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A biorefinery approach to obtain antioxidants, lignin and sugars from exhausted olive pomace

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ABSTRACT

Exhausted olive pomace (EOP) is the main residue of the pomace olive oil extracting industry. In this work, EOP was fractionated into valuable components for valorisation: an aqueous extract rich in hydroxytyrosol and mannitol, lignins with antioxidant properties and fermentable sugars. EOP was first subjected to water extraction at 85 °C for 90 min. Several pretreatments based on liquid hot water and organosolv with 50% or 60% ethanol (catalysed and uncatalysed with 1% sulfuric acid) were then evaluated in terms of delignification ability and efficiency for enzymatic hydrolysis of the pretreated solids. Once the best conditions had been selected (50 % ethanol-1% sulfuric acid at 130 °C for 60 min), an organosolv lignin (OL) with antioxidant properties was obtained through acid precipitation of the pretreatment liquor. This was compared to the enzymatic hydrolysis lignin obtained in the subsequent step and to the lignins purified by acid hydrolysis. OL showed a higher total phenolic content and antioxidant activity than the rest of the lignin samples. Chemical differences were also observed that could explain the results.

Introduction

The industries involved in the production of olive oil generate a large amount of agroindustrial by-products/waste every year. This includes the exhausted olive pomace (EOP), which is main residue of the pomace olive oil extracting industry and around 1.2 million tonnes are generated per campaign in Spain [1,2]. Although EOP is currently used as a biofuel, this use has some drawbacks: its low cost provides a limited income, and different environmental problems also occur during combustion, e.g., particle emission and hazardous gas generation [3]. Alternatively, EOP can be used to obtain bioethanol [4] or xylitol [5] from the hemicellulose fraction and antioxidants from the extractive fraction [6]. Nonetheless, for an efficient use of this biomass in a biorefinery context, these components should be valorised in an integrative manner, and the use of lignin should also be considered.

Lignin is a high molecular weight aromatic polymer, being mainly composed of phenylpropyl alcohols linked by different types of bonds: *p*-coumaryl alcohol (or *p*-hydroxyphenyl unit, H), coniferyl alcohol (or guaiacyl unit, G) and synapyl alcohol (or syringyl unit, S) [7–10]. This basic structure makes lignin a source of aromatic chemicals after selective depolymerisation [11,12]. Moreover, the industrial interest in lignin is growing since some lignins can prevent or delay oxidation processes [13] and act as anti-inflammatory, antibacterial or anti-cancer agents [14].

Besides its natural complexity, the structure of lignin, including the monomeric units and their linkages, and its properties vary according to the biomass type, the type of treatment and the intensity of the conditions applied, which is a consideration for their industrial production and application [7]. In this way, the use of alkalis and ammonia is common in the recovery of lignin [8]. Other options are autohydrolysis and organosolv treatment based on the use of organic solvents [15–20]. The use of inorganic acids as catalysts for the organosolv treatment has also been reported [10]. According to Erdocia et al. [17], organosolv treatment is the most environmentally friendly and economical process, since the solvent can be recycled. This process also represents a significant improvement in the quality of lignin [21], presenting lower impurities [11] and good antioxidant properties [18]. Moreover, the

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application of an organosolv pretreatment can improve the enzymatic hydrolysis of the biomass to convert the polymeric sugars into monomers [20], which can be used to obtain other building block chemicals and biofuels [1,22].

Another important issue is when the lignin is obtained, i.e., in the waste streams from other biorefinery processes or in the early stages of the biomass valorisation. Although this can affect the structure and properties of the lignin, its use in all cases can increase the value of the biorefinery process [11,22].

In this work, several pretreatments based on liquid hot water (LHW) and organosolv pretreatment have been evaluated as a second step in the biorefinery of EOP, which was first treated hydrothermally to recover the antioxidants. The delignification ability of the pretreatments and the enzymatic hydrolysis efficiency to convert cellulose into glucose were established. Once the pretreatment was selected, two lignins were obtained; one of them was recovered from the pretreatment liquor (PL) by acid precipitation, and the other lignin was obtained after enzymatic hydrolysis. Both lignins were purified, characterized and their antioxidant properties studied. Therefore, this work give new insights into the valorisation of EOP through an integrative process and also into the lignin structure and properties obtained from this agro-industrial waste.

Material and methods

Chemicals, standards and reagents

All the chemicals and reagents were of analytical grade and were supplied by Sigma-Aldrich (St. Louis, MO, USA): Folin & Ciocalteu's phenol reagent, sodium carbonate, sodium nitrite, aluminum chloride, sodium hydroxide, acetic acid, sodium acetate, TPTZ (2,4,6,-tri(2pyridyl)-1,3,5,-triazine), iron(III) chloride, DPPH (1,1-diphenyl-2-picrylhydrazyl), sodium chloride, potassium chloride, dipotassium hydrogen phosphate, disodium hydrogen phosphate, ABTS [2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate)], Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) and the standards of gallic acid and rutin. Methanol was obtained from Honeywell (Morristown, NJ, EEUU), sulfuric acid 72% and 96% from PanReac AppliChem (Barcelona, Spain) and ethanol (96%) from VWR Inc. (West Chester, PA, USA). Ultrapure water was obtained using a Milli-Q system (Millipore, Bedford, MA, USA).

Raw and extracted material

EOP, partially pitted and pelletized, was obtained from the olive pomace factory "Spuny SA" (Castellar, Jaén, Spain). Its average moisture content was around 6.5%. EOP was subjected to aqueous extraction (85 °C, 10% solids and 90 min) in a thermostatic water bath provided with mechanical agitation according to Gómez-Cruz et al. [6]. After extraction, the wet material was vacuum filtered, obtaining two fractions: an aqueous extract and a solid fraction (extracted EOP).

Chemical characterization

The raw extracted EOP, pretreated solids (PSs) and lignins were subjected to compositional analysis following the standard method provided by the National Renewable Energy Laboratory (NREL) [23]. Then, the content of moisture, ash, cellulose, hemicelluloses and lignin were estimated. Prior to the analysis of the polymeric fractions, a Soxhlet extraction was applied in two sequential stages using water and ethanol, respectively. The content of the monomeric sugars released after acid hydrolysis was determined in the liquid fraction using high-performance liquid chromatography (HPLC) with a refractive index detector (RID). Acid insoluble lignin was determined by gravimetric analysis after the acid treatment, and acid soluble lignin was determined by spectrophotometry at 205 nm in the liquid fraction. The elemental composition (C, H, N and S) was analysed using a TruSpec Micro device (Leco, St. Joseph, MI, USA).

Liquid hot water and organosolv pretreatments

LHW and organosolv pretreatments were performed on the extracted EOP at 15% (w/v) of solids using a laboratory scale 1-L stirred tank reactor (Parr Instrument Company, Moline, IL, USA). Table 1 summarizes the experimental conditions for all the pretreatments applied to the EOP. In particular, LHW pretreatment was performed at 210 °C for 60 min, once the temperature was reached. Organosolv experiments were carried out using 50% or 60% ethanol, and sulfuric acid at 1% (w/v) was used as a catalyst in some experiments (Table 1). After reaching the target temperature, the reactor was kept sealed, and the slurry was agitated for the pretreatment time. In all cases, the reactor was cooled down to around 50 °C, and the slurry was vacuum filtered to separate the PS from the PL.

