Subcritical carbon dioxide-water hydrolysis of sugarcane bagasse pith for reducing sugars production

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HIGHLIGHTS

• Hydrolysis conditions were optimised by L16(45) orthogonal design to give a reducing sugar yield of 45.8%.
• Hemicelluloses was removed to mainly produce xylose, glucose and arabinose during hydrolysis.
• Simple biomass solubilisation cannot perfectly describe the hydrolysis of sugarcane bagasse pith.
• A consecutive reaction kinetics was proposed.

Abstract

The aim of present study was to obtain total reducing sugars (TRS) by hydrolysis in subcritical CO2-water from sugarcane bagasse pith (SCBP), the fibrous residue remaining after papermaking from sugarcane bagasse. The optimum hydrolysis conditions were evaluated by L16(45) orthogonal experiments. The TRS yield achieved 45.8% at the optimal conditions: 200 °C, 40 min, 500 r min⁻¹, CO2 initial pressure of 1 MPa and liquid-to-solid ratio of 50:1. Fourier transform infrared spectrometry and two-dimensional heteronuclear single quantum coherence nuclear magnetic resonance were used to characterize hydrolysis liquor, treated and untreated SCBP, resulting in the removal of hemicelluloses to mainly produce xylose, glucose and arabinose during hydrolysis. The severity factors had no correlation to TRS yield, indicating that the simple kinetic processes of biomass solubilisation cannot perfectly describe the SCBP hydrolysis. The first-order kinetic model based on consecutive reaction was used to obtain rate constants, activation energies and pre-exponential factors.

1. Introduction

Sugarcane bagasse, the by-product of sugarcane extraction process, is mainly used in papermaking. About 40% of this residue is a smaller fiber, sugarcane bagasse pith (SCBP), which is removed during the process of producing pulp for papermaking to reduce paper brittleness. As most agricultural residues, SCBP is a lignocellulosic material primarily composed of lignin, cellulose, and hemicelluloses. About 209 million tons of SCBP was produced annually throughout the world, given that one ton of sugarcane produces 280 kg of bagasse (Sindhu et al., 2016). The most frequent use for SCBP is steam and electricity production by its combustion, which is a highly inefficient process and provokes a problem of pollution, increasing the emissions of CO2 (Gámez et al., 2006). Since it can easily be collected and readily available during the sugar production process, there is great interest in developing...
methods for the biological production of fuel and chemicals that offer economic, environmental, and strategic advantages. One of the high added value products which can be obtained from SCBP is reducing sugars, a biomass energy precursor that can be further transformed to fuel alcohol by fermentation or gaseous fuel by gasification (Zhu et al., 2011b).

In order to obtain reducing sugars from SCBP, the cellulose and hemicelluloses need to be hydrolyzed. The conventional methods are alkali, acidic, or enzymatic hydrolysis (Cardona et al., 2010). However, using concentrated acids, such as H₂SO₄ and HCl (Velmurugan and Muthukumar, 2011), requires corrosion-resistant reactors. These acids are also toxic and hazardous in nature. The major bottleneck to make enzymatic hydrolysis economically feasible is the long process time and the high cost of producing enzyme (Adsul et al., 2014). Sub- and supercritical water hydrolysis has been developed to be highly environmentally friendly and proven technically feasible in face of acid and enzymatic hydrolysis, with the advantages of short reaction times, less corrosion, no use of toxic solvents and chemical-free hydrolysis (Prado et al., 2014). Pressurised carbon dioxide has been used to acidify the medium through the formation of carbonic acid and to increase the efficiency of subcritical-water-mediated hydrolysis of biomass (Van Walsum et al., 2007; Cantero et al., 2013).

Sub- and supercritical water hydrolysis has been used to produce reducing sugars from agricultural residues, such as sugarcane bagasse (Vallejos et al., 2015), bean dregs waste (Zhu et al., 2011a), municipal solid waste (Goto et al., 2004), corn stalks (Zhao et al., 2009), wheat straw (Zhao et al., 2009), rice bran (Pourali et al., 2009; Baig et al., 2013), and other solid wastes (Prado et al., 2016). However, the application of sub- and supercritical water hydrolysis to agricultural residues is a challenging task because hydrolysis rates and yields depend on the characteristics of the residue, including cell wall composition and structure, as well as the monosaccharide present and the type of bonds between them. Therefore, each raw material represents a technological challenge that needs to be studied individually, since the optimal process conditions for a given raw material may not be the most efficient for other types of residues (Prado et al., 2014).

