



Kinetic study of the extraction of hemicellulosic carbohydrates from sugarcane bagasse by hot water treatment



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ABSTRACT

Sugarcane bagasse is a lignocellulosic agro-industrial waste, which is usually burned in the sugar and bio-ethanol mills to produce heat and electricity. This work presents the kinetic study of the carbohydrates extracted from the mild hot water pretreatment of sugarcane bagasse, to explain the variation of hemicellulosic carbohydrates during the treatment. This could allow the selection of optimum conditions to obtain the desired products in spent liquors, as high concentration of xylans and low concentrations of fermentation inhibitors. Sugarcane bagasse was hydrothermally treated under isothermal conditions at 160, 170, and 180 °C, using a liquid to solid ratio of 14:1. Glucans, xylans, arabans, xylose, glucose, arabinose, acetic acid, formic acid, HMF and furfural were first identified in the spent liquor. A kinetic model was applied, considering the direct extraction of xylose and oligomers from the solid, xylose production from the oligomers, and furfural generation from xylose. It was supposed that the reaction rate constants have first-order kinetics. The fractionation by hydrothermal treatment has proven to be effective for hemicelluloses removal. Most glucans were retained in the solid, and a partial delignification (at 180 °C, 9.8% and 36.3% of the initial lignin at 20 and 240 min, respectively) was achieved. The maximum concentration of xylans in spent liquors with the low furfural content (0.5% on oven dry bagasse) was achieved at 180 °C and 20 min of treatment (17.6% on oven dry bagasse, about 74% of the initial amount). An activation energy of 128.8 kJ mol⁻¹ has been obtained for the fast hydrolysis of xylans from sugar cane bagasse. The maximal concentration of xylans + xylose in liquors was obtained with a *P*-factor of 800.

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1. Introduction

Lignocellulosic biomass is an important sustainable resource of carbohydrates (cellulose and hemicelluloses) due to its renewable nature. Its use allows the production of fuels, cellulosic pulp, biomaterials and a variety of chemicals. Lignocellulosic residues generated by agroindustry are available in large quantities at low cost. The fractionation of this waste in its main components would allow the production of chemical intermediates for the manufacture of various products.

Sugarcane bagasse is an important lignocellulosic waste in South America which account about 50% of the world's sugarcane production (about 0.8 billion tonnes in 2012) (FAO, 2014).

Bagasse is usually burned in sugar or bioethanol mills to produce heat and electricity. It is composed of 32–45% cellulose, 19–24% lignin, 27–32% hemicelluloses (mainly xylans) and minor amounts of extractives and inorganic compounds (Novo et al., 2011; Area et al., 2009; Vallejos et al., 2012). It can, therefore, be an adequate source of glucose for the production of second-generation ethanol and xylose for xylitol (Garrote et al., 1999).

Conventional pulping processes fractionate biomass to obtain a pulp rich in cellulose, and energy through burning lignin and other chemical components. An alternative to further enhance value is to separate all components using sequential processes, and produce high value products that can be used in different applications to improve the profit. This is the conceptual background of the technologies based on the bio-refinery concept.

The commonly used pretreatments to fractionate lignocellulosic biomass are essentially hydrolytic either in acidic or basic media, or catalyzed by enzymes.

Xylans can be depolymerized and extracted from biomass in a strong alkali media, but the reaction products are highly degraded,

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completely deacetylated and their solubility in water is limited (Patil, 2012; Li Jansson and Brannvall, 2011). On the contrary, autohydrolysis occurs in mild acid medium due to the partial breakdown of acetyl groups, and acetic acid release. Moreover, the autohydrolysis at mild temperatures produce high molecular weight xylo-oligosaccharides, without substantially modifying the cellulose and lignin, which allows their recovery for further processing (Garrote et al., 1999). Fractionation by hot water is environmentally friendly since uses pressurized hot water at moderate times and temperatures. It has proven to be effective and selective to remove hemicelluloses present in the lignocellulosic material, as is extensively discussed in the literature (Garrote et al., 1999; Allen et al., 1996).

Water is the best green solvent to be used in biorefinery because of its environmental benefits, safety and low cost. It has been classified recently as a recommended solvent by a survey of solvent selection guides (Prat et al., 2014; Amidon and Liu, 2009). Hot water treatment avoids the use of corrosive reagents for the hydrolysis of xylans to reducing sugars. In addition, autohydrolysis at mild conditions (short times and temperatures under 200 °C, without catalyst) does not modify cellulose and lignin substantially, which can allow their recovery for further treatments and utilization (Qing et al., 2013).

After the hydrolytic pretreatment, the solid fraction (mainly cellulose) is filtered to separate the liquid fraction (spent liquor), rich in xylo-oligomers and sugars derived from hemicelluloses (xylose and arabinose). The chemical and porosity of the solid fraction (lignocellulosic material) has been modified, allowing for a more efficient delignification. Treating the material with adequate reactives in subsequent biorefinery processing, allow to obtain cellulose and lignin fractions of higher added value than the currently available industrial ones (Bujanovic et al., 2012; Bozell and Petersen, 2010).