PSs were dried at 40 °C, and the solid recovery yield was calculated and referred to the extracted EOP. Also, a portion of these solids was milled and characterized as described in Section "Chemical characterization". Moreover, the PLs were analysed to determine their content of soluble sugars, acetic acid, furfural and hydroxymethylfurfural by HPLC-RID analysis with a refractive index detector (RID) [24], and their total phenolic content (TPC) and antioxidant capacity were also measured using the methodology described in the following sections.

Enzymatic hydrolysis

Raw EOP, extracted EOP and PSs were subjected to enzymatic hydrolysis in 100 mL Erlenmeyer flasks containing 25 mL of 0.05 M sodium citrate buffer (pH 4.8) and 5% (w/v) of solids. The hydrolysis was performed at 50 °C on a rotary shaker (INFORS HT ecotron, Surrey, United Kingdom) for 72 h using the commercial enzyme solution Cellic® CTec2 (Novozymes A/S, Bagsværd, Denmark) at 15 FPU/g substrate with β-glucosidase (Novozymes A/S) at 15 IU/g substrate. All enzymatic hydrolysis experiments were performed in triplicate. The glucose concentration in the enzymatic hydrolysate (liquid fraction) was determined by HPLC-RID analysis. The hydrolysates and solid fractions were then separated by vacuum filtration for further analysis.

Lignin recovery

The best delignification method for the extracted EOP was selected, and four lignins were obtained in this work (Fig. 1). Firstly, lignin was precipitated from the liquor obtained in pretreatment 5, according to the procedure described by Garcia et al. [18] with

Table 1
Conditions of the liquid hot water (P1), organosolv (P2, P4–P6) and combined (P3) pretreatments applied for EOP delignification. All experiments were performed using a solid:liquid ratio of 15% for 60 min.

Pretreatment	Solvent	Catalyst	Temperature (ºC)
P1	Water	NA	210
P2	50% ethanol	NA	110
P3	Water + 50% ethanol[a]	NA	110
P4	50% ethanol	1% H_2SO_4	110
P5	50% ethanol	1% H_2SO_4	130
P6	60% ethanol	1% H_2SO_4	110

NA, not added.
[a] The pretreated solid obtained in P1 was subsequently pretreated with 50% ethanol.

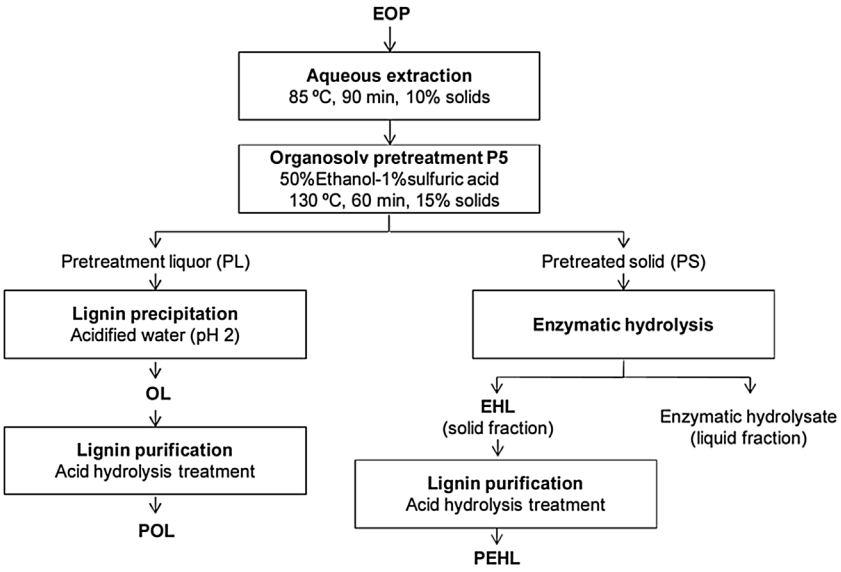

Fig. 1. Scheme summarizing the procedures followed to recover lignin products from exhausted olive pomace (EOP): organosolv lignin (OL), enzymatic hydrolysis lignin (EHL), purified OL (POL) and purified EHL (PEHL).

some modifications. For this, a part of the liquor was evaporated with a Rotavapor® R-210 (BÜCHI Labortechnik AG) up to approximately 50% of the volume. Then, the solubilized lignin was recovered by precipitation, adding two volumes of cold water acidified at pH 2 with H_2SO_4. The precipitate was vacuum filtered, washed twice with 100 mL acidified water and dried at 50 °C for 24 h; this lignin precipitate was named organosolv lignin (OL). Secondly, OL was subjected to a purification process using acid hydrolysis to release potential hemicellulosic impurities bound to the lignin, thus obtaining the acid insoluble lignin fraction. For this, an acid hydrolysis in two-steps was performed, as in the NREL procedure [23]. In the first stage, the acid hydrolysis treatment was carried out with 72% (v/v) H_2SO_4 at 30 °C for 1 h. Then, in the second stage, the mixture was diluted by 4% (v/v) H_2SO_4 and autoclaved at 120 °C for 1 h. After this treatment, the resulting acid insoluble lignin fraction was collected by vacuum filtration and dried in the oven at 50 °C for 24 h; this lignin was named purified OL (POL).

In addition, the solid fraction resulting from the enzymatic hydrolysis, composed mainly of the remaining lignin from the organosolv pretreatment, was named enzymatic hydrolysis lignin (EHL). This was also subjected to the acid hydrolysis treatment to remove minor components, obtaining a purified enzymatic hydrolysis lignin (PEHL).

Total phenol content and antioxidant capacity assays

The TPC and antioxidant capacity were determined in the PLs and in the lignin products dissolved in methanol (4 g/L), using DPPH, ABTS and ferric reducing power (FRAP) assays. Briefly, the TPC was measured by spectrophotometry (at 760 nm) using the Folin-Ciocalteu assay [25]. The measurements were performed in a UV–vis spectrophotometer (UV-1800) from Shimadzu Schweiz GmbH (Reinach BL, Switzerland). Gallic acid was used as standard, and the results were expressed as milligrams of gallic acid equivalents (GAE) per gram of extracted EOP and/or lignin.

Using the aforementioned spectrophotometer, DPPH, ABTS and FRAP were measured at 517 nm, 734 nm and 593 nm, respectively [3,6]. For all three assays, Trolox was used as standard, and results were expressed in milligrams of Trolox equivalents (TE) per gram of extracted EOP and/or lignin. All of the samples were analysed in triplicate.

Table 2
Chemical composition (%, dry weight) of raw exhausted olive pomace (EOP), extracted EOP and pretreated solids (PSs) obtained after liquid hot water (PS1), organosolv (PS2, PS4–PS6) and combined (PS3) pretreatments.