There is only limited information on the hydrolysis of SCBP in sub- and supercritical water, particularly in combination with the use of CO₂. This study aims to investigate the subcritical CO₂-water hydrolysis of SCBP to producing reducing sugars. In the present study, the orthogonal test method was applied to optimize the combination of process parameters: reaction temperature (A), liquid-to-solid ratio (B), CO₂ initial pressure (C), stirring speed (D) and reaction time (E) on total reducing sugars (TRS). The liquid products were analyzed and characterized by the 3,5-dinitrosalicylic acid (DNS) method and Fourier transform infrared spectrometry (FTIR). The treated and untreated SCBP samples were characterized using two-dimensional heteronuclear single quantum coherence nuclear magnetic resonance (2D HSQC NMR) analysis to help elucidate the physical and chemical characteristics of the raw material and the residual solid. The severity factors with the presence of temperature, time and carbonic acid were employed to choose the factor values in the orthogonal experiments and describe the hydrolysis process of SCBP. The hydrolysis kinetic of SCBP for obtaining the reaction kinetic parameters (i.e. rate constant, activation energy and pre-exponential factor) based on a simplified consecutive reaction model were investigated as well.

2. Materials and methods

2.1. Materials

The SCBP used as a raw material in this study was obtained from a local mill (Nan-Ning Sugar Mill, Guang-Xi, China). The component of SCBP was: cellulose (21.0%), hemicelluloses (40.2%) and lignin (17.8%) (Li et al., 2016). Xylose (>98%) was purchased from Toronto Research Chemicals (Toronto, Canada).

2.2. Experimental procedure

The hydrolysis of SCBP was carried out in a high pressure reactor (maximum working pressure 30.0 MPa and temperatures 500 °C, Dalian Jinyi Autoclave Vessel Manufacturing Co. Ltd., Dalian, China) equipped with a stainless steel 2 L reaction vessel. The reactor is equipped with a magnetic driven paddle agitator at the bottom, a temperature controller, a cooling coil, a heat exchanger, a CO₂ inlet, and a sampling device. The reactor was heated with the help of 1.5 kW electric heaters. Temperature inside the reactor was measured using a thermocouple and controlled at operating temperature. The reaction content was mixed continuously via magnetic driven stirrer at desired temperature. For reactions using CO₂, a stainless steel tubing connection equipped with a valve and pressure gage was fitted to the reactor to allow introducing of CO₂ from a gas cylinder. Initial pressure of the CO₂ was regulated using a high pressure regulator on reactor.

The hydrolysis process was run under batch mode. In the experiment, a set amount of the SCBP basing on the liquid-to-solid ratio and 1000 mL of water were introduced into the reactor. The reactor was then closed and capped tightly. The air was pumped out of the reactor to an absolute pressure of approximately 0.003 MPa and pressurized with CO₂ for 10 min. Then, the feeding was heated to the desired reaction temperature. The SCBP hydrolysis process was performed between 180 to 220 °C for 3–150 min reaction time at a stirring speed of 100–500 r min⁻¹. The reaction pressure is the vapor pressure of the system water–carbon dioxide at the reaction temperature. Reaction pressures ranged from 1.8 to 6.0 MPa.

At these conditions, liquid samples were collected through sampling device at different time intervals for DNS and FT-IR analysis. The power controller was switched off and the mixtures were naturally cooled up to room temperature. The hydrolysis mixtures were separated in a vacuum into solid and liquid solutions through filtration. Solid residues were placed in an oven at 80 °C for 8 h to dry the samples.

2.3. Analytical method

2.3.1. TRS analysis

The TRS concentration was estimated by the 3,5-dinitrosalicylic acid (DNS) method (Miller, 1959), using xylose as a standard. The hydrolysis liquor was diluted 10 times. For each 1 mL of the diluted liquor, 1.5 mL DNS reagent and 1 mL deionized water were added. The mixture was then heated in boiling water for 10 min until the red brown color was developed. Then, the mixture was cooled to room temperature in a water bath and diluted to 25 mL. The absorbance was then measured using an ultraviolet–visible spectrophotometer (UV-2100, Unico, Dayton, NJ, USA) at 508 nm. The TRS concentration was calculated based on the standard curve obtained with xylose as represented in Eq. (1).

\[
C_B = \frac{A}{0.36} \times 10
\]  

(1)

where \(C_B\) is the TRS concentration (g L⁻¹), \(A\) is the absorbance at 508 nm.

2.3.2. Fourier transforms infrared spectroscopy (FTIR)

FT-IR spectroscopy (Nicolet 380, Thermo Scientific, Waltham, MA, USA) was used to characterize the hydrolysis liquor. The liquor sample was mixed with spectroscopic grade dried KBr to create a disk. The spectra were collected in the spectral range
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