



Enhanced ethanol production by simultaneous saccharification and fermentation of pretreated olive stones



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ABSTRACT

Olive stones are an agro-industrial by-product in Mediterranean countries that can be regarded as a potential source of bio-fuels and bioactive compounds. In this work, olive stones were pretreated with liquid hot water (LHW), dilute sulphuric acid (DSA) and organosolv delignification at temperatures in the range 190 °C–230 °C. The resulting solids from pretreatments were subjected to simultaneous saccharification and fermentation (SSF) with the yeast *Saccharomyces cerevisiae* IR2-9a for fuel-ethanol production. The composition of prehydrolysates from LHW and DSA pretreatments were strongly dependent of reactor temperature. The highest yields of D-xylose (0.21 kg kg⁻¹) and D-glucose (0.11 kg kg⁻¹) were achieved in DSA assays at 200 °C and 230 °C, respectively, while LHW processes provided the maximum oligosaccharide recovery (0.17 kg kg⁻¹) at 210 °C. The addition of sulphuric acid in organosolv pretreatments was particularly effective to increase the cellulose content of the pretreated solids till percentages close to 83%. Finally, the maximum ethanol concentration achieved by SSF was 47.1 kg m⁻³, and 13 kg ethanol were obtained from 100 kg of raw material.

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1. Introduction

Lignocellulose materials are the most abundant and lowest-cost biomass in the world. A promising approach is to convert these materials into ethanol, a clean motor fuel. Olive cultivation represents a potential local source of green biomass in Mediterranean countries, mainly in Spain, Italy and Greece [1]. Olive stones are by-products derived from the olive oil extraction industry and from manufacturing of pitted-table olives. They are currently used as energy source by combustion. Olive stones have been also employed to produce hydroxytyrosol, activated carbon, and other chemicals at laboratory scale [2]. A great advantage of this raw material is its small size because it is fragmented during the milling of olive fruit. Thus olive stones could be used in many industrial processes without the need of resorting to a grinding stage.

The fractionation of lignocellulose materials, such as olive stones, into value added products derived from their structural components has led to the biorefinery concept [3]. When the main target is the production of fuel-ethanol, the biorefinery scheme is currently composed of four major unit operations: pretreatment, hydrolysis of polysaccharides and oligosaccharides, sugars fermentation to ethanol and, finally, ethanol separation. Pretreatment is required for initial lignocellulose fractionation and hemicellulose is usually solubilised in this step [3]. It is also used to reduce cellulose crystallinity and thereby improve the accessibility of enzymes to polysaccharide [4]. The choice of pretreatment type is critical as it influences all subsequent downstream processing stage and the efficiency of the whole process. With regard to the chemical pretreatments, liquid hot water (LHW) and dilute sulphuric acid (DSA) pretreatments are regarded as two of the most suitable methods for industrial applications and have been studied for pretreating a wide range of lignocellulosic biomasses [3–6]. Because acid catalyst addition is not needed in LHW pretreatment, this alternative offers several potential advantages compared to the dilute acid pretreatment, such as the limited equipment corrosion

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(lower capital investment) as well the absence of a stage of neutralization of hydrolysates (lower environmental impact). LHW and DSA processes performed under optimised conditions lead to the complete removal of hemicelluloses while cellulose fraction remains virtually unaltered. Most hemicellulosic sugars can be found in oligomeric form after LHW pretreatment [7], and the formation of monosaccharides and furaldehydes (furfural, 5-hydroxymethylfurfural ...) is minimised. On the contrary, dilute acid hydrolysis not only solubilises hemicelluloses but also converts solubilised polymers into fermentable sugars in one step.

The susceptibility of pretreated cellulose to enzymatic attack is affected by lignin. Although LHW pretreatment can provoke changes in the lignin structure which would make the cellulose more accessible to enzymes, both LHW and DSA pretreatments have limited effects on biomass delignification. In the last decades several organosolv treatments have been assayed using different solvents (methanol/water, ethanol/water, acetone/water, acetic-acid/water, acetic-acid/formic-acid/water, etc.) for the delignification of lignocellulosic materials [8–13]. For example, it was found that pretreatment of pinewood with 60–80% aqueous methanol solution containing 0.2% HCl for 45 min at 170 °C removed approximately 75% of original lignin, and roughly 90% of pretreated cellulose was hydrolysed to D-glucose using cellulases [13]. Ethanol-based organosolv fractionation is regarded as one of the most promising organosolv processes due to the low cost of solvent and its easy recovery. The addition of mineral acids (sulphuric acid, hydrochloric acid, etc.) to the ethanol/water mixture could accelerate xylan degradation and enhance the delignification process [14].