In the autohydrolysis processes using pressurized hot water, hydronium ions from generated compounds (acetic, uronic, and phenolic acids) catalyze the hydrolysis of the hemicelluloses (Garrote et al., 1999). These processes increase cellulose accessibility, and allow pentosans recovery ($\geq 90\%$), producing hydrolysates almost free of fermentation inhibitors. Hemicelluloses structure and composition vary according to the origin of the lignocellulosic material and in different parts within the same material. The hydrolysis reactions generate a random cleavage of the hemicelluloses, depending of their chemical structure, so the understanding of differences in the hydrolysis reactions allows maximization of biomass use.

Modelling of the changes in the composition of the lignocellulosic materials during the hydrolysis treatment is applied to design and optimize the conversion processes. Kinetic models and severity parameters are different mathematical methods to describe the hydrolysis of hemicelluloses. Severity parameters have been used to compare different pretreatment strategies, whilst kinetic models have been applied to describe the changes of hemicelluloses by hydrolysis in function of treatment conditions (Sixta et al., 2006; Wang et al., 2011).

The effect of time and temperature on the intensity of the hot water treatment can be described by the prehydrolysis factor (*P*-factor) based on the Arrhenius equation. *P*-factor is used to compare the hot water treatments performed at different temperatures and to predict the solubilisation of hemicellulosic components during acid treatments. This factor is similar to the *H*-factor used in the pulp and paper industry (Sixta et al., 2006).

The kinetics of the hydrolysis reaction for extraction of hemicelluloses from sugarcane bagasse using diluted sulphuric acid has been widely studied due its high reaction rates and high extraction yields (Aguilar et al., 2002; Ávila Rodrigues and Guirardello, 2008; Sasikumar and Viruthagiri, 2008; Canilha et al., 2011; Cardona et al.,

2010). However, this pretreatment has some drawbacks, as: (i) its high cost, (ii) its high liquid–solid ratio, making necessary a subsequent concentration of sugars for their recovery, and (iii) the high formation of degradation products, inhibitors of the fermentation (Cardona et al., 2010).

Several kinetic models for autohydrolysis have been proposed to describe the hydrolysis reactions of wood and grass species, and to optimize the production of xylo-oligosaccharides and xylose. Nevertheless, no works on kinetic of autohydrolysis reactions of sugarcane bagasse have been found (Kabel et al., 2002; Nabarlitz et al., 2004; Gullón et al., 2009; Carvalheiro et al., 2004; Garrote et al., 2001; Zhuang et al., 2009).

This work presents the kinetic study of mild hot water pretreatment of sugarcane bagasse, to explain the variation of hemicellulosic carbohydrates released during the treatment. This could allow the selection of optimum conditions to obtain the desired products in spent liquors, as high concentration of xylans and low concentrations of fermentation inhibitors.

2. Experimental

2.1. Raw materials

Sugar cane bagasse was supplied by a local mill (San Javier Sugar Mill, Misiones, Argentina). Bagasse pith was removed in two stages. In the former, bagasse was wet-depithed to break its structure in a Bauer disc refiner (plate gap of 0.01 in), after which the bagasse pith was removed by screening, using a plate with 2 mm wide slits (Wenmber). Finally, depithed bagasse was centrifuged and preserved in a refrigerator. The pretreatments were performed in a MK digester with a capacity of 7 L using 350 g OD of bagasse.

2.2. Hot water pretreatment

The conditions of hydrothermal pretreatments were: water/dry bagasse ratio: 14/1, maximum temperatures: 160, 170 and 180 °C, maximum time at temperature: 4 h.

As a fraction of the hemicelluloses (mainly xylans) was hydrolyzed in the pre-heating step (time to reach the maximum temperature), the initial time (0 min) for the isothermal process was set after the initial 60 min.

Samples of liquor were obtained at different times of treatment, and the content of organic compounds was determined. The remaining xylans in the solid were calculated by subtracting the xylans, xylose and furfural present in the liquor (all species expressed as xylose) to the xylans content (expressed as xylose) in raw material.

2.3. Analysis of liquor samples

The samples were characterized by the determination of sugars content (glucose, xylose, and arabinose) and degrading products: furfural, 5-hydroxymethylfurfural and organic acids (formic and acetic), according to Technical Report NREL/TP-510-42623 (January 2008) “Determination of Sugars, Byproducts, and Degradation Products in Liquid Fraction Process Samples”, National Renewable Energy Laboratory.

The quantification of sugars, organic acids and degradation products was carried out by HPLC liquid chromatography (Waters HPLC System), using an Aminex-HPX87H column (BIO-RAD) with the following chromatographic conditions: H₂SO₄ 4 mM as eluent, 0.6 mL min⁻¹, 35 °C and refractive index and diode array detectors. The structural carbohydrates in the raw material and in the pretreated solid (glucans, xylans, arabans and acetyl groups) were

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