Biomass and Bioenergy 93 (2016) 227–242

Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: http://www.elsevier.com/locate/biombioe

Research paper

Biochemical conversion of sugarcane bagasse into bioproducts

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ARTICLE INFO

Article history:
Received 10 October 2015
Received in revised form
18 June 2016
Accepted 8 July 2016

Keywords:
Sugarcane bagasse
Soaking in aqueous ammonia treatment
Ethyl-hydro-oxides treatment
Pulp
Solvent based extract
Enzymatic saccharification at high substrate loadings

ABSTRACT

The ground sugarcane bagasse conversions were examined through chemical treatment methods employing soaking in aqueous ammonia (SAA), and ethyl-hydro-oxides (EHOs). To characterize a chemical treatment method, both generated solvent based extract and pulp were examined. The generated pulps were evaluated through chemical composition and enzymatic saccharification. The enzyme mixtures were investigated including *Trichoderma reesei* Rut C-30 originated cellulase, *T. reesei* Rut C-30 originated cellulase with external added β-glucosidase, Accellerase® 1500, and Cellic® CTec2. The physiochemical effects of chemical treatments on the structural-chemical properties of treated-bagasse were also analyzed at high substrate enzymatic saccharification. The substrate loadings (using both SAA-treated and EHOs-treated bagasse) of 125, 150, 175, 200, and 225 g L^{-1} were examined during enzymatic saccharification process. The generated phenolic compounds were characterized based on density, antioxidant activity, and anticancer activity. All findings are discussed in relation to developing a self-sustainable integrated biorefinery.

1. Introduction

Agriculture crops such as sugarcane, can be sustainably produced in large quantities in the tropical and sub-tropical regions of the world. The generated agriculture residues, such as sugarcane bagasse (after juice extraction), can be utilized in different industrial processes for paper pulp, (bio)-chemicals, and biofuels production. The polysaccharides and lignin contents of sugarcane bagasse ranges from 55 to 73 g (per 100 g of dried biomass) and 20–27 g (per 100 g of dried biomass), respectively. The major polysaccharide contents of sugarcane bagasse consist of 35–43 g cellulose (per 100 g of dried biomass), and 20–30 g hemicellulose (per 100 g of dried biomass) [1–8]. The composition of lignin in sugarcane bagasse consists of: gallic acid, protocatechuic acid, *p*-hydroxybenzoic acid, *p*-hydroxybenzaldehyde, vanillic acid, vanillin, syringic acid, syringaldehyde, *p*-coumaric acid, and ferulic acid [9]. Hydrocinnamic acids (*p*-coumaric acid and ferulic acid) are important antioxidants for the treatment of cancer and cardiovascular diseases [10]. *p*-Coumaric acid inhibits a growth of tumor cell and ferulic acid increases viable cell counts [11].

However, structural-chemical properties of lignocellulosic biomass provide a rigid framework of plant matter and inhibit its conversion. The cellulose content of sugarcane bagasse occurs in both crystalline (cellulose I) and amorphous contents. To access the crystalline polysaccharides content of lignocellulosic biomass, both physical and thermochemical treatments are required. A physical treatment, such as milling, is required to increase the surface area of the sized particle per unit of volume. Whereas, thermochemical treatments are required to convert polysaccharide content from crystalline to amorphous with lignin removal. Several different thermochemical treatments employing steam [1,7], sulfuric acid based reagent [4,12], soda-ethanol [3], alkaline hydroxide (including sodium hydroxide [6,8], and soaking in aqueous ammonia (SAA) [5]), and alkaline hydrogen peroxide [2] have been reported for sugarcane bagasse conversion. The effects of thermochemical treatments on structural-chemical properties of lignocellulosic biomass can be measured through X-ray diffraction, scattering electron microscopy, kappa number, and enzyme digestibility [1–8,12].

The selection of reactants in a solvent formulation is the most critical challenge towards complete utilization of lignocellulosic biomass. Based on the pH of the solution, the chemical treatment is either acidic or basic in nature. The breakage of bonds in

Abbreviations: SAA, soaking in aqueous ammonia; EHOs, ethyl-hydro-oxides.

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http://dx.doi.org/10.1016/j.biombioe.2016.07.015
0961-9534/

lignocellulosic biomass occurs due to formation of hydronium ions (in acidic pH) and hydroxyl ions (in basic pH). In order to understand different chemical treatments, it is important to have knowledge of the physio-chemical properties of reactants with reference to different fractions of lignocellulosic biomass (Table 1). A reduction in crystallinity (due to removal or alteration of hydrogen bonding) and a delignification (due to removal of phenolic compounds) of lignocellulosic biomass is dependent on an acid dissociation (pKa value) of reactant constituents in the chemical treatment formulation. A pKa value represents the strength of acid solution and directly proportional to Gibbs energy change [18]. Similar pKa values of two reactants indicate the maximum dissolution and interaction in a solution.