Component	Raw EOP [6]	Extracted EOP	PS1	PS2	PS3	PS4	PS5	PS6
Extractives	41.78 ± 1.85	15.24 ± 0.27	–	–	–	–	–	–
Aqueous	37.94 ± 1.89	8.24 ± 0.23	–	–	–	–	–	–
Ethanolic	3.83 ± 0.16	7.00 ± 0.18	–	–	–	–	–	–
Cellulose	9.67 ± 0.84	12.81 ± 0.55	22.14 ± 1.94	17.78 ± 0.39	23.89 ± 1.48	23.50 ± 0.64	25.11 ± 2.01	18.30 ± 0.62
Hemicellulose	10.94 ± 0.53	17.98 ± 0.82	10.28 ± 0.64	21.68 ± 0.27	10.05 ± 0.22	20.31 ± 0.32	13.33 ± 0.82	17.36 ± 0.52
Xylan	9.79 ± 0.53	13.00 ± 0.54	5.17 ± 0.64	18.17 ± 0.27	4.69 ± 0.22	15.51 ± 0.32	8.82 ± 0.82	13.82 ± 0.52
Galactan	0.31 ± 0.31	3.27 ± 0.61	2.72 ± 0.07	2.69 ± 0.05	2.87 ± 0.10	3.24 ± 0.06	2.48 ± 0.09	2.52 ± 0.04
Arabinan	1.82 ± 0.03	2.12 ± 0.07	1.85 ± 0.08	2.13 ± 0.08	1.68 ± 0.00	2.36 ± 0.02	2.03 ± 0.01	1.67 ± 0.02
Mannan	0.42 ± 0.02	1.21 ± 0.06	1.76 ± 0.09	1.41 ± 0.06	1.98 ± 0.07	1.70 ± 0.06	1.62 ± 0.05	1.50 ± 0.03
Acetyl groups	1.51 ± 0.17	1.00 ± 0.06	0.71 ± 0.07	0.40 ± 0.02	0.61 ± 0.03	1.32 ± 0.04	0.36 ± 0.03	1.07 ± 0.02
Lignin	21.82 ± 0.89	34.21 ± 0.38	58.13 ± 0.33	42.81 ± 0.87	54.82 ± 0.36	45.82 ± 0.47	47.40 ± 0.05	43.77 ± 0.63
AIL	20.29 ± 0.68	33.62 ± 0.28	56.77 ± 0.31	41.15 ± 0.87	54.25 ± 0.36	44.64 ± 0.45	46.44 ± 0.02	42.85 ± 0.63
ASL	1.54 ± 0.47	0.93 ± 0.41	1.36 ± 0.11	1.66 ± 0.00	0.57 ± 0.00	1.18 ± 0.14	0.96 ± 0.05	0.92 ± 0.01
Ash	6.41 ± 0.21	0.18 ± 0.01	1.59 ± 0.18	1.89 ± 0.07	2.64 ± 0.22	2.39 ± 0.04	3.18 ± 0.04	2.56 ± 0.07
Solids recovery	–	59.00[a]	63.56[b]	90.78[b]	77.51[b]	70.81[b]	55.50[b]	74.01[b]

AIL: acid insoluble lignin; ASL: acid soluble lignin. The data is expressed as mean ± standard deviation (n = 3).
[a] With respect to EOP.
[b] With respect to extracted EOP.

Lignin characterization

UV–vis spectra of the different lignins dissolved in methanol were measured between 190 and 800 nm on the above mentioned device, with a 1 cm quartz cuvette. The spectra were processed by UVProbe version 2.32.

Pyrolysis–gas chromatography–mass spectroscopy analyses (Pyr–GC–MS) were performed using a SCION GC–MS System from Bruker Daltonics (Bremen, Germany), according to García et al. [18] with some modifications. Concretely, the pyrolysis step was performed in a Multi-Shot Pyrolyzer® EGA/Py-3030D (Frontier Lab, Koriyama, Fukushima) at 580 °C for 2 s [26] and the heating ramp was 2 °C/ms. The data processing was performed using MS Data Review software (version 8.0), and the compounds were characterized according to their *m*/*z* value and fragmentation pattern, compared to data from the NIST database version 17. All of the samples were analysed in triplicate.

HPLC analyses

PLs and the enzymatic hydrolysates were filtered (0.45 μm nylon syringe filter) (Sinerlab Group) (Madrid, Spain) and analysed by a HPLC 1260 series system connected with RID from Agilent Technologies (Palo Alto, CA, USA). An ICSep ICE-COREGEL 87 H3 column (Transgenomic, Inc., Omaha, NE, USA) was used, set at 65 °C with a mobile phase of 5 mM sulfuric acid at 0.6 mL/min.

Results and discussion

Water extraction step and chemical composition of the resulting fractions

EOP was mainly composed of around 42% aqueous-ethanolic extracts, 22% lignin and 20% of structural carbohydrates (cellulose and hemicelluloses); glucose and xylose, the major sugars in EOP, were in a similar percentage, i.e., around 10% (Table 2) [6]. Other olive-derived biomasses, such as olive mill leaves and olive pomace, also contain extractives and lignin in high amounts [27,28]. Accordingly, it seems reasonable to firstly take advantage of the extractive fraction, which includes the phenolic fraction. Therefore, a water treatment (85 °C for 90 min) was applied to obtain an antioxidant extract as a first step in the valorisation cascade of EOP. This contained around 0.6 g/L of hydroxytyrosol (1.47 g hydroxytyrosol/100 g dry extract EOP), which is one of the most promising phenolic compounds from olive products due to its great biological properties [6]. In addition, the extract was rich in mannitol (4.8 g/L or 11.74 g/100 g dry extract EOP), which is also an interesting bioactive compound.

After this water extraction step, the chemical composition of the EOP was modified, with the extracted EOP enriched in lignin and polymeric sugars due to the partial removal of around 63.5% and 97.2% of the initial content of extractives and ash, respectively. The solid recovery efficiency of the water extraction step was 59%. These results agreed with those obtained by Manzanares et al. [29] after the treatment of EOP with water at 100 °C for 30 min. Therefore, some delignification methods were tested as a second step to recover lignin and to evaluate how this step affects the enzymatic digestibility of the PSs.

Chemical composition of the pretreated solids recovered after LHW and organosolv pretreatments

The material resulting from the water extraction step was used as a raw material for the subsequent fractionation step, to continue with the biorefinery scheme. As commented before, the pretreatment conditions are shown in Table 1 and consisted of LHW and organosolv pretreatments, and combined treatments. The composition of the PSs obtained from these pretreatments, as well as the composition of raw and extracted EOP, is shown in Table 2. The solid recovery after pretreatment ranged from 90.78% (P2) to 55.50% (P5) at the most severe conditions; thus more components were solubilized under severe conditions, i.e., using organosolv pretreatment at higher temperature and with catalyst.

