Bioresource Technology 149 (2013) 546–550

Contents lists available at ScienceDirect

Bioresource Technology

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

Short Communication

Subcritical CO_2 pretreatment of sugarcane bagasse and its enzymatic hydrolysis for sugar production

Hongdan Zhang, Shubin Wu *

State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, PR China

HIGHLIGHTS

- Sugarcane bagasse is an interesting raw material for sugar production.
- Subcritical CO_2 pretreatment was investigated to enhance enzymatic hydrolysis.
- Liquid fractions and solid residues were thoroughly analyzed.
- The optimal pretreatment conditions based on the total sugar yields was obtained.
- The proposed process is a contribution to bioconversion of biomass to bio-fuels.

ARTICLE INFO

Article history:
Received 30 July 2013
Received in revised form 28 August 2013
Accepted 31 August 2013
Available online 12 September 2013

Keywords:
Sugarcane bagasse
Subcritical CO_2 pretreatment
Enzymatic hydrolysis
Total sugar

ABSTRACT

The present work investigated the effects of subcritical CO_2 pretreatment of sugarcane bagasse at different CO_2 pressure, pretreatment time, and temperature with relative high-solid concentration (15% w/v) to the composition of prehydrolyzate and the enzymatic hydrolysis. The results indicated that the maximum xylose yields in prehydrolyzate liquid were 15.78 g (combined 3.16 g xylose and 12.62 g xylo-oligosaccharides per 100 g raw material). Due to the effective removal of hemicellulose, the maximum glucose yield in enzyme hydrolyzate reached 37.99 g per 100 g raw material, representing 91.87% of glucose in the sugarcane bagasse. The maximal total sugars yield (combined xylose and glucose both in prehydrolyzate and enzymatic hydrolyzate) were 52.95 g based on 100 g raw material. These results indicated that subcritical CO_2 pretreatment can effectively improve the enzymatic hydrolysis, so it could be successfully applied to sugarcane bagasse.

1. Introduction

Due to the inevitable depletion and negative environment impact of fossil fuels, increasing attention has been focused on the conversion of lignocellulosic biomass. Lignocellulosic biomass as a renewable and suitable energy resource can be used for the generation of bio-based fuels and chemicals (Alvira et al., 2010). Sugarcane bagasse, as an agricultural residue, is a low-cost, available, abundant, and renewable raw material worldwide for the bioconversion of lignocellulosic biomass to bio-fuels (ethanol and biodiesel) (Pandey et al., 2000).

Sugarcane bagasse is difficult to digest due to the complex matrix formed by the three main polymers of lignocellulosic biomas (cellulose, hemicellulose, and lignin). And a pretreatment process is essentially required to break down it (Himmel et al., 2007). Numerous pretreatment methods are available, such as dilute-acid hydrolysis, alkaline hydrolysis, liquid hot water pretreatment, biological process and supercritical fluid pretreatment (Yang et al., 2012; Mohsenzadeh et al., 2012; Zhang et al., 2013; Hendriks and Zeeman, 2009), each had their advantages and disadvantages.

Recent attention has focused on supercritical CO_2 because of several potential benefits. CO_2 has a low critical temperature (31.1 °C) and pressure (7.36 MPa) (Muzafera et al., 2007), can form weak acid catalyst with water ($CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \rightleftharpoons 2H^+ + CO_3^{2-}$) by acting as easily separable green co-solvent (Luterbacher et al., 2012), which is benefit to the degradation of hemicellulose and lignin, the disrupt of polymerization degree. Moreover, CO_2 is nontoxic and friendly to the environment, leaves no residue, and is inexpensive and readily available. However, the supercritical pressure of CO_2 need high resist reaction equipments which limited the extensive use of critical CO_2 pretreatment. The subcritical CO_2 (pressure <7.36 MPa) can help to overcome this hurdle and the subcritical CO_2 pretreatment were investigated in this study.

Based on the above viewpoint, we proposed a subcritical CO_2 pretreatment process to improve the enzymolysis efficiency of sugarcane bagasse. The subcritical CO_2 pretreatment is to obtain

* Corresponding author. Tel.: +86 20 22236808; fax: +86 20 87518783.
E-mail address: shubinwu@scut.edu.cn (S. Wu).

