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Sugarcane bagasse mild alkaline fractionation and production of purified fractions by pulse chromatography with water

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ABSTRACT

Sugarcane bagasse (SCB) was treated under mild alkaline conditions (solid:liquid ratio of 1:20 (w/v), 1.5% NaOH (w/v), 60 °C, 6 h) to fractionate the lignocellulose in order to produce a typical mild alkaline extract from a lignocellulosic biomass. The solid residue was enriched in cellulose, while the SCB alkaline extract contained lignin and hemicelluloses, but also inorganic salts, five phenolic monomers and acetic acid. After concentration of the alkaline extract by evaporation, low pressure chromatography with water as eluent was performed to produce purified fractions. Two different strong acid cation (SAC) exchange resins were tested: one gel-type resin and one macroporous-type resin. The lignin and hemicelluloses were separated from the inorganic salts by the gel-type SAC exchange resin. On this resin, the phenolic monomers were partitioned regarding the presence or absence in their structure of a carboxyl group. On the macroporous-type SAC exchange resin, the largest sugar oligomers and lignin oligomers were obtained in a fraction free of inorganic salts, phenolic monomers and acetic acid.

1. Introduction

Sugarcane was the most produced crop in the world in 2013 with 1.9 billion tons (FAO, 2015). Sugarcane bagasse (SCB) is a lignocellulosic by-product of the sugar and alcohol industry from sugarcane, and is nowadays mainly burnt to produce electricity. However, in the last decade, SCB has been widely studied as a substrate to produce ethanol by fermentation of the glucose coming from the cellulose, or of the other C6 and C5 sugars coming from the hemicelluloses (Cardona et al., 2010). The pretreatment of the incoming lignocellulosic material into the second generation ethanol biorefinery, consisting in the separation of the three main components, cellulose, hemicelluloses and lignin, is a key step for economic viability and environmental efficiency in the overall process (Mosier et al., 2005; Yang and Wyman, 2008). Acidic conditions for the pretreatment were extensively studied and have been applied industrially for twenty years, and present the advantage of obtaining monomeric sugars in a single step process (Farone and Cuzens, 1997; Mosier et al., 2005).

Chromatography was investigated to purify the monomeric sugars resulting from lignocellulosic biomass treatment by concentrated acid (usually H_2SO_4 at 70–75%), using gel-type SAC exchange resin under H^+ form and water as eluent (Neuman et al., 1987; Hester et al., 1995). Monomeric sugars can be separated from sulfuric acid and other impurities such as acetic acid, furfural and hydroxymethylfurfural (HMF) (Heinonen and Sainio, 2010). Once the acid and other impurities are removed, the mixture of sugars can be purified by another chromatographic step with water as eluent. When the monomeric sugars are a mixture of glucose, xylose and arabinose, gel-type SAC resin with Ca^{2+} as counter ion was found to be the most efficient resin for their separation (Caruel et al., 1991; Lei et al., 2010; Chen et al., 2018). However, prior to this second chromatographic step, the extract had to undergo decationization through ion exchange and neutralization with the addition of NaOH inducing extra economic and environmental cost to the process (Lodi et al., 2017).

Inspired from pulp and paper processes, alkaline pretreatment is gaining importance in the second generation ethanol biorefinery (Hayes, 2009) due to improved overall ethanol yields (Saha and Cotta, 2007; Kim et al., 2016), mild reaction conditions and possible valorization of the solubilized lignin and hemicelluloses (Cardona et al., 2010; Kim et al., 2016). Among the different alkaline pretreatments mentioned in the literature, mild sodium hydroxide conditions appear to lead to the highest lignin and hemicelluloses extraction yields at reasonable costs (Peng et al., 2012; Kim et al., 2016). These conditions also induce the hydrolysis of ester bonds – between hemicelluloses and lignin, phenolic monomers and lignin, and acetate groups from hemicelluloses (Xiao et al., 2001; Chen et al., 2012). Purifying the alkaline

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extract components to enable their further valorization is of major importance to give value to the whole process of lignocellulosic ethanol production after alkaline pretreatment (Ragauskas et al., 2014).

Recovery of lignin or hemicelluloses from lignocellulosic alkaline extracts (black liquors in the pulp and paper industry) have been investigated by acid precipitation (Uloth and Wearing, 1989; Sun and Tomkinson, 2001), ethanol precipitation (Peng et al., 2009; Bian et al., 2012) and membrane filtration (Uloth and Wearing, 1989; Wallberg et al., 2003). However, purification through precipitation led to high chemical consumption, while membrane filtration generated fractions of mediocre purity due to difficult salt removal. Resin adsorption process has also been investigated either for the production of pure phenolic compounds such as *p*-coumaric acid (*p*-CA) (Ou et al., 2009) and ferulic acid (FA) (Ou et al., 2007), or for hemicelluloses purification (Zeitoun et al., 2010). These operations can lead to high economic and environmental costs through a significant consumption of chemicals and numerous process steps - loading, rinsing, desorption, regeneration, equilibration - and so far, no industrial development has been reported.

Chromatography is an interesting alternative purification technique, implying both size exclusion and ionic repulsion phenomena. It presents the advantage of using only one eluent and an easier process set-up - loading, elution - both for batch (pulse chromatography) and continuous process (Sequential Moving Bed). However, unlike for lignocellulosic acid extracts, very few studies can be found on chromatography to purify lignocellulosic alkaline extracts. In the case of liquors from soda-anthraquinone pulping process, separation was not performed directly on the alkaline extract. The media was first treated with acid until pH 1.2 to precipitate the lignin, then by chromatography on SAC exchange resin with water as eluent at 65 °C to specifically separate aliphatic carboxylic acids from sodium sulfate (Alén et al., 1991). More recently, chromatography was tested on a corn stover alkaline extract, but mesoporous silica materials were used as stationary phase, acidic water or organic solvent as mobile phase and the goal was to specifically separate monomeric C5 sugars from monomeric C6 sugars (Modenbach, 2013).

