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Monomeric carbohydrates production from olive tree pruning biomass: Modeling of dilute acid hydrolysis

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HIGHLIGHTS

- Olive tree pruning was converted to monomers by a one-step hydrolysis reaction.
- Response surface methodology was applied for statistical modeling and optimization.
- D-Xylose recovery of 85% was achieved at optimized conditions, confirming the model.
- Low concentration of toxic substances provided a high quality D-xylose substrate.

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ABSTRACT

Statistical modeling and optimization of dilute sulfuric acid hydrolysis of olive tree pruning biomass has been performed using response surface methodology. Central composite rotatable design was applied to assess the effect of acid concentration, reaction time and temperature on efficiency and selectivity of hemicellulosic monomeric carbohydrates to D-xylose. Second-order polynomial model was fitted to experimental data to find the optimum reaction conditions by multiple regression analysis. The monomeric D-xylose recovery 85% (as predicted by the model) was achieved under optimized hydrolysis conditions (1.27% acid concentration, 96.5 °C and 138 min), confirming the high validity of the developed model. The content of D-glucose (8.3%) and monosaccharide degradation products (0.1% furfural and 0.04% 5-hydroxymethylfurfural) provided a high quality subtract, ready for subsequent biochemical conversion to value-added products.

1. Introduction

Currently, due to the rapid depletion of fossil resources, researches of alternative renewable energy sources, such as biomass, is taking great interest. The conversion of different biomass feedstocks to fuel and other products, i.e., the biorefinery concept of biomass processing, is being considered now as a more potential way to guarantee sustainable bio-based economy (Kamm and Kamm, 2007). The agro-based lignocellulosic materials, such as industrial crop residues and various grasses represent an abundant and cheap feedstock for lignocellulosic feedstock biorefinery.

Among the largest agricultural crop waste generation in Spain may be mentioned the wheat straw and especially the olive tree pruning for its high concentration in southern. The olive tree is one of the most important crops in Spain. The pruning, operation that is usually applied to the branches and leaves after harvest, generates $5.0 \cdot 10^6 - 5.5 \cdot 10^6$ t/year of lignocellulosic biomass (Moya et al., 2008). The large volumes of waste generated, together with the great environmental damage caused by its uncontrolled burning has suggested the possibility of exploiting this biomass resource to produce oligosaccharides and monomeric carbohydrates (Mateo et al., 2013a).

In agro-based biomass the proportion of xylan may amount to 95% of the total non-cellulosic polysaccharides (Hurter, 1988). The monomeric D-xylose can be used as substrate for a wide variety of products production, such as xylitol, a five-carbon sugar alcohol that has attracted much attention because of its potential use in food and pharmaceutics (as a natural food sweetener, dental caries reducer, sugar substitute for diabetics, thin coating of tablets) (Granstrom and Leisola, 2009). Xylan isolation and depolymerization to D-xylose can therefore be an important first step in the complex biorefinery scheme.

The dilute sulfuric acid hydrolysis under moderate reaction conditions was proved to be a reliable and easily performed low cost method for quantitative conversion of hemicellulosic xylan

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to monomeric sugars. Hemicellulose hydrolysis of different lignocellulosic materials by dilute sulfuric acid solutions has been reported, rice straw (Karimi et al., 2006;Roberto et al., 2003), sugarcane bagasse (Rodrigues et al., 2010), sunflower stalks (Du et al., 2012), Eucaliptus wood (Gutsch et al., 2012), cauliflower mushroom (Lee et al., 2013), corn fiber (Noureddini and Byun, 2010) or triticale, barley, oats, canola and mustard straws (Pronyk and Mazza, 2012). The results showed that the amount of sugars released during the hydrolysis treatment is dependent on the type of raw material used and operational conditions (reaction time, temperature and acid concentration) applied for the hydrolysis reaction. The minimal monosaccharide decomposition to furans and cellulose degradation can be achieved under optimized conditions, providing high effectiveness and selectivity of the overall hydrolysis process.

D-Xylose production from olive tree pruning biomass has been studied using a low temperature dilute sulfuric acid hydrolysis. The response surface methodology (RSM) was employed for process modeling and optimization to maximize effectiveness and selectivity of xylan conversion to monomeric D-xylose within one-step reaction.

2. Methods

2.1. Raw material and chemical

The olive tree pruning biomass, collected during the pruning season, consisted of leaves, branches and pieces of trunks from olive trees and was collected in an olive grove situated in Jaén, Spain. The material was air-dried, milled, screened to select the fraction of particles with a diameter 0.425–0.60 mm and homogenized in a single lot.

