Dilute acid pretreatment of olive stones: experimental optimization of xylose recovery

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Olive stones is a by-product generated in the olive oil production process. The main steps of the process are milling of olives, mixing or malaxation, and the oil separation in a horizontal centrifuge (decanter). In Spain, most of the olive mills operate by the called 2-phase extraction process, in which a semi-solid pomace (*alpeorujo*) was obtained from the decanter. This residue contains the part of the olives that do not have oil: pulp, peel and crushed stones. It also contains a little amount of residual oil that is recuperated in the olive pomace extracting industry. In the last years, it has been becoming the more and more frequent in Spain the separation of the crushed stones from the 2-phase olive pomace, to use them as a fuel in domestic heating systems or in small industrial boilers. The content of stones represent around 10 % of olive weight. Thus, in an average olive campaign in Spain (6 million tons / year), around 600,000 tons of olive stones can be generated (Ruiz *et al.*, 2017). The aim of this work was the optimization of the hemicellulose solubilization by dilute acid pretreatment of olive stones, as a first step for the valorization of this lignocellulosic biomass in a biorefinery context.

The chemical characterization of olive stones revealed that it contains a high amount of structural sugars, 21 % glucan and 26 % hemicellulose (mainly xylans, 23.4%). It also contains 33% of lignin and 6% of extractives, one third of them as soluble sugars. A biorefinery scheme to valorize olive stones can include a first pretreatment step to solubilize hemicellulose in the liquid fraction. The sugars released can be used as molecular platform to obtain different products, such as furfural, ethanol, xylitol, etc. The cellulose recovered in the insoluble solid could be further converted into ethanol by a biochemical process. The final lignin-rich solid residue can be used for the production of chemicals or for the energetic supply of the biorefinery (Hernández *et al*., 2014).

In this work, dilute acid pretreatment of olive stones was performed in laboratory autoclave, through a Boxh-Benhken experimental design (Table 1). Temperature, solid concentration and acid dosage were selected as independent variables. Temperature was modified in the range 120-130ºC, solid concentration in the range 20-60 %, and acid dosage between 7.5 and 17.5 % of sulfuric acid referred to solid biomass. Time was fixed in 60 minutes, taking into account previous results (Lama-Muñoz *et al*., 2014). The design included five replicates at the center of the domain selected for each independent variable studied.

The solid and liquid fractions issued from pretreatment were separated by filtration. The solid was washed with distilled water, dried in an oven at 40ºC and weighed for solid recovery determination. This material was stored for further characterization and evaluation of the additional steps needed for the valorization of the cellulose and lignin it contains. Liquid fraction was analyzed by HPLC (Waters, Milford, USA, equipped with a refractive index detector, model 2414). A CAR-BOSep CHO-782 Pb (Transgenomic, Inc., Omaha, USA) carbohydrate analysis column was used for the monomeric sugars determination (glucose, xylose, galactose, arabinose and mannose) operating at 70ºC with ultrapure water as eluent at a flow rate of 0.6 mL/min. Furfural, hydroxymethylfurfural, acetic acid and formic acid content were also analyzed by HPLC with a ICSep ICE-COREGEL 87H3 column operating at 65ºC with 5 mM sulfuric acid as mobile phase (0.6 mL/min).

Table 1 shows the concentrations of sugars released from dilute acid pretreatment of olive stones at the different experimental conditions assayed. As expected, xylose is the main solubilized sugar. The optimization of the recovery of xylose in the liquid fraction was carried out by response surface methodology using the Design Expert 8.0.7.1 software (Stat-Ease Inc., Minneapolis, USA). Different optimization criteria were applied. On the one hand, considering the yield of xylose as response for the model (% recovery of xylose in the liquid fraction referred to the xylose content in the raw material) better results were obtained for low solid concentration and high temperatures in the range assayed, for a medium acid concentration. For example, the model predicted 95 % of xylose yield at 129ºC, 20 % of solid concentration and 9.6 % of acid dosage. On the other hand, when focusing on xylose concentration, better results were obtained for high solid concentration and low temperatures in the range assayed, i.e. maximum xylose concentrations were predicted for the model at 120ºC, 60% of solid concentration and 14 % of acid dosage. However, at the conditions that maximize xylose concentration a drop in xylose yield (up to 75-85%) was evidenced. Consequently, a third optimization criterion was applied, considering both xylose concentrations and yields as responses. When 50 % of the weight in the optimization was attributed to each response, the predicted results were quite similar to the case of considering only xylose concentration as response. For example, at 120ºC, 60% of solid concentration and 14 % of acid dosage, until 114 g/L of xylose can be obtained with a xylose yield of 85%. Further techno-economic analysis would be necessary to evaluate the relevance of the concentrations or yields of xylose in the viability of the full process, within the final proposed biorefinery scheme.

Table 1. Boxh-Benhken experimental design and sugar concentrations obtained from dilute acid pretreatment of olive stones.

Std	Run	Factor 1 A: Temperature (ºC)	Factor 2 B: % Acid dosage	Factor 3 C: % Solid concentration	Glucose (g/L)	Xylose (g/L)	Galactose (g/L)	Arabinose (g/L)
4	1	130	17.50	40	4.28	61.17	4.01	2.60
9	2	125	7.50	20	0.09	33.28	2.33	1.03
1	3	120	7.50	40	0.33	50.36	3.12	2.49
5	4	120	12.50	20	0.13	32.55	1.16	0.95
6	5	130	12.50	20	0.22	44.89	1.99	1.31
11	6	125	7.50	60	1.88	88.55	8.30	5.25
14	7	125	12.50	40	3.03	62.22	3.32	2.14
10	8	125	17.50	20	0.09	44.77	1.95	1.43
2	9	130	7.50	40	1.49	73.60	4.59	3.40
13	10	125	12.50	40	2.18	94.09	6.37	4.36
17	11	125	12.50	40	1.18	78.02	4.94	3.33
3	12	120	17.50	40	0.94	67.09	4.31	3.03
16	13	125	12.50	40	3.14	81.78	6.30	4.63
7	14	120	12.50	60	4.43	117.20	10.42	6.76
8	15	130	12.50	60	7.90	96.27	7.81	2.27
15	16	125	12.50	40	3.69	74.88	4.96	3.29
12	17	125	17.50	60	6.97	84.35	7.41	4.44

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