LHW pretreatment mainly affected the hemicellulose and solubilized about 76% of this fraction. Consequently, this caused an increase in the cellulose and lignin content with respect to the extracted EOP, e.g., 73% and 70%, respectively. Previous studies have reported the solubilisation of xylans through LHW treatments, which is more noticeable when high temperatures are applied [1]. This also agreed with previous studies on other biomasses, but the pretreatment results are variable and depend on the feedstock [30]. For example, using LHW at 200 °C for 30 min with corncob, all hemicellulose was solubilized. Similarly, the glucan and lignin content increased after this treatment [31].

For organosolv pretreatments with aqueous ethanol, there was an increase in the percentages of cellulose and lignin content of the resulting PSs with respect to the raw material and extracted EOP. This depended on the temperature and ethanol concentration, as well as whether sulfuric acid was added. In this way, the highest value of cellulose was obtained when 50% ethanol was used at 130 °C with 1% sulfuric acid (P5). These pretreatment conditions reached 55% of hemicellulose solubilisation and the highest value of delignification in this work, 23%. Alternatively, P2, P4 and P6, which were carried out at gentler conditions, solubilized less than 30% of hemicellulose and only 5% of lignin in the case of P4 and P6, whilst P2 (without acid catalyst) did not affect the lignin fraction. This agreed with Díaz et al. [20] who showed that the hemicellulose content is highly affected by the temperature in the organosolv pretreatment. The addition of sulfuric acid as catalyst has also been reported as a way to increase delignification [32], agreeing with our results. It seems that acidic conditions contribute to the breakage of ether bonds in lignin, favouring the delignification process [10].

The combination of LHW and organosolv pretreatment (P3) slightly increased the cellulose content in PS3 compared to PS1, which was obtained using only LHW. This pretreatment mainly favoured the solubilisation of the xylan fraction.

Enzymatic digestibility of the pretreated solids

The effectiveness of enzymatic saccharification on the pretreated biomass is principally evaluated by the degree of conversion of cellulose to glucose monomers. Therefore, the effect of the LHW and organosolv pretreatments on the enzymatic digestibility of the PSs was evaluated. This parameter estimates the percentage of glucose released by enzymes with respect to the initial glucose content in the PSs (Fig. 2).

The highest values, even higher than 70%, were reached when the PSs obtained from the LHW pretreatment (P1) and the organosolv pretreatment (P5) were hydrolysed with the enzymatic cocktail. However, when these values were expressed in terms of the total glucose content in the raw EOP, pretreatment P5 resulted in the best conditions to recover the maximum amount of glucose, i.e., the enzymatic hydrolysis yield (EHY) was 69.2%. In addition, this pretreatment produced the highest delignification, being around 28%. This made the ratio of cellulose to lignin reach the highest value, around 60%. According to Yang et al. [33] a higher ratio of cellulose to lignin and the gradual removal of lignin is generally accompanied by an increase in the conversion of cellulose. This fact is, for example, manifested when the organosolv pretreatment P5 was compared with diluted acid pretreatments, which were also applied to EOP using sulfuric acid in the range 1–

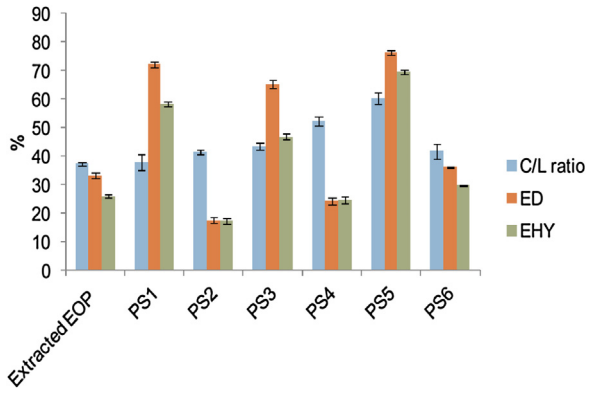

Fig. 2. Ratio of cellulose to lignin (C/L), enzymatic digestibility (ED) of the pretreated solids (PS), expressed as % of the glucose released with respect to the total content in this solid, and enzymatic hydrolysis yield (EHY), expressed as % of the glucose released with respect to the total content in raw exhausted olive pomace (EOP).

2% (w/v) and at 170–210 °C [1]. Using this type of pretreatment, the maximum enzymatic yield was around 40% [1,34].

These results and the fact that the organosolv pretreatment P5 also led to a lower content of acetyl groups (Table 2) make it the best choice as a second step in the biorefinery cascade of EOP to produce glucose.

Composition of the pretreatment liquors and antioxidant activity

The liquors obtained through the application of the different pretreatments were analysed in terms of sugars and inhibitors that provide a direct insight into the effect of LHW and organosolv pretreatments in terms of their solubilisation (Table S1 of the Supporting Information). All pretreatments mainly released hemicellulosic sugars, from 0.27 g/L (PL3) to 15.8 g/L (PL5), while the content of glucose varied between 0.32 g/L (PL1) and 1.51 g/L (PL5) and was not detected in PL3. Not surprisingly, the stronger conditions (P5, 50% ethanol–1% sulfuric acid, 130 °C for 60 min) led to the solubilisation of more monomeric hemicellulosic sugars (15.8 g/L or 10.53 g/100 g EOP). As commented before, xylan was the fraction most affected by the pretreatments. Regarding sugar derivatives, EOP contains mannitol, a large part of which was solubilized in the aqueous extract obtained in the first valorisation step. Nonetheless, a little was solubilized by the pretreatments, up to 2.13 g/L (1.42 g/100 g EOP) (PL5). The liquors also contained formic acid (up to 5.53 g/L, PL6) and acetic acid (up to 2.39 g/L, PL5), agreeing with other authors that applied LHW and organosolv pretreatments to olive tree pruning [20] and corncob [31]. Some authors suggest that the poor delignification provided by LHW is due to the limited solubility of lignin in acid medium caused by the solubilisation of acetic acid from hemicelluloses [31]. However, our results show similar values of acetic acid in the liquors from the pretreatment P1 (LHW) (2.27 g/L) and P5 (organosolv) (2.39 g/L), but different delignification rates.

Moreover, the presence of furfural and hydroxymethylfurfural was found in low concentrations (<0.79 g/L), also agreeing with previous studies for olive-derived biomass [20,29]. Therefore, for further valorisation of hemicellulosic sugars into other valuable compounds, such as bioethanol or xylitol via fermentation, a detoxification step to reduce the content of organic acids will be required.

The TPC and antioxidant activity of the PLs were also determined (Fig. 3). Since the first valorisation step was focused on the extraction of antioxidant phenolic compounds from the non-structural fraction, it is expected that the phenolic components measured in these liquors by TPC correspond to the phenolic hydroxyl groups of the solubilized lignin [31], at least in part. The highest TPC value was obtained in the liquor from the pretreatment P5, which also exhibited a high antioxidant activity, especially in the FRAP assay.