This paper focuses on the purification of raw SCB extract, obtained under mild alkaline conditions, to give a higher value to the overall biorefinery scheme. Pulse chromatography, using water as mobile phase and SAC exchange resins as adsorbents was studied in order to produce purified fractions from the SCB alkaline extract, composed mainly of lignin oligomers, hemicelluloses, acetic acid, phenolic monomers and inorganic salts.

2. Materials and methods

2.1. Chemicals

Sodium hydroxide (≥98.5%), sulfuric acid 72% for analytical hydrolysis, sulfuric acid 95% and acetonitrile (≥99.9%) to prepare HPLC eluents, and methanol (≥99.8%) used as a tracer for column void volume, were purchased from VWR. Calcium carbonate (≥98.5%) was purchased from Merck. HPLC standards: D-(+)-cellobiose (≥98%), D-(+)-glucose (≥99.5%), D-(+)-galactose, L-(+)-arabinose (99%), D-(+)-xylose (99%), D-(+)-mannose (≥99%), fructose (≥99%), acetic acid (≥99%), furfural (99%), 5-hydroxymethyl-2-furfuraldehyde (99%), gallic acid (97%), 4-hydroxybenzoic acid (≥99%), caffeic acid (≥98%), vanillic acid (97%), syringic acid (≥95%), 4-hydroxybenzaldehyde (98%), vanillin (99%), *p*-coumaric acid (≥98%), syringaldehyde (99%), *trans*-ferulic acid (≥99%), sinapic acid (≥98%), trans-3-hydroxycinnamic acid (99%), were all purchased from Sigma Aldrich. Blue Dextran, 2,000,000 Da molecular weight, came from Sigma Aldrich too. Both SAC exchange resins, XA2004-30Na$^+$ and XA2054Na$^+$ (Table 1) were provided by Novasep Process, France.

Table 1
Characteristics of the resins.

	XA2004-30Na$^+$	XA2054Na$^+$
Nature	SAC	SAC
Matrix	Styrene + DVB	Styrene + DVB
Type	Gel (pore size: 3 nm)	Macroporous (max pore size: 20–50 nm)
Active site	-SO_3^-	-SO_3^-
Capacity	1.4 Eq/L	1.1 Eq/L

2.2. Alkaline extraction

Dry SCB was provided by eRcane (La Réunion, France) and ground on a 2 mm mesh by a knife mill (Mill F6 N V, Electra). The alkaline extraction conditions are based on Sun et al., (1995) to optimize the extraction yield of lignin and hemicelluloses (Sun et al., 1995). The conditions were the following: 150 g of SCB in 3 L of sodium hydroxide solution at 1.5% (w/v) in a 4 L jacketed glass reactor, leading to a solid:liquid ratio of 1:20 (w/v) and a NaOH:SCB ratio of 0.3:1 (w/w), under continuous stirring (200 rpm) for 6 h at 60 °C. The SCB solid residue was removed from the alkaline extract on Whatman filters grade 3 (150 mm diameter) on a Büchner filtration device, then dried at 50 °C for 48 h and finally ground by a microfine grinder (IKA MF 10 basic) on a 1 mm sieve prior to analysis. The filtrated alkaline extract was concentrated by Rotavap at 55 °C under 100 mbar. A dry solid content of at least 20% is generally required to reach a good productivity on the chromatographic purification step and make it economically viable at industrial scale.

2.3. Pulse tests

Pulse tests were run on 500 mL resin packed in a 1 m high and 26 mm diameter jacketed glass column. Two resins were tested, their characteristics are indicated in Table 1. Both resins are under Na$^+$ form as the main cation in the alkaline extract is Na$^+$ due to the sodium hydroxide introduced during the extraction step. The resin was mixed with water at 60 °C for degassing and packed from the top of the column. The upper piston was brought as close as possible to the top of resin to minimize the dead volume. A Y-valve successively enabled the injection of 5 mL feed (Blue Dextran, methanol, synthetic solutions or concentrated alkaline extract) or eluent (distilled water) on top of the column. The eluent was circulated from the top to the bottom of the column thanks to a peristaltic pump and its volume was accounted as resin Bed Volume (BV). The temperature of the column was maintained at 40 °C thanks to a water bath. At the outlet of the column, a fraction collector (GradiFrac, from Pharmacia Biotech) was set to collect 15 mL fractions representing 0.03 BV. The collected samples were analyzed after the run was completed. Blue Dextran (Sigma Aldrich, France) at 0.1% (w/v), was used to determine the void volume of the resin bed (i.e., inter-particles porosity), as it cannot enter the pores of the resins (2,000 kDa molecular weight) or interact with the resin matrix (Ladisch, 2001). A pulse test was also run with methanol at 5% (v/v) in order to determine the total void volume of the resin bed (i.e., inter- and intra-particles porosity), since methanol, a small uncharged molecule, can penetrate all the pores of the resins without adsorbing on the styrene-DVB matrix of the resins thanks to its polarity (Lodi et al., 2017).

2.4. Analytical methods

2.4.1. Dry solid and ash

Dry solid (DS) content was gravimetrically determined at 103 °C for 12 h and ash content at 500 °C for 12 h. The conductivity (mS/cm) was measured for every fractions of the pulse tests and converted into ash concentration (g/L) from a linear relationship with a coefficient of 0.443.