Bioresource Technology 102 (2011) 6254–6259

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Liquid hot water and alkaline pretreatment of soybean straw for improving cellulose digestibility

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ARTICLE INFO

Article history:
Received 16 December 2010
Received in revised form 16 February 2011
Accepted 17 February 2011
Available online 20 February 2011

Keywords:
Soybean straw
Liquid hot water
Alkaline pretreatment
Cellulose digestibility

ABSTRACT

Soybean straw was pretreated with either liquid hot water (LHW) (170–210 °C for 3–10 min) or alkaline soaking (4–40 g NaOH/100 g dry straw) at room temperature to evaluate the effects on cellulose digestibility. Nearly 100% cellulose was recovered in pretreated solids for both pretreatment methods. For LHW pretreatment, xylan dissolution from the raw material increased with pretreatment temperature and time. Cellulose digestibility was correlated with xylan dissolution. A maximal glucose yield of 70.76%, corresponding to 80% xylan removal, was obtained with soybean straw pretreated at 210 °C for 10 min. NaOH soaking at ambient conditions removed xylan up to 46.37% and the subsequent glucose yield of pretreated solids reached up to 64.55%. Our results indicated LHW pretreatment was more effective than NaOH soaking for improving cellulose digestibility of soybean straw.

1. Introduction

With soaring increases in world energy consumption and growing concerns about climate change, biomass-based renewable energy, such as cellulosic ethanol, is considered to be one solution to the energy crisis and global warming. Lignocellulosic biomass, such as crop residue, woody biomass, and energy crops, is widely and sufficiently available for cellulosic ethanol production. However, the recalcitrance of lignocellulosic biomass to chemical and enzyme conversion hinders efficient production of cellulosic ethanol. Thus, a suitable pretreatment process is important to reduce the recalcitrance and to make bioconversion processes more efficient, economic, and environmentally friendly.

Liquid hot water (LHW) pretreatment has been shown to improve cellulose digestibility of various types of lignocellulosic biomass. LHW pretreatment differs from other current leading pretreatment methods (e.g., diluted acid, alkaline, steam explosion) with respect to chemical usage and formation of inhibitory compounds (e.g., HMF and furfural). It is a chemical free process which hydrolyzes hemicellulose at elevated temperature and pressure. Acetic acid and other organic acids generated from autohydrolysis can catalyze further hydrolysis (Kim et al., 2009). In the meantime, accumulation of hydrogen ions accelerates degradation of fermentable sugars. However, compared to steam explosion to which no chemical catalyst is added, fewer inhibitory compounds to fermentation are formed during LHW pretreatment (Laser et al., 2002). The pH controlled, LHW pretreatment can prevent degradation of fermentable sugars but involves the use of a base (Mosier et al., 2005a).

Alkaline pretreatment is one of the current leading chemical pretreatment methods, particularly for dissolving lignin. In addition, acetyl groups and various uronic acid substitutes, which lower susceptibility of hemicellulose and cellulose to hydrolytic enzymes, are also removed by alkaline pretreatment (Mosier et al., 2005b). Agricultural residues and herbaceous crops have been shown to be more suitable to alkaline pretreatment than woody biomass (Galbe and Zacchi, 2007). Reaction temperature, pretreatment time, and alkali loading are critical to alkaline pretreatment (Silverstein et al., 2007). Varga et al. (2002) reported that more than 95% lignin and about 88% hemicellulose in corn stover were removed as a result of pretreatment with 10% NaOH at 120 °C. Alkaline soaking at room temperature instead of elevated temperatures was also found to be effective in improving cellulose digestibility of corn stover (Li et al., 2004). As alkaline pretreatment does not need a complicated reactor, there is an increased interest in applying alkaline pretreatment on-farm (Digman et al., 2007). The major problem of chemical pretreatments is washing and/or neutralization of the pretreated slurry. In order to reduce the environmental impacts of chemical waste disposal,

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doi:10.1016/j.biortech.2011.02.075

extra processes are needed for wastewater treatment and chemical recycling.

As one of the major food and energy crops, soybean plantings occupy large land areas all over the world. In 2009, nearly 77.5 million acres of soybeans were planted in the U.S. (USDA, 2009). Soybean straw, left after soybean harvesting, is partially collected for use as animal feed (Gupta et al., 1978). With the annual demand for soybeans increasing, there is growing interest in soybean straw as a potential feed stock for cellulosic ethanol production. However, there is little information related to bioconversion of soybean straw. The only test to date on pretreatment of soybean straw used ammonia soaking, which resulted in 51% cellulose digestibility (Xu et al., 2007). It was our goal to evaluate the efficacy of LHW and alkaline pretreatment on soybean straw in terms of cellulose digestibility. The degradation of xylan and formation of inhibitory compounds were also investigated.