Chemical characteristics and antioxidant properties of the lignin products

The pretreatment P5 was chosen on the basis of the previous results, and OL was obtained from the liquor via direct acid precipitation. In addition, a lignin-rich residue was also recovered after enzymatic hydrolysis (EHL). The yields of both lignins were 7.1% and 19.2% of extracted EOP, respectively. The mass balance of the whole process, including aqueous extraction, organosolv pretreatment P5, lignin precipitation, and enzymatic hydrolysis, is shown in Fig. 4

The chemical composition of the aforementioned lignin products obtained in this process is shown in Table 3. The purity of OL was closer to 90%, being higher than that for EHL (78%). In this regard, EHL showed a higher sugar and ash content compared to OL, since it could be contaminated with the part of cellulose that the enzymes did not hydrolyse during the saccharification step and also with the salts added to the medium.

Moreover, OL and EHL were subjected to further purification by a two-step acid hydrolysis, obtaining two additional products, POL and PEHL, as commented before. The elemental composition of all these lignin products, the raw and extracted EOP, and the PS5 is shown in Table 4. The OL contained nitrogen, indicating protein contamination. This component is naturally associated with lignin in the raw plant source, being removed along with the lignin fragments released during the delignification process [16,35]. Moreover, a part of the nitrogen was removed from OL during the purification step, while another part seemed to be strongly linked to the lignin. As regards carbon, its amount in all lignins is similar and higher than 50%. This agreed with other authors who have reported that carbon and oxygen are the highest components of lignins, which were obtained from different sources and methods. However, their content is variable and depends on the biomass, extraction technique and purity [36,37]. Remarkably, the amount of sulphur in the lignin products from EOP was very low, avoiding the generation of harmful emissions if any of these products were destined for thermal conversion [36]. Also, the ash content was low, thus lowering the possibility of corrosion processes in the boiler in the absence of appropriate maintenance [38].

Besides their use as a fuel, the lignin products were evaluated in terms of their TPC and antioxidant activity to preliminary consider the application as antioxidant additives (Table 5). OL had the

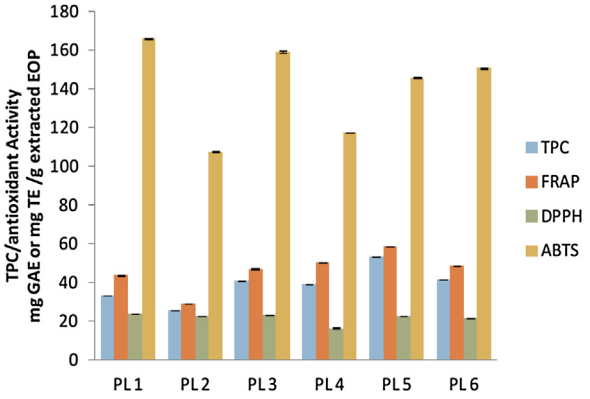

Fig. 3. Antioxidant activity of the pretreatment liquors (PL) obtained from LHW (PL1), organosolv (PL2, PL4–PL6) and combined pretreatments (PL3).

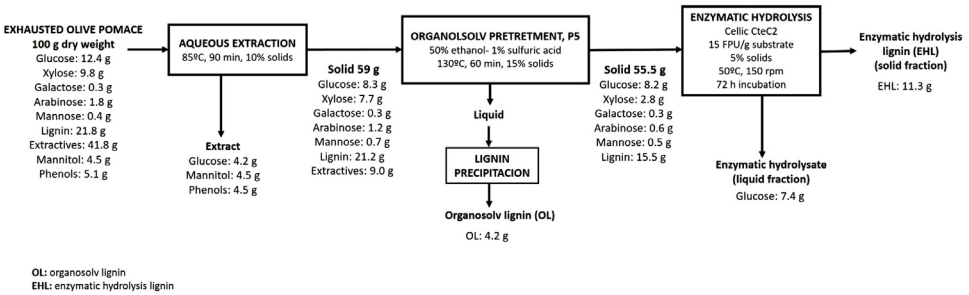

Fig. 4. Material balance flow scheme of the overall process for lignin production from EOP after organosolv pretreatment at 130 °C, 60 min and 15% solids.

Table 3
Chemical components of the organosolv lignin (OL) and the lignin obtained after enzymatic hydrolysis (EHL).

Component	OL (%)	EHL (%)
Glucose	1.42 ± 0.23	12.14 ± 1.66
Xylose	2.05 ± 0.33	3.77 ± 0.25
Galactose	1.40 ± 0.09	ND
Arabinose	1.73 ± 0.69	1.49 ± 0.06
Acid soluble lignin	1.78 ± 1.78	0.58 ± 0.08
Acid insoluble lignin	87.69 ± 2.38	78.34 ± 1.10
Ash	0.0018 ± 0.0001	0.13 ± 0.04

ND, not detected. The data is expressed as mean ± standard deviation (n = 3).

highest TPC and antioxidant activity. Its TPC value (86.37 mg of GAE/g lignin) is in the range between the values found for lignins obtained from bamboo [16] and apple tree pruning [18] using organosolv treatments, and similar to that of olive pomace lignin obtained by ionic liquids [39]. Alternatively, lower TPC values were observed for corncob lignin obtained by LHW and ethanol organosolv treatments applied sequentially [31], although the antioxidant activity cannot be compared due to the use of different units.

In addition, our study also showed that EHL contains antioxidant activity, but this was lower than that for OL. This can be at least partially explained by its lower purity, as commented before. Concerning the loss of activity after the purification step, it seems that the acid hydrolysis can cause degradation of the aromatic units and then modify the antioxidant properties of the lignin [18]. Thus, the lignin samples were analysed by UV–vis spectroscopy and Pyr–GC–MS.

UV–vis and Pyr–GC–MS characteristics of the lignin products

All the lignins have similar UV–vis profiles (Fig. S1 of the Supporting information), but OL required more dilution to avoid signal saturation. This suggests that OL has higher amounts of chromophores and thus phenolic units, which can explain the previous TPC and antioxidant activity results. In this regard, two main UV peaks between 210–220 nm and 270–290 nm were observed and a shield at 230–240 nm. The former sharp peak is typical for lignin, while the maximum around 280 is consistent with a G-rich lignin, since the syringyl unit exhibit its band at lower wavelength, around 268–276 nm [40]. Moreover, the presence of absorbance around 340 nm could derive from a small quantity of the hydroxycinnamic acids [41]. In part, it resembles the UV spectrum of softwood lignin due to the higher presence of G-units [42].

The EOP lignin products were also analysed by Pyr–GC–MS, which enables the determination of the basic structures of lignin through to the detection of pyrolysis products [18]. A total of 30 compounds could be characterized: 28 compounds derived from phenolic compounds (Table 6, Fig. S2 of the Supporting information) along with 3-furaldehyde and 3-ethyl pyridine from sugar and nitrogen compounds, respectively. Most of these compounds were present in all samples, suggesting that OL and EHL are HGS-

Table 4
Elemental composition of the raw exhausted olive pomace (EOP), extracted EOP, pretreatment solid 5 (PS5), and lignin products: organosolv lignin (OL), enzymatic hydrolysis lignin (EHL) and their purified fractions, POL and PEHL.

