Bioresource Technology 124 (2012) 306–310

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

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

Pretreatment of wheat straw using SO_2 dissolved in hot water

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HIGHLIGHTS

- Wheat straw hemicellulose was efficiently pretreated in an H_2O–SO_2 system.
- SO_2 in the H_2O–SO_2 system could be recovered and reused after reaction.
- SO_2 in water favors hemicellulose conversion rather than xylose dehydration.
- Kinetic analysis was performed by Saeman modeling and Arrhenius equation.

ARTICLE INFO

Article history:
Received 21 February 2012
Received in revised form 9 July 2012
Accepted 9 August 2012
Available online 17 August 2012

Keywords:
Pretreatment
Wheat straw hemicellulose
Recoverable catalyst
H_2O–SO_2 system

ABSTRACT

Efficient pretreatment is important for complete enzymatic conversion of lignocellulosic materials. Pretreatment of wheat straw with sulfur dioxide (SO_2) dissolved in hot water achieved xylose and total product yields of up to 61.1% and 93.9%, respectively, based on the mass of lignocellulose in wheat straw. The apparent activation energies for hemicellulose conversion and xylose dehydration were 7.8 and 9.0 kJ/mol. FT-IR spectra of the residual solid after treatment showed that the hemicellulosic components were converted, the hydrogen bonds in cellulose were broken, but the lignin structure was not changed. Importantly, the SO_2 was recovered from the product mixture by steam stripping and could be reused. Thus, the SO_2–H_2O system is an efficient and environmentally friendly way for the conversion of hemicellulose in wheat straw into monosaccharides, such as xylose, glucose and arabinose.

1. Introduction

The utilization of lignocellulosic materials for the production of value-added chemicals or biofuels generally requires a pretreatment process (Dadi et al., 2006; Grous et al., 1986; Kumar et al., 2009; Qi et al., 2009). Chemical pretreatment processes such as dilute acid hydrolysis are efficient, but create waste, require additional recovery steps and can lead to degradation of products. When sulfuric acid is used, the derived sugars, mainly xylose, are easily converted into furfural, which has an inhibitory effect on the subsequent enzymatic hydrolysis (Almeida et al., 2009).

Orozco et al. (2007) reported that H_3PO_4, a medium strong acid, could promote the yield of glucose from cellulose, since its acidity is just sufficient to break the bonds of cellulose, but not too strong to control the reaction process. SO_2 dissolved in water can react with water to form sulfurous acid as a medium strong acid, like H_3PO_4, to generate H^+ (Donaldson et al., 2009) and also can exist as a Lewis acid (Jonas et al., 1994). Thus, SO_2 in water may potentially be able to convert hemicellulose with a high sugar yield, but a low yield of furfural. Moreover, SO_2 can be removed by steam stripping from an aqueous solution, and the recovered SO_2 can be reused. However, pretreatment of wheat straw in an H_2O–SO_2 system has not been reported in the literature. Therefore, in the present study wheat straw was treated in hot water using SO_2 as a recoverable catalyst. Kinetics analysis of the hemicellulose conversion and xylose degradation with time were established, and the reaction rate constants and apparent activation energy were calculated according to Saeman models and Arrhenius equation.

2. Experimental

2.1. Chemicals

Wheat straw was dried at 105 °C for 12 h and milled to small particles (less than 0.5 mm). The contents of cellulose and hemicellulose in the wheat straw were 40.7% and 30.1%, respectively, as measured with an ANKOM A2000i automatic fiber analyzer. Aqueous 6% solutions of SO_2 were purchased from Aladdin Reagent Inc. (Shanghai, China). N_2 with a volume fraction purity of 0.9995 was supplied by Beijing Haipu Gases Ltd. (Beijing, China). Anhydrous D-glucose, xylose, arabinose, furfural and levulinic acid (LA) with

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http://dx.doi.org/10.1016/j.biortech.2012.08.028

mass fraction purities of 0.998, 0.98, 0.99, 0.99 and 0.99, respectively, were purchased from Aladdin Reagent Inc. (Shanghai, China). All reagents and solvents were of analytical grade.

2.2. Pretreatment of wheat straw

The pretreatment of wheat straw was carried out in a stainless steel reactor of 25-mL in capacity with a magnetic stirrer. The reactor was heated by a furnace and the temperature of the reactor was controlled by a temperature controller with an accuracy of ±0.5 °C. The pressure was determined by a calibrated pressure transducer with an accuracy of ±0.025 MPa.

In a typical procedure, 0.3 g of wheat straw, 6.0 mL of SO_2 aqueous solution and 9.0 mL of H_2O were loaded into the reactor. The reactor was sealed and purged with N_2 at a low flow rate to decrease the loss of SO_2. The reactor was submerged into the furnace which had attained a given temperature, and the contents were stirred for a desired time (the reaction was considered to have started when the reactor was placed into the furnace, and the time of heating the reactor from room temperature to a required temperature was about 12 min). After the reaction, the reactor was placed into ice water. When the temperature of the reactor was about 100 °C, the valves on both ends of the reactor were opened and the solution was purged by steam produced at 120 °C for 20 min, and the concentration of SO_2 in the solution was validated to be less than 10.0 mg/L (limit of detection) by the standard iodimetry method (Johnstone and Leppla, 1934; also see HJ/T 56-2000, a standard method of State Environmental Protection Administration of China). The stripped SO_2 was collected at the outlet of the reactor. The solution was filtered through a filter with a membrane of 0.45 μm, washed with water for 3 times and analyzed by HPLC to determine the yield of products including xylose, glucose, arabinose, furfural, levulinic acid (LA), acetic acid, and 5-hydroxymethylfurfural (HMF). Three parallel experiments were carried out, and the average error was calculated as 3.4%.

