic system, thus dilute hydrochloric acid could be reused after the organic phase was removed. The other way would be converting xylose to other chemicals by fermentation. Generally, lime is used to neutralize pH to an appropriate value before fermentation. After fermentation and distillation, the wastewater containing Cl^- is left which is not friendly to environment if discharged. But, through double acids method, the chloride can be recovered. The processing method has been presented in a previous literature (Li et al., 2008): Initial hydrolysis is conducted by dilute hydrochloric acid, after which, the hydrolysate is neutralized with lime to an appropriate pH value for the enzymatic conversion of the sugars. After conversion and distillation, the wastewater containing Cl^- is left. An appropriate amount of sulfuric acid is added to the wastewater, calcium sulfate is precipitated and dilute hydrochloric acid are formed. The dilute hydrochloric acid can be used for hydrolysis again.

Lime was used in the second stage so as to further alter the lignin structure and swell the internal surface of cellulose. Lime is considered as a weak base for its low solubility in water, but under appropriate conditions, a significant increase in sugar yield could also be achieved. Different temperatures, residence times, lime loadings and enzyme dosages were investigated. SEM images, degree of polymerization, and porosity were used to characterize the features of corn stover in a two-stage pretreatment.

2. Methods

2.1. Materials

Corn stover was collected from the north of Anhui province of China. The biomass was firstly ground to pass through a 40-mesh screen and then washed with tap water to remove the clay from the surface. After washing process, the solids were air-dried and then stored in sealed plastic bags at room temperature.

2.2. Two-stage pretreatment of corn stover

In the first stage, the biomass (on a dry basis) was treated with 1 wt% dilute hydrochloric acid in a 100 ml batch reactor with agitation. The solid/liquid ratio was 1:10. Different reaction temperatures (100, 110, 120 and 130 °C) and reaction times of 20 and 40 min at temperature were investigated. It took approximately 20 min to reach the target temperature for the different pretreatment conditions. After pretreatment, the reactor was removed from the heating jacket and cooled down with circulating water. The hydrolysate was collected by filtration and an aliquot was used to analyze the concentrations of different sugars and calculate the sugar yields. The optimal condition was chosen according to a maximum xylose yield. The solid phase (with washing) obtained from the optimal condition was used for a second stage treatment with lime.

In the second stage, the wet biomass after dilute hydrochloric acid pretreatment was further pretreated with lime in a 50 ml flask with agitation. The solid/liquid ratio was kept constant at 1:10. Two sets of experiments were conducted with low temperature (60 °C) in a water bath and high temperature (100 °C) in an oil bath for 1, 3, 6, 12, 24 h and 1, 2, 3, 4, 6 h respectively. Different lime loadings (0.05, 0.10, 0.15, 0.20, and 0.25 g lime/g dry biomass after dilute hydrochloric acid pretreatment) at the same temperature and reaction time were also investigated. After pretreatment, the solid phase was recovered by filtration with a vacuum pump and washed with 500 ml deionized water to remove excess alkali, solubilized lignin and other byproducts.

2.3. Enzymatic hydrolysis

Celluclast 1.5 L (cellulase complex, produced by Trichoderma reesei) and Novozyme 188 (β-glucosidase, produced by Aspergillus niger) were kindly donated by Novozymes (China) Investment Co., Ltd. The enzyme activities were determined to be 74.5 filter paper units (FPU)/mL (expressed as micromoles of glucose produced per minute, with filter paper as a substrate) and 261.4 cellobiose units (CBU)/mL (expressed as micromoles of cellobiose that is converted to glucose per minute, with cellobiose as a substrate) for Celluclast 1.5 L and Novozyme 188, respectively (Ghose, 1987). Enzymes were directly used without further purification.

Enzymatic hydrolysis was conducted in a shaking incubator at 50 °C and 120 rpm. Wet pretreated biomass (0.3 g dry biomass) was mixed with a specific amount of 0.05 M sodium acetate buffer (pH 4.8) and the mass concentration of substrate is 5%. Sodium azide (0.3%, w/v) was added to the hydrolysis mixture to inhibit microbial growth. Cellulase (5, 10, and 15 FPU per gram substrate) and β-glucosidase (20 CBU per gram substrate) were added into the mixture. The excessive dosage of β-glucosidase was used to eliminate the cellobiose accumulation. After 72 h hydrolysis, the hydrolysate was collected by centrifugation and the supernatant was used for further analysis.

2.4. Analysis methods

2.4.1. Composition analysis of raw and pretreated biomass

The Laboratory Analytical Procedures (LAP) established by National Renewable Energy Laboratory (NREL) were used to measure total solids, ash, structural carbohydrates and acid-insoluble lignin in the raw and pretreated biomass (Templeton and Ehrman, 1995; Sluiter et al., 2005a,b, 2008).