2.2. Dilute acid hydrolysis

Hydrolysis experiments (replicated for each condition set) were carried out in a discontinuous reactor (2 dm^3 volume) heated with silicon V50 from a bath. For this study, the reactor was loaded with 100 g (on dry basis) of olive tree pruning residue and 1 dm^3 of sulfuric acid solution. The process variables were reaction time (20–220 min), temperature (86–103 °C) and acid concentration (0.2–1.8 mass%). The heating-up period for each experiment was around 5 min. Solid residue after hydrolysis was separated from solution by vacuum-filtration. The collected hydrolyzate was examined on degree of monosaccharide recovery and degradation products formed. Xylan conversion after hydrolysis (Y_1) was defined as a ratio of D-xylose content in hydrolyzate to hemicellulosic content in olive tree pruning raw biomass. Y_2 was defined as a ratio of D-xylose to D-glucose in hydrolyzate.

2.3. Analytical methods

The quantification of carbohydrates (D-glucose, D-xylose and L-arabinose) as well as acetic acid concentrations (in order to estimate the acetyl groups content) were determined by high-performance liquid chromatography (HPLC) using a WATERS instrument, in the conditions: a BIO-RAD Aminex HPX-87H (300 × 7.8 mm) column at 45 °C, 0.005 M sulfuric acid as eluant, flow rate of 0.6 $cm^3\ min^{-1}$, refraction index (RI) detector and 20 μL sample volume.

Furfural and HMF were analyzed by HPLC using a WATERS instrument with a UV detector (at 276 nm), in the following conditions: a Waters Resolve C18 5 μm (300 × 3.9 mm) column at ambient temperature, acetonitrile/water (1/8 with 1% of acetic acid) degassed with addition of phosphoric acid for pH correction to 2.5 as eluant, flow rate of 0.8 $cm^3\ min^{-1}$ and 20 μL sample volume. The samples were previously diluted with ultrapure water and filtered through membranes HAWP 04700 with 0.45 μm pores. The concentrations of these compounds were calculated from calibration curves obtained from standard solutions.

To calculate the cellulose and hemicellulose percentage and Klason lignin, the methodology proposed by Irick et al. (1988) was utilized and moisture composition by the TAPPI norm T12 os-75. Furthermore, the concentration of acid-soluble lignin was determined by the method described in a previous work (Mateo et al., 2013b), and ash composition using the procedure established by Browning (1967).

Extractives (nonstructural components such as pectins, fatty matters, terpenes, phenols, tannins, uronic acids, etc.) were determined gravimetrically using a two-step sequential extraction process by Soxhlet to remove water and ethanol soluble material according to a procedure adapted from Sluiter et al. (2008).

2.4. Statistical modeling

Response surface methodology (RSM) was employed for statistical data treatment and optimization of hydrolysis conditions by multiple regression analysis, using Statistica 6.0 (Statsoft, USA) software. The 2^3 central composite rotatable design (CCRD) with three independent variables at five different levels, six star (axial) points and five central points (total 19 runs) was adopted to find linear, quadratic and interaction effects of independent process variables on experimental responses. A second-order polynomial model was fitted to each set of experimental data to predict optimal reaction conditions by the following equation:

$$Y_z = b_0 + \sum_{i=1}^{3} b_i X_i + \sum_{i=1}^{3} b_{ii} X_i^2 + \sum_{i<j,j=2}^{3} b_{ij} X_i X_j \quad (1)$$

where Y is a predicted response (xylan conversion or D-xylose/D-glucose ratio), b_0 is an interception coefficient (regression coefficient at central point), b_i are the linear coefficients; b_{ii} are the quadratic coefficients, b_{ij} are the interaction coefficients, X_i and X_j are the independent variables (temperature, time and acid concentration).

The statistical significance of regression coefficients and effects was checked by analysis of variance (ANOVA) using the software STATISTICA 6.0 (Statsoft, USA).

3. Results and discussion

3.1. Compositional analysis of raw material

Detailed chemical analysis of olive tree pruning biomass used in this study revealed some general features typical for other industrially important agro-crops and woody species. The hemicellulose content represent 18.63 ± 0.27 % of dry matter.

The content of cellulose, as the principal chemical constituent, accounting for 33.85 ± 0.76 of dry residue, does not differ greatly from wheat straw (29–35%), bamboo (26–43%) and sugarcane bagasse (32–44%), but somewhat lower in comparison with woods (38–50%) (Hurter, 1988). However, it should be mentioned that cellulose and hemicellulose contents depend on the methods used for the determination of these components. Olive tree pruning has less lignin (23.13 ± 0.04 % of dry matter, being 18.93 ± 0.08 acid-insoluble and 4.20 ± 0.03 acid soluble) and more extractives (19.20 ± 0.39 % of dry matter), in relation to woods (25–30% and 1–5%, respectively) (Atchison, 1987). The particularly high proportion of water-soluble substances, (17.39 ± 0.28 % of dry matter), indicates the high accessibility and therefore reactivity of this biomass during chemical processing. The minerals (ash) comprise