2. Methods

2.1. Materials

Soybean straw, collected from the farm of The Ohio Agricultural Research and Development Center (OARDC) in Wooster, OH, was dried at 40 °C to moisture content less than 5%, ground to pass a 3/16 inch screen, and stored in an airtight container at room temperature prior to use. Raw soybean straw was composed of 34.09% cellulose, 16.05% hemicellulose(11.43% xylan, 1.83% galactan, 1.00% arabinan, and 1.79% mannan), 21.6% lignin, 11.01% extractives, 5.16% ash, and 12.09% other non-identified compounds (e.g., protein, pectin, acetyl groups, glucuronic acid substitutes). Spezyme CP was obtained from Genencor (Palo Alto, CA) and its activity was determined to be 50 FPU/mL according to NREL Laboratory Analytical Procedure (LAP) 006 (Adney and Baker, 1996).

2.2. LHW pretreatment

LHW pretreatment was conducted in a 1-L Parr reactor (Parr Instrument Company, Moline, IL). Forty grams of soybean straw (dry mass) were evenly mixed with 400 mL of deionized (DI) water in the stainless steel vessel of the reactor. The temperature and pressure of the reactor were automatically controlled. The reactor was heated to the target temperatures of 170, 180, 190, 200, or 210 °C from room temperature (21 ± 2 °C) within 30–45 min and with continuous agitation (approximately 400 rpm). The corresponding pressures at the target temperatures were 6.9, 9.3, 12.1, 15.2, and 18.6 bar, respectively. After being held at each target temperature for 3, 5, or 10 min, the reactor was cooled down to room temperature by turning on the cooling water for approximately 30 min. The pretreated slurry was washed with 1000 mL DI water and filtered by vacuum filtration using glass fiber filters (1.6 μm). The liquor and retained solid on the filter paper were collected separately for analysis.

2.3. Sodium hydroxide pretreatment

Fifty grams of soybean straw (dry mass) were soaked in 500 mL NaOH solution in a1-L beaker to obtain 4–40 g NaOH loading based on 100 g dry mass. The ratio of solid to liquid was 1:10. The beaker was covered with plastic wrap and placed at room temperature (24 ± 1 °C) for 24 h. The pretreated slurry was extensively washed with tap water using a sieve (325 mesh) until the pH reached around 8 then was further neutralized with HCl to a pH value between 6.5 and 7.0. The neutralized solid was then drained, washed, and collected for further analysis.

2.4. Enzymatic hydrolysis

The enzymatic hydrolysis was conducted following NREL protocol LAP-008 (Dowe and McMillan, 2001). The solid and Spezyme CP loading were 2.5% (w/w) and 20 FPU/g solid, respectively. The hydrolysis lasted 48 h at 50 °C with an agitation speed of 130 rpm on a rotary shaker (Excella E24, Newbrunswick, NY, USA). After 48 h, the hydrolysate was boiled for 5 min to deactivate enzymes and then chilled in an ice bath. The supernatant was filtered through a 0.2 μm nylon membrane filter and solids collected for sugar analysis.

2.5. Analytical methods

Compositions of untreated and pretreated soybean straw were determined following NREL protocols (Sluiter et al., 2008). The sugar concentrations were determined by high performance liquid chromatography (HPLC) (Agilent 1200 series, MN, USA) with a BioRad Aminex HPX-87P column (BioRad Inc., Hercules, CA) and a refractive index detector (RID). The mobile phase was HPLC grade water, eluting at a flow rate of 0.6 mL/min. The temperatures of the column and detector were maintained at 80 and 55 °C, respectively. HMF and furfural were analyzed by HPLC using a Phenomex Rezex RFQ Fast Acid column (Phenomex, Torrance, CA). The mobile phase was 0.005 N sulfuric acid at a flow rate of 0.6 mL/min. The temperatures of the column and detector were maintained at 55 and 45 °C, respectively.

The solid content in the pretreated materials was determined using a 105 °C drying oven. Solid recovery were calculated as the mass of pretreated solids or water soluble solids in the pretreated slurry expressed as a percentage of the total mass in the raw material. Total mass recovered was determined by the amount of pretreated solid residue plus the soluble solids in the liquor.

Cellulose or xylan recovery in the solids or liquor was calculated as the mass of cellulose or xylan in each fraction expressed as a percentage of total glucan or xylan in the raw material. The sugar concentration in the liquor was determined according to NREL protocols (Sluiter et al., 2006). Sugar (glucose or xylose) yield by enzymatic hydrolysis was defined as the total mass of sugar produced by enzymatic hydrolysis as a percentage of its total mass in the raw material.

The monomeric sugar was degraded into HMF or furfural in severe pretreatment conditions. The converting factors for HMF to glucose, and furfural to xylose were 180/126 and 150/96, respectively (Zeng et al., 2007). HMF and furfural yields were thus calculated as the amount of corresponding degraded glucose or xylan expressed as a percentage of total glucan or xylan in the raw material.

2.6. Statistical analysis

All data reported were the average values of duplicates. A 95% confidence level was applied for statistical analysis and one-way analysis of variance (ANOVA) was performed with Turkey simultaneous tests (SAS Inc., Cary, NC).

3. Results and discussion

3.1. LHW pretreatment

3.1.1. Biomass degradation

As shown in Table 1, recovery of mass in the solid residue after pretreatment decreased with pretreatment temperature and time. In contrast, recovery of solids dissolved in the liquor increased with pretreatment time and temperature except a significant