0960-8524/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.08.159

the maximal hemicellulose degradation and make enzyme more accessibility to cellulose. Hence, the effect of subcritical CO_2 pretreatment of sugarcane bagasse at various pressures, times and temperatures were investigated. The composition of monomers and oligosaccharides in prehydrolyzate liquid, as well as inhibitors were comparatively analyzed. Subsequently, enzymatic hydrolysis of different pretreated solids were carried out to evaluate the efficiency of subcritical CO_2 pretreatment process. Finally, the total sugars (glucose and xylose) obtained both in prehydrolyzate and enzymatic hydrolyzate were also discussed.

2. Methods

2.1. Raw material

Sugarcane bagasse obtained in Guangdong, China, was milled to a particle size <1 mm using a laboratory knife mill (XuLang Machinery, Guangzhou, China). Then the milled raw material was air-dried for further use. The chemical composition of the raw material (on a dry weight basis) was 37.22% glucan, 24.60% xylan, 1.54% arabinan, 0.55% galactan, 22.63% acid-insoluble lignin (AIL), 2.24% acid-soluble lignin (ASL) and 4.59% ash.

CO_2 was purchased from Guangzhou Junduo Gases Co. (Guangzhou, China) and was purified to 99.99% purity using an activated carbon column.

2.2. Subcritical CO_2 pretreatment

Subcritical CO_2 pretreatment was performed in a 1 L Parr reactor with an electric heater at various pressures, times, and temperatures. 45 g of sugarcane bagasse (o.d.) and 300 mL of de-ionized water (15% (w/v)) were added to the reactor. Then a certain amount of CO_2 was loaded into the reactor to reach the desired pressure. During the reacting process, the agitation was set at 300 rpm to allow better mixing of biomass with CO_2. It took about 20–35 min to reach the desired temperature (140–180 °C). After the biomass had been subjected to the preset pressure and temperature for a specific time period, the reactor was immediately cooled down by cooling water (until below 40 °C). Then the pressure was released instantaneously using a quick release ball valve. The pretreated solution was then separated by filtration. The liquid fraction of prehydrolysate was analyzed by Ion chromatography (IC) and high-pressure liquid chromatography (HPLC) to determine the concentration of sugars and inhibitors, respectively. Then the solid fraction was stored in refrigerator for further enzymatic hydrolysis.

2.3. Enzymatic hydrolysis

Enzymatic hydrolysis tests were performed on samples under various pretreatment conditions to determine improvements to the system. Enzymatic digestibility tests were conducted as follows: reaction conditions were 50 °C, pH 4.8 (0.05 mol/L acetic acid sodium acetate buffer), 2 wt% dry matter, with incubation in a shake flask at 150 rpm for 60 h. Cellulase was purchased from Genencor (Shanghai, China), with a filter paper activity of 20 FPU/mL. The enzyme (cellulase) were added at the loading of 20 FPU/g substrate for all hydrolysis experiments. At the same time, two drops of acetic ether were added to inhibit microbial contamination or growth. After the enzymatic hydrolysis process was completed, the sugars in enzyme hydrolyzate were analyzed by IC system.

2.4. Analysis methods

The chemical composition of sugarcane bagasse and enzymatic hydrolysis residues were determined using the standard provided by the National Renewable Energies Laboratory in USA (Sluiter et al., 2006). Since some of the sugars present in the liquid fractions obtained after subcritical CO_2 pretreatment were oligosaccharides, a acid hydrolysis (4% (w/w) H_2SO_4, 121 °C and 60 min) was performed to obtain monosaccharides for analysis (Zhang et al., 2013).

All liquid products from pretreatment and enzymatic hydrolysis were analyzed by IC system. The operation conditions were described in Supplementary material.

3. Results and discussion

3.1. Subcritical CO_2 pretreatment

Weak acid condition formed by subcritical CO_2 and water was employed to remove amorphous hemicellulose, Table 1 showed the composition of the prehydrolyzate obtained after subcritical CO_2 pretreatment referred to 100 g raw material. Xylose (including xylose monomers and xylo-oligosaccharides) were the major products obtained by subcritical CO_2 pretreatment due to the degradation of amorphous hemicellulose. Xylose reached maximal yield of 15.78 g per 100 g raw material (including 3.16 g xylose monomers and 12.62 g xylo-saccharides) at 5 Mpa, 160 °C with 80 min

Table 1
Composition of the prehydrolysate after subcritical CO_2 pretreatment of sugarcane bagasse under different pretreatment conditions.