Sample	N (%)	C (%)	H (%)	S (%)	Ash (%)
Raw EOP	1.31 ± 0.06	42.42 ± 0.24	5.55 ± 0.08	ND	6.41 ± 0.21
Extracted EOP	1.85 ± 0.08	45.41 ± 0.68	5.88 ± 0.05	ND	0.18 ± 0.01
PS5	1.14 ± 0.01	45.81 ± 0.48	5.93 ± 0.01	0.61 ± 0.09	3.18 ± 0.04
OL	2.18 ± 0.05	55.59 ± 0.41	6.23 ± 0.02	ND	0.0018 ± 0.0001
POL	1.78 ± 0.02	56.39 ± 0.20	5.80 ± 0.03	ND	ND
EHL	1.89 ± 0.17	52.18 ± 0.71	6.45 ± 0.13	ND	0.13 ± 0.04
PEHL	1.79 ± 0.06	56.01 ± 0.56	6.41 ± 0.05	ND	0.05 ± 0.01

ND: not detected. The data is expressed as mean ± standard deviation (n = 3).

Table 5
Total phenolic content (TPC) and antioxidant activity of the lignin products, determined by the DPPH, FRAP, and ABTS assays: organosolv lignin (OL), enzymatic hydrolysis lignin (EHL) and their purified fractions, POL and PEHL.

Lignin type	TPC (mg GAE/g lignin)	DPPH (mg TE/g lignin)	FRAP (mg TE/g lignin)	ABTS (mg TE/g lignin)
OL	186.37 ± 0.005	131.10 ± 0.007	254.66 ± 0.02	880.20 ± 0.03
POL	71.63 ± 0.006	68.04 ± 0.01	101.82 ± 0.01	347.67 ± 0.06
EHL	25.86 ± 0.004	25.85 ± 0.05	42.87 ± 0.04	134.34 ± 0.006
PEHL	18.81 ± 0.0015	13.13 ± 0.02	14.19 ± 0.02	81.74 ± 0.001

The data is expressed as mean ± standard deviation (n = 3).

Table 6
Phenolic compounds derivatives found in organosolv lignin (OL), enzymatic hydrolsys lignin (EHL) and their purified fractions, POL and PEHL, by pyrolysis-gas chromatography-mass spectrometry.

No	Retention time (min)	Name	Structure	Main fragments	Monomer assignment	Relative amount (%)[a]			
						OL	POL	EHL	PEHL
1	2.6	Toluene	C_7H_8	65, 91, 92	G, S or H	100	70	45	25
2	3.7	Ethylbenzene	C_8H_{10}	91, 106	G, S or H	100	65	36	32
3	4.1	Styrene	C_8H_8	78, 103, 104	G, S or H	100	98	51	43
4	5.9	Phenol	C_6H_6O	66, 94	H	100	66	50	37
5	6.6	Benzaldehyde, 2-hydroxy	$C_7H_6O_2$	65, 121, 122	H	100	74	17	48
6	6.9	Phenol, 2-methyl-	C_7H_8O	77, 79, 107, 108	H	100	93	26	30
7	7.3	*p*-Cresol	C_7H_8O	77, 107, 108	H	100	57	37	27
8	7.3	Phenol, 2-methoxy	$C_7H_8O_2$	81, 109, 124	G	100	130	119	54
9	8.1	Phenol, 2-ethyl	$C_8H_{10}O$	77, 79, 107, 122	H	100	134	–	–
10	8.3	2,4-Dimethylphenol	$C_8H_{10}O$	77, 79, 107, 121, 122	H	100	47	22	28
11	8.6	Phenol, 4-ethyl	$C_8H_{10}O$	77, 107, 122	H	100	68	53	32
12	8.8	4-Methylguaiacol (creosol)	$C_8H_{10}O_2$	95, 123, 138	G	100	105	68	41
13	9.4	Benzofuran, 2,3-dihydro-	C_8H_8O	91, 120	G, S or H	100	27	74	32
14	9.5	Catechol	$C_6H_6O_2$	64, 110	G	100	93	51	62
15	10.2	1,2-Benzenediol, 3-methoxy-	$C_7H_8O_3$	97, 137, 140	S	100	80	24	62
16	10.4	1,2-Benzenediol, 3-methyl-	$C_7H_8O_2$	78, 123, 124	G	100	–	–	64
17	11.0	Phenol, 5-ethenyl-2-methoxy	$C_9H_{10}O_2$	107, 135, 150	G	100	38	56	26
18	11.2	1,2-Benzenediol, 4-methyl-	$C_7H_8O_2$	78, 123, 124	G	100	62	25	37
19	11.6	3-Methoxy-5-methylphenol	$C_8H_{10}O_2$	107, 138	G	100	–	42	48
20	12.2	Phenol, 2,6-dimethoxy	$C_8H_{10}O_3$	96, 139, 154	S	100	70	34	36
21	13.8	4-Ethylcatechol	$C_8H_{10}O_2$	123, 138	G	100	–	–	–
22	15.2	3,5-Dimethoxy-4-hydroxytoluene	$C_9H_{12}O_3$	125, 153, 168	S	100	87	50	–
23	17.2	Guaiacol, 4-butyl	$C_{11}H_{16}O_2$	122, 137, 180	G	100	26	32	20
24	17.7	Phenol, 4-ethenyl-2,6-dimethoxy	$C_{10}H_{12}O_3$	165, 180	S	100	36	56	24
25	18.1	1-propanone, 1-(4-hydroxy-3-methoxyphenyl)-	$C_{10}H_{12}O_3$	123, 151, 180	G	100	49	22	40
26	19.7	(E)-2,6-Dimethoxy-4-(prop-1-en-1-yl)phenol	$C_{11}H_{14}O_3$	91, 179, 194	S	100	–	–	–
27	20.7	Syringylacetone	$C_{11}H_{14}O_4$	167, 210	S	100	78	49	52
28	21.2	1-Propanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)	$C_{11}H_{14}O_4$	153, 181, 210	S	100	74	42	44
					Total H	100	68	33	31
					Total G	100	63	43	42
					Total S	100	71	35	35

[a] With respect to OL.

type. The H/G/S ratio of OL and EHL was around 2:4:1 and 2:5:1, explaining the UV results due to the predominance of G-units. This unusual H/G/S ratio was also observed in olive pomace [43]. Alternatively, lignins derived from olive tree pruning contained a S/G ratio higher than those values observed here, but it was highly variable, from 1 to 5.1 [44–46]. In this sense, the S/G and H/G/S ratios depend on the type of source, i.e., hardwood/softwood or angiosperm/gymnosperm, and also on the plant part and lignin type [46,47]. Moreover, a loss of H-, G- and S-units was observed after purification, which could explain the lower antioxidant activity of POL (Table 5). As commented before, oxidation can affect the phenolic components during this acid purification step [18]. In this sense, syringyl, phenolics and guaiacyl hydroxyls have shown correlation with the antioxidant activity in the DPPH and ABTS test measured in *Broussonetia papyrifera* lignin [48].

