



Hydrothermal production and gel filtration purification of xylo-oligosaccharides from rice straw



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ABSTRACT

Hydrothermal treatment (autohydrolysis) is an advantageous alternative to fractionate biomass that was not yet explored for rice straw. In this work, the process was optimised and proved to be highly selective towards hemicellulose. Hydrolysates containing a mixture of oligomeric compounds (mainly xylo-oligosaccharides, XOS), could be obtained under relatively mild operation conditions (210 °C, $\log R_0 = 3.59$), yielding a maximum of 40.1 g/100 g of initial xylan. The produced XOS were separated by molecular mass using gel filtration chromatography (GFC). Different fractions of purified XOS were obtained ranging from small polysaccharides and high DP oligosaccharides ($DP \geq 23$), to medium and low DP oligosaccharides ($DP \geq 3$), and separated fractions of by-products (acetic acid, furan derivatives and phenols) as well as di-, and monosaccharides. GFC was an efficient purification method enabling the recovery of interesting categories of XOS that can have potential applications to the pharma, food and feed industries.

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1. Introduction

Agricultural residues and by-products have gained increased attention as potential substrates for the production of fuels, chemicals and bio-materials (Kamm and Kamm, 2007).

Rice is one of the major grain crops worldwide and its residues (straw and husks) are produced in large quantities. Rice straw is usually considered a residue or even a waste material although it may be used as mulching material, feed, compost substrate, cattle house flooring, as well as for straw handicraft and combustion (Kadam et al., 2000; Matsumura et al., 2005). But, conversely to other similar materials, the use of rice straw for feeding or for combustion for energy production may cause problems due to its high silica content (Domínguez-Escribá and Porcar, 2009) and thus most of this material is left unused in the fields.

An alternative for rice straw valorisation can be the production of oligosaccharides within the biorefinery framework along with the production of biofuels. Rice wastes can be a major single feedstock for bioethanol production as both straw and husks have high polysaccharide and low lignin contents, with the straw presenting higher hemicellulose content (Binod et al., 2010;

Domínguez-Escribá and Porcar, 2009). Prior to bioethanol production, several pretreatments have to be applied to rice straw in order to increase its upgradability. Previously studied pretreatments mainly include dilute acid, alkali (including ammonia) and enzymatic methods (Binod et al., 2010). However such pretreatments are expensive and/or time-consuming, not selective, require neutralisation, or result in the formation of by-products that can inhibit subsequent fermentation. Furthermore, none of these methods is suitable for oligosaccharides production from biomass, as either they degrade oligosaccharides (dilute acid hydrolysis), are not selective (alkaline treatments), or present very low yields (enzymatic processes).

An alternative option for the valorisation of rice straw under the biorefinery approach is the hydrolysis of hemicellulose by hydrothermal processing (autohydrolysis), which is an effective pretreatment enabling a high recovery of soluble saccharides in oligomeric form. Since no chemicals other than water are added, hydrothermal processes have important advantages over the processes referred above. Nevertheless, as demonstrated by reported data in the literature for other materials, e.g. corn straw (Moniz et al., 2013), corn cobs (Moura et al., 2007), wheat straw (Carvalheiro et al., 2009), brewery's spent grains (Carvalheiro et al., 2004), or eucalypt wood (Garrote and Parajó, 2002), the careful optimisation of the operational conditions is of paramount importance to achieve a high yield and the balanced distribution

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of oligosaccharides degree of polymerisation (DP) for each material. XOS are potentially bioactive compounds, as they can be used as food ingredients and classed as nutraceuticals. In fact, XOS are receiving substantial attention due to their functional properties and health benefits as active ingredients in functional foods (Carvalho et al., 2013; Moura et al., 2008; Nabarlatz et al., 2007; Vazquez et al., 2005). As compared to the many existing oligosaccharides in the market, XOS are the only oligosaccharides that can be produced from lignocellulosic biomass residues. Other oligosaccharides are produced from sugars used in food such as sucrose, lactose, inulin and starch or from soy (Moreno et al., 2014; Rastall, 2010) and are mainly produced by enzymatic processes synthesis/hydrolysis, making XOS a particular case among oligosaccharides. Chemically, XOS are oligomers containing 2–10 xylose molecules linked by β -1-4 glycosidic bonds (IUPAC, 1980), but molecules with DP higher than 20 have also been considered as oligosaccharides (Moure et al., 2006; Vazquez et al., 2005). The biological activity of XOS depends on its molecular weight (DP) distribution and prebiotic properties, i.e. those associated to the proliferation of beneficial microorganisms in human gut such as bifidobacteria (Hughes and Kolida, 2007). Low/medium DP oligosaccharides have been described as promising fermentable substrates (Moura et al., 2007; Moure et al., 2006).

Besides the selective hydrolysis of hemicellulose aiming at oligosaccharides production, the autohydrolysis process also enables the recovery of cellulose and lignin in a solid phase in advantageous conditions for further processing, i.e. towards an integrated valorisation in a biorefinery approach.