Conditions			Sugar analysis (g/100 g raw material)						Inhibitors (g/L)		
Press/ Mpa	Time/ min	Temp/ °C	Xylose monomer	Xylo-oligo saccharide	Total xylose	Glucose monomer	Glucooligosaccharide	Total glucose	HMF	furfrural	Acetic acid
0			0.68 ± 0.07	11.35 ± 0.74	12.03 ± 0.81	0.04 ± 0.00	0.40 ± 0.08	0.44 ± 0.08	0.02 ± 0.00	0.23 ± 0.04	0.07 ± 0.02
1			1.08 ± 0.24	11.41 ± 0.19	12.49 ± 0.43	0.05 ± 0.00	0.43 ± 0.10	0.48 ± 0.10	0.02 ± 0.00	0.53 ± 0.06	0.36 ± 0.07
3	60	160	1.39 ± 0.23	11.19 ± 0.82	12.58 ± 1.05	0.05 ± 0.00	0.40 ± 0.09	0.45 ± 0.09	0.04 ± 0.01	0.68 ± 0.05	0.62 ± 0.08
5			2.35 ± 0.28	12.56 ± 0.82	14.91 ± 1.10	0.07 ± 0.02	0.33 ± 0.04	0.40 ± 0.06	0.07 ± 0.02	1.21 ± 0.12	1.73 ± 0.14
7			2.18 ± 0.14	11.70 ± 0.98	13.88 ± 1.12	0.03 ± 0.01	0.34 ± 0.04	0.37 ± 0.05	0.05 ± 0.00	0.90 ± 0.10	1.52 ± 0.02
	20		0.66 ± 0.09	9.24 ± 0.55	9.90 ± 0.64	0.03 ± 0.00	0.48 ± 0.12	0.51 ± 0.12	0.02 ± 0.01	0.31 ± 0.07	0.80 ± 0.09
	40		1.50 ± 0.28	11.90 ± 0.15	13.40 ± 0.43	0.03 ± 0.00	0.37 ± 0.08	0.40 ± 0.08	0.04 ± 0.00	0.65 ± 0.09	0.72 ± 0.06
5	60	160	2.35 ± 0.28	12.56 ± 0.82	14.91 ± 1.10	0.07 ± 0.02	0.33 ± 0.04	0.40 ± 0.06	0.07 ± 0.02	1.21 ± 0.12	1.73 ± 0.14
	80		3.16 ± 0.34	12.62 ± 0.42	15.78 ± 0.76	0.05 ± 0.01	0.43 ± 0.04	0.48 ± 0.05	0.06 ± 0.01	1.59 ± 0.01	1.90 ± 0.22
	100		3.40 ± 0.20	11.07 ± 0.16	14.47 ± 0.36	0.09 ± 0.03	0.40 ± 0.06	0.49 ± 0.09	0.07 ± 0.02	2.07 ± 0.24	2.63 ± 0.17
		140	0.08 ± 0.00	5.67 ± 0.47	5.75 ± 0.47	0.01 ± 0.00	0.26 ± 0.03	0.27 ± 0.03	0.01 ± 0.00	0.01 ± 0.00	0.69 ± 0.12
		150	0.85 ± 0.06	10.03 ± 0.55	10.88 ± 0.61	0.03 ± 0.00	0.26 ± 0.05	0.29 ± 0.05	0.02 ± 0.00	0.22 ± 0.02	1.18 ± 0.18
5	100	160	3.40 ± 0.20	11.07 ± 0.16	14.47 ± 0.36	0.09 ± 0.03	0.40 ± 0.06	0.49 ± 0.09	0.07 ± 0.02	2.07 ± 0.24	2.63 ± 0.17
		170	4.21 ± 0.34	0.98 ± 0.16	5.19 ± 0.50	0.26 ± 0.07	0.40 ± 0.07	0.66 ± 0.14	0.26 ± 0.07	5.18 ± 0.60	4.06 ± 0.38
		180	0.57 ± 0.17	0.18 ± 0.05	0.75 ± 0.22	0.52 ± 0.04	0.26 ± 0.01	0.78 ± 0.05	0.46 ± 0.09	6.19 ± 0.38	5.41 ± 0.52