In addition, EHL and PEHL presented lower values for all these units (Table 6). In this regard, Zhao et al. [22] have shown that demethoxylation occurs during the hydrolysis process, while other reactions should not be ruled out since –H, –G, and –S units were affected in this step. In any case, antioxidant lignins can be obtained before and after enzymatic hydrolysis without further purification, but the former has better antioxidant properties and purity.

Conclusions

An integrative valorisation process is proposed to valorise EOP. After a water treatment to recover an aqueous extract rich in hydroxytyrosol and mannitol, an organosolv pretreatment can be performed using 50% ethanol–1% sulfuric acid at 130 °C for 60 min. This provided around 28% of delignification and facilitated the enzymatic hydrolysis (EHY = 69.4%). From the PL, an antioxidant lignin (OL) (purity closer to 90%) was obtained through acid precipitation, which was rich in G-units. Moreover, the solid fraction recovered after enzymatic hydrolysis (EHL) is highly rich in lignin (around 78% of purity) and also has antioxidant properties.

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jiec.2021.01.042.

References

[1] P. Manzanares, E. Ruiz, M. Ballesteros, M.J. Negro, F.J. Gallego, J.C. López-Linares, E. Castro, Span. J. Agric. Res. 15 (2017) 1, doi:http://dx.doi.org/10.5424/sjar/2017153-10868.

