Maximization of xylose production from olive stones by acid pretreatment

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In the Mediterranean basin, olive growing is the most widespread crop. Olive growing and the associated industry produce a large amount of by-products and wastes. One of the main residues is the olive stone (OS), which represents about 10% of the olive. In Spain, an average of 6 million tonnes of olives are harvested each season, which would mean around 600,000 tons of OS (Manzanares et al., 2017). In recent years, OS is separated in olive mills and olive pomace mills for being used as a fuel. This material is located in the industries, which is a logistic advantage, compared to other wastes such as pruning biomass.

OS are of interest as a feedstock for a biorefinery due to their composition consisting of 21% cellulose, 25% hemicelluloses (with xylose accounting for 24%), 33% lignin and 4% extracts. This work is focused on the dilute acid solubilisation of hemicelluloses which is recognised as one of the most used and efficient methodologies for the recovery of the hemicellulosic fraction (Padilla-Rascón et al., 2020). The resulting monomeric sugars can be converted into value-added products, such as furfural, ethanol, xylitol, etc. The cellulosic fraction can in turn be exploited with other pretreatments to obtain ethanol. This work aimed to determine the optimal conditions of dilte acid extraction at which the solubilisation of the hemicellulosic fraction is maximised.

The experiments were carried out in a 1 L Parr reactor, according to a Box-Behnken experimental design, as shown in Table 1. The factors studied were the temperature, which was varied between 170 and 200 °C, and the concentration of H_2SO_4 ranging from 0.5 to 2% (w/v), while the solid/liquid ratio was set at 40%. The design consists of 13 experiments, including 5 central points and two star points for each factor, one above and one below the experimental range of each factor, to verify that the selected range.

Table 1. Box-Benhken experimental design.

Run	Temperature (ºC)	Sulphuric acid (% p/v)	Xylose (g/L)
1	170	2	79.03
2	185	1.25	62.58
3	185	1.25	64.36
4	185	2.31	32.56
5	185	1.25	58.00
6	185	1.25	62.63
7	185	0.19	12.24
8	185	1.25	60.40
9	200	2	4.41
10	170	0.5	39.65
11	163.79	1.25	54.00
12	206.21	1.25	9.30
13	200	0.5	58.68

The slurries obtained after pretreatment were separated by filtration. Subsequently, the solid fraction was washed with distilled water, dried and stored for possible future valorisation. The liquid fraction was characterised in an HPLC, the monomeric sugars were determined with CARBOSep CHO-782 Pb column operating at 70 °C with ultrapure water as a mobile-phase (0.6 mL/min), these samples were previously neutralized with $CaCO_3$ and filtered. Furfural, hydroxymethylfurfural, acetic acid and formic acid content were also analyzed by HPLC with a ICSep ICE-COREGEL 87H3 column operating at 65 ºC with 5 mM sulfuric acid as mobile phase (0.6 mL/min), these samples were previously filtered.

Xylose was the major solubilised sugar, reaching 79 g/L at 170 ºC and 2 % H_2SO_4 (Table 1). The data obtained from the hydrolysates were statistically analysed with the Design Expert 7.0.0, Stat-Ease Inc. software. As can be seen in Figure 1, the xylose concentration increased with sulphuric acid concentration at low temperatures. At high temperatures the behaviour is reversed, xylose concentration decreased with increasing sulphuric acid concentration. For process optimisation, the conditions at which xylose solubilisation is maximal, 170 ºC and 2% sulphuric acid (w/v), were determined. The optimal conditions were replicated in triplicate, the slurries were treated as for the design. Under optimal conditions, 19.5 g xylose/100g OS was obtained, representing 81% xylose recovery.

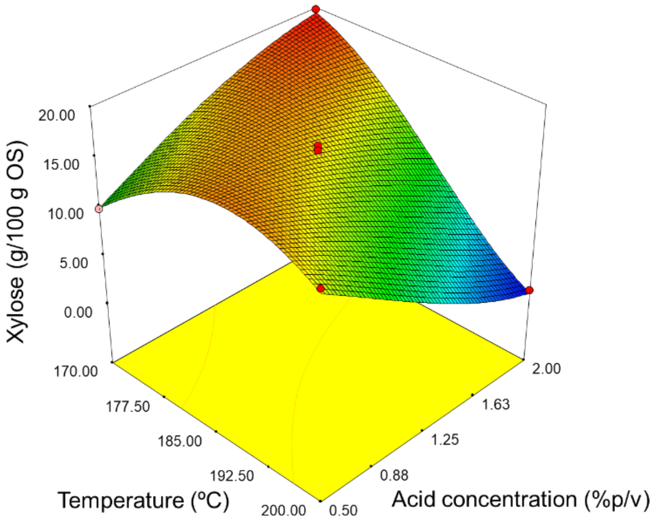

Figure 1 . Response surface curve representing the effect of temperature and sulphuric acid concentration on the xylose concentration.

The solubilisation of OS hemicelluloses by diluted acid hydrolysis is confirmed to be an effective pretreatment for the recovery of xylose contained in olive stones. Further work is envisaged for the utilisation of the other major fractions of OS, cellulose and lignin.

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References

Manzanares, P., Ruiz, E., Ballesteros, M., Negro, M.J., Gallego, F.J., López-Linares, J.C., Castro, E., 2017. Residual biomass potential in olive tree cultivation and olive oil industry in Spain: valorization proposal in a biorefinery context. Span J Agric Res 15, e0206. https://doi.org/10.5424/sjar/2017153-10868

Padilla-Rascón, C., Ruiz, E., Romero, I., Castro, E., Oliva, J.M., Ballesteros, I., Manzanares, P., 2020. Valorisation of olive stone by-product for sugar production using a sequential acid/steam explosion pretreatment. Industrial Crops and Products 148, 112279. https://doi.org/10.1016/j.indcrop.2020.112279