Several strategies may be used for XOS purification. These include membrane separation or chromatographic techniques (Cara et al., 2012; Gonzalez-Munoz et al., 2013; Moure et al., 2006; Vegas et al., 2004). Membrane technologies have had an increased interest in recent years since they may be less expensive although the separation of XOS can be affected by the structural characteristics of the oligosaccharides and even by their solubility (Pinelo et al., 2009). Sequential membrane-based steps for concentration and fractionation to achieve XOS fractions free from monosaccharides and by-products have been employed in multistage purification processes (dos Santos et al., 2011; Gonzalez-Munoz et al., 2013). Conversely, to membrane processes, the less explored chromatographic separation has the potential advantage to yield XOS with high purity and separated by molecular weight and/or chemical structure. In this work, rice straw was subjected to autohydrolysis at different final temperatures (150–240 °C) and the optimal operational conditions leading to the maximal recovery of XOS were established. The yields and composition of both liquid and solid phases were evaluated, and the yields of the solubilised products, namely oligosaccharides, monosaccharides, acetic acid and degradation compounds, such as furfural and HMF were determined and interpreted using the severity factor ($\log R_0$) (Overend and Chornet, 1987). The XOS-rich hydrolysates were further purified by GFC and the target fractions were characterised in terms of XOS content and degree of polymerisation.

2. Materials and methods

2.1. Raw material

Rice straw was supplied by Orivárzea (Salvaterra de Magos, Portugal) as a heterogeneous sample containing stalks and leaves as the field agricultural residue after crop harvest. The raw material was air dried and milled with a knife mill (Fritsch Industriestr., Germany) to particles smaller than 6 mm. The material was homogenised in a combined lot, and stored in plastic containers at room temperature.

2.2. Hydrothermal processing of rice straw

Autohydrolysis treatments of rice straw were performed in a stainless steel reactor (Parr Instruments Company, USA) with a total volume of 600 mL. Temperature was controlled through a Parr PID controller (model 4842). The raw material (25 g) was mixed with water in the reactor to reach a liquid-to-solid ratio of 10 (g water/g dry raw material). The agitation speed was set at 150 rpm and the reactor was operated under non-isothermal conditions, i.e. heated to reach final temperatures and rapidly cooled down. Several treatments were performed to study different final temperatures ranging between 150 and 240 °C. Typically, the average heating rate (from 100 °C onwards) was 4 °C min⁻¹ and the average cooling rate (down to 100 °C) was 25 °C min⁻¹. The liquid and solid phases were separated by pressing (up to 200 bar) using an hydraulic press (Sotel, Portugal). The liquid phase was filtered (Whatman filter paper no. 1) and the solid phase was washed with twice the amount of water, filtered, dried at 40 °C and stored, at room temperature, until further use.

The effects of temperature on rice straw autohydrolysis were interpreted based on the severity factor, $\log R_0$ (Overend and Chornet, 1987) defined as:

$$R_0 = \int_0^t \exp\left(\frac{T(t) - T_{\text{ref}}}{14.75}\right) dt$$

where the temperature T (°C) is a function of time t (min) and T_{ref} is the reference temperature (100 °C). The value 14.75 is an empirical parameter related with activation energy and temperature.

2.3. Gel filtration chromatography (GFC)

The preparative gel filtration chromatography for the purification of XOS was carried out in an Amersham Pharmacia Biotech system (Sweden) equipped with a refractive index (K-2401 Knauer, Germany) detector. A 400 mL sample of rice straw hydrolysate obtained under the optimised condition of 210 °C (see Section 3) was eluted with deionized water at a flow rate of 25 mL min⁻¹ through a BPG 100/950 column (Amersham Pharmacia Biotech, Sweden) with a Superdex 30™ gel bed volume of 4.2 L, suitable to separate the target XOS from the lower molecular weight carbohydrates, phenolic compounds, acetic acid, and furan derivatives (HMF and furfural). The sample was fractionated into 28 fractions of 125 mL, and collected every 5 min using a Super-frac™ collector (Amersham Pharmacia Biotech, Sweden). All fractions were freeze-dried (Labconco, Missouri, USA) and weighted for mass quantification. After analytical determination it was verified that the sample started to elute only after a 30 min running period, corresponding to an elution volume of 1250 mL. The carbohydrates were separated according to their molecular size. The smallest molecules, such as the monosaccharides, were the last to be eluted, after the disaccharides, whereas the higher molecular weight compounds were the first to elute.

2.4. Analytical methods

2.4.1. Chemical characterisation of raw material and processed solids

The materials were ground in a knife mill (IKA, Germany) to a particle size smaller than 0.5 mm and the moisture content was determined by oven-drying at 100 °C to constant weight. The ash content was determined at 550 °C using NREL/TP-510-42622 protocol (Sluiter et al., 2005). For extractives determination, the samples were successively extracted with dichloromethane, ethanol, and water (during 8 h, 8 h and 16 h, respectively), with a Soxtec extraction system.

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