[2] M. del M. Contreras, I. Romero, M. Moya, E. Castro, Process Biochem. 97 (2020) 43, doi:http://dx.doi.org/10.1016/j.procbio.2020.06.013.
[3] J.C. Martínez-Patiño, I. Gómez-Cruz, I. Romero, B. Gullón, E. Ruiz, M. Brnčićc, E. Castro, Energies 12 (2019) 2679, doi:http://dx.doi.org/10.3390/en12142679.
[4] J.C. López-Linares, I. Gómez-Cruz, E. Ruiz, I. Romero, E. Castro, Processes 8 (2020) 533, doi:http://dx.doi.org/10.3390/pr8050533.
[5] J.C. López-Linares, E. Ruiz, I. Romero, E. Castro, P. Manzanares, Appl. Sci. 10 (2020) 6966, doi:http://dx.doi.org/10.3390/app10196966.
[6] I. Gómez-Cruz, C. Cara, I. Romero, E. Castro, B. Gullón, Antioxidants 9 (2020) 1010, doi:http://dx.doi.org/10.3390/antiox9101010.
[7] J.I. Santos, Ú. Fillat, R. Martín-Sampedro, M.E. Eugenio, M.J. Negro, I. Ballesteros, A. Rodríguez, D. Ibarra, Int. J. Biol. Macromol. 105 (2017) 238, doi:http://dx.doi.org/10.1016/j.ijbiomac.2017.07.030.
[8] D. Ahuja, A. Kaushik, G.S. Chauhan, Int. J. Biol. Macromol. 97 (2017) 403, doi: http://dx.doi.org/10.1016/j.ijbiomac.2017.01.057.
[9] L. Da Costa Sousa, M. Foston, V. Bokade, A. Azarpira, F. Lu, A.J. Ragauskas, J. Ralph, B. Dale, V. Balan, Green Chem. 18 (2016) 4205, doi:http://dx.doi.org/10.1039/c6gc00298f.
[10] M. Tayier, D. Duan, Y. Zhao, R. Ruan, Y. Wang, Y. Liu, BioResources 13 (2018) 412, doi:http://dx.doi.org/10.15376/biores.13.1.412-424.
[11] D.S. Zijlstra, C.W. Lahive, C.A. Analbers, M.B. Figueirêdo, Z. Wang, C.S. Lancefield, P.J. Deuss, ACS Sustain. Chem. Eng. 8 (2020) 5119, doi:http://dx.doi.org/10.1021/acssuschemeng.9b07222.
[12] A.J. Ragauskas, G.T. Beckham, M.J. Biddy, R. Chandra, F. Chen, M.F. Davis, B.H. Davison, R.A. Dixon, P. Gilna, M. Keller, P. Langan, A.K. Naskar, J.N. Saddler, T.J. Tschaplinski, G.A. Tuskan, C.E. Wyman, Science 344 (2014) 6185, doi:http://dx.doi.org/10.1126/science.1246843.
[13] R. Bhat, H.P.S.A. Khalil, A.A. Karim, C.R. Biol. 332 (2009) 827, doi:http://dx.doi.org/10.1016/j.crvi.2009.05.004.
[14] P.C.H. Hollman, J. Sci. Food Agric. 81 (2001) 842, doi:http://dx.doi.org/10.1002/jsfa.900.
[15] X. Meng, A. Parikh, B. Seemala, R. Kumar, Y. Pu, C.E. Wyman, C.M. Cai, A.J. Ragauskas, Bioresour. Technol. 272 (2019) 202, doi:http://dx.doi.org/10.1016/j.biortech.2018.09.130.
[16] B. Ramakoti, H. Dhanagopal, K. Deepa, M. Rajesh, S. Ramaswamy, K. Tamilarasan, Bioresour. Technol. Rep. 7 (2019)100293, doi:http://dx.doi.org/10.1016/j.biteb.2019.100293.
[17] X. Erdocia, R. Prado, M.Á. Corcuera, J. Labidi, J. Ind. Eng. Chem. 20 (2014) 1103, doi:http://dx.doi.org/10.1016/j.jiec.2013.06.048.
[18] A. García, G. Spigno, J. Labidi, Ind. Crops Prod. 104 (2017) 242, doi:http://dx.doi.org/10.1016/j.indcrop.2017.04.063.
[19] P. Moniz, C. Serralheiro, C.T. Matos, C.G. Boeriu, A.E. Frissen, L.C. Duarte, L.B. Roseiro, H. Pereira, F. Carvalheiro, Process Biochem. 65 (2018) 136, doi:http://dx.doi.org/10.1016/j.procbio.2017.11.012.
[20] M.J. Díaz, W.J.J. Huijgen, R.R. Van, D. Laan, J.H. Reith, C. Cara, E. Castro, Holzforschung 65 (2011) 177, doi:http://dx.doi.org/10.1515/HF.2011.030.
[21] A. Tagami, C. Gioia, M. Lauberts, T. Budnyak, R. Moriana, M.E. Lindström, O. Sevastyanova, Ind. Crops Prod. 129 (2019) 123.
[22] C. Zhao, X. Qiao, Q. Shao, M. Hassan, Z. Ma, Energy Fuels 34 (2020) 5938, doi: http://dx.doi.org/10.1021/acs.energyfuels.0c00293.
[23] A. Sluiter, B. Hames, R. Ruiz, C. Scarlata, J. Sluiter, D. Templeton, D.C. Nrel, Determination of Structural Carbohydrates and Lignin in Biomass Determination of Structural Carbohydrates and Lignin in Biomass NREL/TP-510-42618, (2012) .
[24] J.C. Martínez-Patiño, E. Ruiz, I. Romero, C. Cara, J.C. López-Linares, E. Castro, Bioresour. Technol. 239 (2017) 326, doi:http://dx.doi.org/10.1016/j.biortech.2017.04.102.
[25] V.L. Singleton, S.A. Rossi, Am. J. Enol. Vitic. 16 (1965) 144.
[26] T. Ohra-Aho, M. Tenkanen, T. Tamminen, J. Anal. Appl. Pyrolysis 74 (2005) 123, doi:http://dx.doi.org/10.1016/j.jaap.2004.11.010.
[27] B. Gullón, P. Gullón, G. Eibes, C. Cara, A. De Torres, J.C. López-Linares, E. Ruiz, E. Castro, Sci. Total Environ. 645 (2018) 533, doi:http://dx.doi.org/10.1016/j.scitotenv.2018.07.155.
[28] M. del M. Contreras, A. Lama-Muñoz, F. Espínola, M. Moya, I. Romero, E. Castro, Food Chem. 314 (2020)126218, doi:http://dx.doi.org/10.1016/j.foodchem.2020.126218.
[29] P. Manzanares, I. Ballesteros, M.J. Negro, J.M. Oliva, A. González, M. Ballesteros, Renew. Energ. 145 (2020) 1235, doi:http://dx.doi.org/10.1016/j.foodchem.2020.126218.
[30] E. Tomás-Pejó, P. Alvira, M. Ballesteros, M.J. Negro, in: A. Pandey, C. Larroche, S. C. Ricke, C.G. Dussap, E. Gnansounou (Eds.), Biofuels, Academic Press, Cambridge, 2011, doi:http://dx.doi.org/10.1016/B978-0-12-385099-7.00007-3 p. 149.
[31] M. Michelin, S. Liebentritt, A.A. Vicente, J.A. Teixeira, Int. J. Biol. Macromol. 120 (2018) 159, doi:http://dx.doi.org/10.1016/j.ijbiomac.2018.08.046.
[32] M. Hochegger, B. Cottyn-Boitte, L. Cézard, S. Schober, M. Mittelbach, Int. J. Chem. Eng. (2019)1734507, doi:http://dx.doi.org/10.1155/2019/1734507.
[33] S. Yang, Y. Zhang, W. Yue, W. Wang, Y.Y. Wang, T.Q. Yuan, R.C. Sun, Biotechnol. Biofuels 9 (2016) 1, doi:http://dx.doi.org/10.1186/s13068-016-0656-1.
[34] M.C. Fernandes, I. Torrado, F. Carvalheiro, V. Dores, V. Guerra, P.M.L. Lourenço, L.C. Duarte, Bioethanol 2 (2016) 103, doi:http://dx.doi.org/10.1515/bioeth-2016-0007.
[35] M. del M. Contreras, A. Lama-Muñoz, J.M. Gutierrez-Pérez, F. Espínola, M. Moya, I. Romero, E. Castro, Foods 8 (2019) 531, doi:http://dx.doi.org/10.3390/foods8110531.
[36] O. Gordobil, R. Moriana, L. Zhang, J. Labidi, O. Sevastyanova, Ind. Crops Prod. 83 (2016) 155, doi:http://dx.doi.org/10.1016/j.indcrop.2015.12.048.
[37] T.D.M. Florian, N. Villani, M. Aguedo, N. Jacquet, H.G. Thomas, P. Gerin, D. Magali, A. Richel, Ind. Crops Prod. 132 (2019) 269, doi:http://dx.doi.org/10.1016/j.indcrop.2019.02.022.
[38] A.J. Perea-Moreno, M.J. Aguilera-Ureña, F. Manzano-Agugliaro, Fuel 186 (2016) 358, doi:http://dx.doi.org/10.1016/j.fuel.2016.08.101.
[39] E. Cequier, J. Aguilera, M. Balcells, R. Canela-Garayoa, Biomass Convers. Biorefin. 9 (2019) 241, doi:http://dx.doi.org/10.1007/s13399-019-00400-w.
[40] R. El Hage, N. Brosse, L. Chrusciel, C. Sanchez, P. Sannigrahi, A. Ragauskas, Polym. Degrad. Stab. 94 (2009) 1632, doi:http://dx.doi.org/10.1016/j.polymdegradstab.2009.07.007.
[41] K. Wang, F. Xu, R. Sun, Int. J. Mol. Sci. 11 (2010) 2988, doi:http://dx.doi.org/10.3390/ijms11082988.
[42] S.Y. Lin, in: S.Y. Lin, C.W. Dence (Eds.), Methods in Lignin Chemistry, Springer, Berlin, Heidelberg, 1992, pp. 217–232.
[43] I. Sampedro, T. Cajthaml, S. Marinari, M. Petruccioli, I. Sampedro, S. Grego, A.D. Annibale, Process Biochem. 44 (2009) 216, doi:http://dx.doi.org/10.1016/j.procbio.2008.10.016.
[44] J. Rencoret, A. Gutiérrez, E. Castro, J.C. Del Río, Holzforschung 73 (2018) 25, doi: http://dx.doi.org/10.1515/hf-2018-0077.
[45] A. Sequeiros, J. Labidi, Ind. Crops Prod. 97 (2017) 469, doi:http://dx.doi.org/10.1016/j.indcrop.2016.12.056.
[46] J.I. Santos, R. Martín-Sampedro, Ú. Fillat, J.M. Oliva, M.J. Negro, M. Ballesteros, M.E. Eugenio, D. Ibarra, Int. J. Polym. Sci. 105 (2015) 238, doi:http://dx.doi.org/10.1155/2015/314891.
[47] A. Lourenço, H. Pereira, in: M. Poleppo (Ed.), Lignin - Trends and Application, InTech, Rijeka, Croatia, 2018, pp. 65–98.
[48] L. Yao, L. Xiong, C.G. Yoo, C. Dong, X. Meng, J. Dai, A.J. Ragauskas, C. Yang, J. Yu, H. Yang, X. Chen, Sustain. Energy Fuels 4 (2020) 5114, doi:http://dx.doi.org/10.1039/d0se00940g.llll

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Corrigendum

Corrigendum to "A biorefinery approach to obtain antioxidants, lignin and sugars from exhausted olive pomace" [J. Ind. Eng. Chem. 96 (2021) 356–363]

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The authors regret having detected an error in the publication "A biorefinery approach to obtain antioxidants, lignin and sugars from exhausted olive pomace". In the original paper, the antioxidant activity measured by ABTS assay was calculated incorrectly. As a consequence, the values of ABTS in Fig. 3 and Table 5 must be corrected by multiplying by 0.626. We ensure that the discussion of the results and the conclusions of the work are valid because the error did not affect to the data analysis.

The authors would like to apologise for any inconvenience caused.

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