2.3. Analysis of products

An HPLC (Waters 2695, USA) with SHODEX SH 1011 column (Shodex, Tokyo) and differential refractive index detector (Waters, USA) were employed for the analysis of liquid samples. The temperature of the column oven was 55 °C and the mobile phase was 0.01 mol/L sulfuric acid at a flow rate of 0.5 mL/min. The conversion of wheat straw was calculated by the mass difference before and after the reaction, and the yield of products was calculated by the following equation:

$$\text{Yield of products} = \frac{\text{Mass of products (g)}}{\text{Mass of wheat straw added (g)} \times 0.301} \times 100\% \quad (1)$$

2.4. FT-IR analysis

The original wheat straw and the residual solids after treatment were ground into powder for FTIR measurement. FTIR spectra were recorded on a Thermo Scientific Nicolet 6700 FT-IR spectrophotometer (Thermo, USA) using KBr pellets, and each sample was recorded with 32 scans in the range of 4000–400 cm^{-1} at an effective resolution of 2 cm^{-1}.

3. Results and discussion

3.1. Conversion of wheat straw hemicellulose in the H_2O–SO_2 system

Fig. 1 shows the effect of SO_2 concentration on yield of products at 160 °C for 30 min. Even a small amount of SO_2 could enhance the yield of products considerably. For example, the yield of xylose was 56.3% at a SO_2 concentration of 0.012 g/mL, while the yield was only 1.6% in the absence of SO_2. However, with a further increase in SO_2 concentration, the xylose yield decreased and the degradation products, such as furfural and LA, occurred, which can lead to the formation of humin.

The effect of temperature on the yields of products from wheat straw hemicellulose for 30 min is shown in Fig. 2. Temperature greatly influenced the yields and distribution of products from wheat straw hemicellulose. At 130 °C, the main products were xylose, arabinose, glucose and acetic acid. As the temperature increased from 130 to 160 °C, the yield of xylose first increased and then decreased, because the sugar was further converted into furfural whose yield gradually increased with temperature. Fig. 3 shows that temperature had a pronounced effect on the reaction time needed to reach the maximum yield of xylose. The time to reach the maximum yield of xylose at 130, 140, 150, and 160 °C was 75, 75, 30 and 30 min, and the maximum yields of xylose were 57.5%, 59.2%, 61.1%, and 53.5%, respectively. The lower yield at the highest temperature studied is due to the degradation of xylose into furfural (Fig. 3d).

Fig. 3 also shows the effect of reaction time on the yield of products at different temperatures with a SO_2 concentration of 0.024 g/mL. With increasing reaction times, the yields of xylose and arabinose first increased and then decreased due to degradation of the sugars. The yield of acetic acid gradually increased at the beginning time and then remained constant since the acetyl content in wheat straw is fixed and acetic acid shows good stability

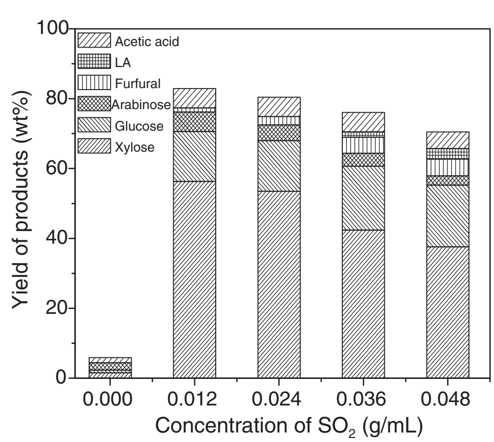

Fig. 1. Product yields after treatment of wheat straw at 160 °C for 30 min in the presence of different concentrations of SO_2.

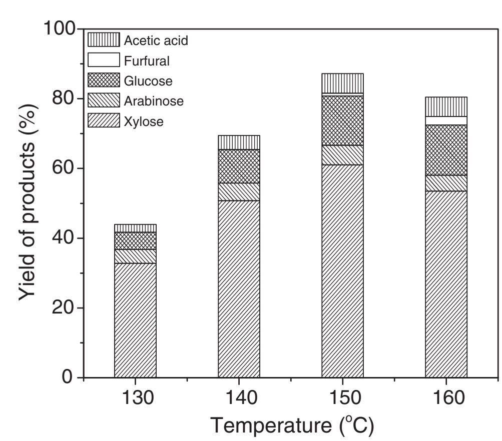

Fig. 2. Product yields after treatment of wheat straw in the presence of 0.024 g/mL of SO_2 for 30 min at different temperatures.