Simultaneous saccharification and fermentation (SSF) is a process in which D-glucose is converted into ethanol as soon as it is formed. The SSF scheme minimizes the inhibition by end-product on the enzyme activity and prevents microbial contamination. Besides, the combination of the two steps (enzymatic hydrolysis and fermentation) results in lower capital cost [15]. Recently, overall ethanol yields close to 80% of the maximum theoretical yield, based on the amount of available hexoses in the raw material, have been obtained from simultaneous saccharification and fermentation of different materials [16]. In relation to the final stage for ethanol separation, a minimum bio-product concentration of 40–50 kg m⁻³ is required if distillation is used [15,17].

The generation of fuel-ethanol from olive stones has been previously studied by using steam explosion and liquid hot water pretreatments [18,19], but not by dilute sulphuric acid hydrolysis or organosolv process. The aims of this work were (a) to compare the impact of LHW and DSA pretreatments on the solubilisation of native hemicelluloses and on the production of monosaccharides and oligosaccharides in prehydrolysates, (b) to analyse whether an ethanol organosolv pretreatment with (E&DSA) and without (E&LHW) sulphuric acid addition is suitable for increasing the cellulose content of pretreated solids, and (c) to assess the effect of pretreatment type and particle solid size on the SSF stage for obtaining substrates with great potential for fuel-ethanol production.

2. Materials and methods

2.1. Raw material and chemicals

Olive stones (OS), olive pits crushed into fragments kindly supplied by a local industry ('S.C.A. San Juan', Jaén, Spain), were air-dried at room temperature to a moisture content of about 8%. The raw material, with particle sizes ranging from 0.51 to 7.00 mm, was homogenised in a single lot and stored until used. Particle size distribution was determined using a vibratory screen (Restch, Mod.

Vibro). The fraction between 1.40 and 7.00 mm represented roughly 95% of the total weight. Only 2.3% and 2.7% of the total solid weight corresponded to endocarps with diameters between 0.85 and 1.40 mm and below 0.85 mm, respectively. All chemicals employed in this work were of analytical grade purity.

2.2. Pretreatments

Liquid hot water (LHW) pretreatments, also called hydrothermal pretreatments, and dilute sulphuric acid (DSA) pretreatments were conducted in a 2-dm³ Parr reactor, Series 4522 (Moline, IL, USA). The reactor was loaded with 50 g of dry raw material and 300 cm³ of water for LHW experiments, and with 50 g of dry raw material and 300 cm³ of a dilute sulphuric acid solution (1.5 g sulphuric acid per 100 g of olive stones) for DSA trials. The suspension was heated to a specific temperature by passing an electrical current through coils surrounding the reactor. The assayed temperatures were 190 °C, 200 °C, 210 °C, 220 °C and 230 °C. These temperatures were selected because we previously found that complete hemicellulose extraction of olive stones is achieved within this range of temperatures, largely preserving cellulose in the resulting solid after both LHW [19,20] and DSA [21] pretreatments.

Organosolv delignification was carried out in a 1-dm³ Parr reactor, Series 4521 (Moline, IL, USA). The reactor was loaded with 50 g of dry olive stones and 300 cm³ of a 50% v/v water-ethanol solution (E&LHW experiments) and with 50 g dry OS and 300 cm³ of a 50% v/v water-ethanol solution that contained 1.5 g of sulphuric acid per 100 g dry OS (E&DSA trials). The reactor was heated to 220 °C for all the delignification assays.

When the desired temperature was attained, the reactor was quickly removed from the heating system and cooled in a water bath to below 100 °C in less than 10 min Fig. 1 shows the temperature profiles for eight experiments. The severity factor ($\log R_0$) was used to express the intensity of pretreatment by combining process time and temperature into a single variable [22]. Because the reactor worked under non-isothermal conditions, and the heating and cooling stages influenced the pretreatments, the evolution of temperature over time was recorded throughout the processes. From this data the equations (1) and (2) could be applied to calculate the severity factor.

$$(R_0)_{\text{Total}} = (R_0)_{\text{Heating}} + (R_0)_{\text{Cooling}} \quad (1)$$

$$R_0 = \int_0^t \exp\left(\frac{T(t) - 100}{14.75}\right) dt \quad (2)$$

where $T(t)$ is a function that links the reactor temperature (T) to a given time (t) in each stage. The function was fitted to a straight line ($T = a_1 + b_1 t$) in the heating zone and to a third-degree polynomial equation ($T = \alpha t^3 + \beta t^2 + \chi t + \delta$) in the cooling stage. Thus, the expression obtained to calculate $(R_0)_{\text{Heating}}$ was,

$$(R_0)_{\text{Heating}} = \frac{14.75}{b_1} \left[\exp\left(\frac{a_1 - 100 + b_1 t_1}{14.75}\right) - \exp\left(\frac{a_1 - 100}{14.75}\right) \right] \quad (3)$$

where t_1 is the time in which the maximum pretreatment temperature was reached. In the cooling region, trapezoidal rule was used to numerically integrate equation (2).

After pretreatment, the prehydrolysate was separated from the remaining solid by filtration. The solid was washed with ultrapure water after LHW and DSA pretreatment and with an ethanol/water solution (50%, v/v) after E&LHW and E&DSA assays. The solids were

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