



# Agricultural residue valorization using a hydrothermal process for second generation bioethanol and oligosaccharides production



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## HIGHLIGHTS

- An environmentally friendly process for barley straw valorization has been developed.
- High amounts of xylooligomers have been obtained.
- Fed batch simultaneous saccharification and fermentation was optimized.
- 52 g ethanol/L was obtained working at high solids loading (4 g liquid/g solid).

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## ABSTRACT

In the present work, the hydrothermal valorization of an abundant agricultural residue has been studied in order to look for high added value applications by means of hydrothermal pretreatment followed by fed-batch simultaneous saccharification and fermentation, to obtain oligomers and sugars from autohydrolysis liquors and bioethanol from the solid phase. Non-isothermal autohydrolysis was applied to barley straw, leading to a solid phase with about a 90% of glucan and lignin and a liquid phase with up to 168 g kg<sup>-1</sup> raw material valuable hemicellulose-derived compounds. The solid phase showed a high enzymatic susceptibility (up to 95%). It was employed in the optimization study of the fed-batch simultaneous saccharification and fermentation, carried out at high solids loading, led up to 52 g ethanol/L (6.5% v/v).

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## 1. Introduction

During this century, due to depletion of traditional energy sources, and the need of an environmentally sustainable economy, structural changes in the global economy will be mandatory. According to the analysis of the Energy Watch Group (Zittel et al., 2013) it is quite likely that, in 2030, world oil production will have declined by 40% compared to 2012. This situation will be a problem for the supply of energy and materials, and requires a transition to an economy based on renewable sources. By 2030, the European Union expects an increase up to the 30% of heat and power generated from biomass (Star-COLIBRI, 2011). One of the most promising options is the second generation bioethanol.

The bioethanol production from biomass is an important alternative to fossil fuels that will ensure the supply, reduce the greenhouse emissions and dependence on imports and can be easily implemented in current vehicles with few modifications (Cook and Devoto, 2011).

Biomass can be obtained from several sectors, but agricultural residues are expected to play a major role in the future biorefineries (Star-COLIBRI, 2011). There is a considerable interest in using straw, a byproduct, for industrial fiber or biofuel (ethanol) production (Soon and Lupwayi, 2012). Cereal straw is a residue of harvesting obtained in important amounts that constitutes a considerable biomass resource which could be used as an important byproduct for bioethanol production. A part of these residues is burnt *in situ*, producing non-desirable emissions, or used as animal feed, but it presents a low nutritional value and digestibility (López et al., 2005). Barley is an abundant cereal with a yearly world production of 142 ± 2 million tons (average value of the last 20 years, according to FAO). Spain is the fifth largest world producer, with an

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average value of  $8.5 \pm 0.4$  million tons per year. The main byproduct of barley is straw, with a ratio of up to 0.53 kg straw/kg grain (Larsen et al., 2012) that implies a high amount of barley straw (up to 4.505 million tons/year in the case of Spain), which can be an important and cheap source of lignocellulosic raw material for second generation bioethanol production.

For the conversion into liquid fuels, lignocellulosic materials (LCM) must be broken to obtain the sugar monomers that can be used by the microorganisms. The enzymatic hydrolysis is the most common method used for the conversion to sugars, which can be further fermented to ethanol or other valuable chemicals. However, enzymatic hydrolysis without pretreatment is not so effective because of the high stability of the materials to enzymatic attacks due to their structure and composition (Taherzadeh and Karimi, 2008). Some of the major problems for the enzymatic hydrolysis are the crystallinity, the degree of polymerization, the surface area, and the LCM composition. The hemicelluloses prevent the access of enzymes to the cellulose surface, and consequently they have been found to be physical barriers in the hydrolysis of the cellulose (Zhang et al., 2012). The hemicellulose fraction removal increments the pore size of the substrate, increasing the hydrolysis owing to a better access of the enzymes to the cellulose (Hendriks and Zeeman, 2009). Thus, a pretreatment becomes necessary in order to disrupt the cellulose structure and remove some of the compounds that can be inhibitors in the fermentation to ethanol.

The pretreatment, necessary for the production of second generation bioethanol from LCM, is one of the most important and expensive stages and it has a high incidence in the operational cost (Wyman et al., 2005; Krishnan et al., 2010; Romaní et al., 2010). Although there is a wide variety of methods for pretreatment, liquid hot water extraction (autohydrolysis) has many advantages over other treatments. The autohydrolysis not only produces a substrate easy to hydrolyzed, but it is also an economic pretreatment, with reduced chemicals consumption. Besides, all the fractions can be recovered and used for obtaining valuable products with limited generation of inhibitors and undesirable products (Romaní et al., 2012). Furthermore, the autohydrolysis carried out by heating an aqueous suspension of LCM in a pressurized reactor solubilizes mostly the hemicellulose fraction from LCM and a small part of lignin, increasing the mean pore size of the obtained solid (with increased proportion of cellulose), which enhances the enzymatic digestibility of this substrate (Hendriks and Zeeman, 2009). The hemicelluloses present in the liquid phase are recovered in form of valuable compounds as xylooligosaccharides, useful in several industries, as chemical, food or pharmaceutical industries (Moura et al., 2008; Zampa et al., 2004) or converted into sugars and used in biofuels production (Rodríguez-López et al., 2012).