Water is the most polar solvent and form hydrogen bonding with cellulosic hydroxyl groups. However, the hydrophobic nature of lignin inhibits water molecule interaction with cellulose. To overcome the physical barrier of lignin on sugarcane bagasse conversion, steam (or liquid hot water) treatment is utilized at a high temperature of 180 °C for 20 min [1]. Steam treatment at high temperature penetrates lignocellulosic biomass through formation of a hydronium ion [1]. The steam treatment promotes hemicellulose degradation and transforms lignin, thereby increasing access to cellulose content [1]. The application of steam treatment on sugarcane bagasse removes 75% of xylan content and 25% of phenolic compounds without affecting its cellulose content [1]. During enzyme hydrolysis, steam treated bagasse converts up to 28% and 17% of total polysaccharides into fermentable sugars at substrate loadings of 100 g L^{-1} and 200 g L^{-1}, respectively [1]. Phosphoric acid and sulfuric acid (based reactants) have been used with water to enhance sugarcane bagasse conversion and to reduce processing temperature [4,7,12]. The paper pulp industry utilizes a combination of sulfuric acid and alkaline hydroxide based reactants at a temperature range of 120–150 °C for several minutes for sugarcane bagasse conversion [4,12]. The use of high temperature converts xylose (from hemicellulose) and glucose (from cellulose) to furfural and hydroxymethylfurfural, respectively [12]. Both furfural and hydroxymethylfurfural inhibit microbial fermentation towards biofuel production [12]. The generated lignin (through sulfuric acid based reactant) is mainly utilized by burning for production of steam in the paper pulp industrial processes. For biofuel production using herbaceous crops, SAA treatment (ammonium hydroxide concentration: 150–200 g L^{-1}) is an economically viable option due to moderate operating temperature (30–80 °C for 12–15 h), relative ease of solvent recovery and an abundance of ammonia as a commodity chemical. SAA treatment preserves cellulose and hemicellulose contents of lignocellulosic biomass in a solid state with removal of 60–70% of phenolic compounds [19–24]. During simultaneous saccharification and fermentation process, SAA-treated lignocellulosic biomass (with enzymatic xylan removal) at substrate loading of 283 g L^{-1} have been reported to produce 70 g L^{-1} of ethanol in the product stream [21]. No research has been found in the literature on properties of the generated lignin through SAA treatment towards a valuable byproduct development (such as pharmaceutical grade extract). On the contrary, sodium hydroxide treatment (concentration: 18–20 g L^{-1}, conditions: 80–110 °C for 1–6 h) using lignocellulosic biomass removes up to 67–76% of phenolic compounds and decreases hemicellulose content by 20–25% [6,8]. Moreover, sodium hydroxide treated lignocellulosic biomass have been reported in enzyme hydrolysis at high substrate loadings of 300–330 g L^{-1} [6,8]. The major difference between different reactant loadings and different processing times of ammonium hydroxide and sodium

Table 1
Physio-chemical properties of chemical reactants.[13–17]

Reactant	Molecular weight [g mol^{-1}]	Boiling point [°C]	pKa [25 °C]	Reference
Potassium hydroxide	56.1	1 327	16.0	[13]
Ethanol	46.1	78.2	15.5	[14]
Methanol	32.0	64.6	15.5	[14]
Sodium hydroxide	40.0	1 388	14.8	[14]
Water	18.0	100	14.0	[14]
Cellulosic hydroxyl group			14.0	[15]
Glucose	180.1		12.5	[14]
Xylose	150.1		12.1	[14]
Hydrogen peroxide	34.0	150.2	11.6	[14]
Lignin			10.0-11.0	[16]
Gallic acid	170.1		$pKa_1 = 4.2$, $pKa_2 = 8.3$, $pKa_3 = 9.2$	[17]
			($pKa_1 = 4.2$, $pKa_2 = 8.8$, $pKa_3 = 10.1$)	[17]
Protocatechuic acid	154.1		$pKa_1 = 4.4$, $pKa_2 = 8.7$, $pKa_3 = 10.7$	[17]
			($pKa_1 = 4.7$, $pKa_2 = 9.1$, $pKa_3 = 10.9$)	[17]
p-Hydroxybenzoic acid	138.1		$pKa_1 = 4.4$, $pKa_2 = 9.0$	[17]
			($pKa_1 = 4.7$, $pKa_2 = 9.2$)	[17]
Vanillic acid	168.1		$pKa_1 = 4.3$, $pKa_2 = 8.8$	[17]
			($pKa_1 = 4.6$, $pKa_2 = 9.2$)	[17]
Syringic acid	198.2		$pKa_1 = 4.2$, $pKa_2 = 9.0$	[17]
			($pKa_1 = 4.5$, $pKa_2 = 9.3$)	[17]
p-coumaric acid	164.1		$pKa_1 = 4.4$, $pKa_2 = 8.4$	[17]
			($pKa_1 = 4.6$, $pKa_2 = 9.4$)	[17]
ferulic acid	194.2		$pKa_1 = 4.6$, $pKa_2 = 8.6$	[17]
			($pKa_1 = 4.8$, $pKa_2 = 8.9$)	[17]
Ammonium hydroxide	35.0	24.7*	9.2	[14]
Phosphoric acid	98.0	407	$pKa_1 = 2.1$, $pKa_2 = 7.2$, $pKa_3 = 12.4$	[14]
Sulfuric acid	98.1	337	$pKa_1 = -3.0$, $pKa_2 = +2.0$	[14]

Note
*The boiling point corresponds to 350 g L^{-1} of ammonium hydroxide solution.
Bracketed pKa values are listed using 20% aqueous methanol solvent, otherwise using water solvent.