This work deals with the optimization of a process for barley straw valorization, following a biorefinery scheme with a first step of hydrothermal pretreatment, with recovery of valuable hemicellulose-derived compounds in a separate liquid stream, followed by simultaneous saccharification and fermentation in fed-batch mode in order to obtain high bioethanol concentrations.

## 2. Methods

### 2.1. Raw material

Barley straw used to carry out the experiments was kindly provided by a local farmer (Jaen, southern Spain). It was milled through a 2 mm screen, air-dried, homogenized and stored at room temperature until use.

### 2.2. Composition of the raw material

The chemical characterization of the raw material was determined according to TAPPI® standards for the analysis of moisture, TAPPI 264 cm-07; ash, TAPPI T 211 om-12; extractives, TAPPI T 264 cm-07; two-step Quantitative Acid Hydrolysis (QAH) and Klason Lignin, TAPPI T 249 cm-09. The content of glucose, xylose, arabinose and acetic acid was quantified from the filtered QAH liquid phase by a 0.45 µm membrane by using an Agilent Technologies 1100 Series HPLC with a Refractive Index Detector and a BioRad Aminex HPX-87H column, using 0.006 M H<sub>2</sub>SO<sub>4</sub> at 60 °C as mobile phase. The results allowed the determination of glucan, xylan, arabinan and acetyl groups that make the raw material up. All the analyses were carried out by quadruplicate. The composition of raw material was as follows (g of component/1000 g raw material, on dry basis, ±standard deviation): glucan  $351.0 \pm 0.9$ , xylan  $199.5 \pm 1.2$ , arabinan  $46.1 \pm 0.2$ , acetyl groups  $19.8 \pm 0.3$ , Klason lignin  $197.7 \pm 2.3$ , extractives  $67.5 \pm 1.7$ , and ash  $76.1 \pm 0.2$ .

### 2.3. Barley straw autohydrolysis

Barley straw was pretreated using non-isothermal hydrothermal processes. In order to determine the optimal conditions, trials at different maximum autohydrolysis temperature ( $T_{MAX}$ , °C) between 200 and 230 °C were carried out in Parr reactors (Parr Instruments Company, Moline, Illinois, USA) of 0.6 or 3.75 L of total volume following the standard time–temperature profile. Severity ( $S_0$ ) was employed to measure the intensity of the hydrothermal pretreatments, defined as the logarithm of the severity factor  $R_0$  (Lavoie et al., 2010), in terms of the combined effects of time and temperature along the hydrothermal process, including heating and cooling periods. The equation applied is the following:

$$S_0 = \log R_0 = \log [R_{0\text{ HEATING}} + R_{0\text{ COOLING}}]$$

$$= \log \left[ \int_0^{t_{MAX}} \exp \left( \frac{T(t) - T_{REF}}{\omega} \right) dt + \int_{t_{MAX}}^{t_F} \exp \left( \frac{T'(t) - T_{REF}}{\omega} \right) dt \right] \quad (1)$$

where  $t_{MAX}$  is the time (in min) needed to achieve the maximum temperature ( $T_{MAX}$ , °C);  $t_F$  is the time (in min) required for the entire heating–cooling cycles;  $T(t)$  and  $T'(t)$  (°C) are the temperature profiles in heating and cooling, respectively, and  $\omega$  and  $T_{REF}$  are parameters whose values have been reported in the literature ( $\omega = 14.75$  °C;  $T_{REF} = 100$  °C).

Liquid–Solid Ratio (LSR) was fixed in 8 g liquid/g dry material. When the mixture reached  $T_{MAX}$ , the system was cooled down immediately by flowing water through an inner loop. After finishing the pretreatment, liquid and solid phases were separated by filtration in order to perform further analysis.

### 2.4. Analysis of liquid and solid phases from autohydrolysis

The solid obtained after the autohydrolysis pretreatment was washed with distilled water, filtered and centrifuged. Moisture and weight were measured in order to determine the yield ( $Y_A$ , autohydrolysis yield, defined as g solid phase obtained after autohydrolysis/kg raw material, dry basis). The solids were stored in closed plastic bags until analyses and use. Aliquots of solids were air-dried for analysis by QAH (as described in Section 2.2).

An aliquot of the liquid phase from the hydrothermal pretreatment was filtered and analyzed by HPLC to determine the concentration of monomeric sugars (glucose, xylose, and arabinose), acetic acid, Furfural and Hydroxymethylfurfural. A second aliquot of the liquid phase was subjected to quantitative posthydrolysis (performed with 4% w/w sulphuric acid at 121 °C for 40 min) in

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