Recovery of pentoses-containing olive stones for their conversion into furfural in the presence of solid acid catalysts


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Abstract

Olive stones were employed as feedstock for furfural production in two stages: 1) autohydrolysis of hemicellulosic fraction to recover their pentoses, mainly xylose, and 2) subsequent dehydration of pentoses into furfural. Autohydrolysis step was optimized by using different experimental conditions (temperature: 160-200 °C and time: 30-75 min), giving rise to liquors with different xylose concentrations, since hydrolysis was incomplete in some cases. The combined use of a commercial \( \gamma \)-Al\(_2\)O\(_3\) and CaCl\(_2\) led to total hydrolysis of non-hydrolyzed pentosans after autohydrolysis step, and the subsequent dehydration of pentoses into furfural. The maximum values of furfural yield and efficiency were 23 and 96%, respectively, after only 60 minutes at 150 °C by using liquor obtained by autohydrolysis at 180 °C and 30 min (L5.1) as source of pentoses. This liquor, L5.1, provided better catalytic results than other liquors which had shown higher xylose concentration after autohydrolysis, probably due to
these latter also exhibited a higher concentration of organic acids; thus, the presence of organic acids such as acetic and lactic acid could promote side undesired reactions leading to lower furfural yields. Finally, $\gamma$-$\text{Al}_2\text{O}_3$ was more effective for furfural production under these experimental conditions than other solid acid catalysts, such as mesoporous Nb$_2$O$_5$, Nb-doped SBA-15 and Zr-doped HMS silicas, probably due to alumina has a higher density of acid sites.

**Keywords:** lignocellulosic biomass, hemicellulosic liquors, olive stones, xylose dehydration; furfural, solid acid catalysts.

1. **Introduction**

Awareness of climate change and the rapid depletion of non-renewable fossil sources, together with the high volatility in crude oil price, have led to the search and development of alternative sustainable processes for the production of chemicals and fuels from non-fossil carbon sources (Werpy and Petersen, 2004). In this sense, a very promising environmentally friendly raw material is biomass, mainly lignocellulosic biomass, as it is the only widely available and renewable source of carbon (Stocker, 2008; Alonso et al., 2010; Van Putten et al., 2013), with an estimated annual production of approximately $2 \cdot 10^{11}$ metric tons (Wang et al., 2014). Lignocellulosic biomass is mainly composed of lignin, cellulose and hemicellulose, which possess specific properties that provide different uses (Garrote et al., 2007; Willför et al., 2008). For this, the use of local biomass, such as agricultural, forestry, agro-industrial and industrial waste, is of great interest due to its low cost and high availability, specially in countries such as Spain, highly dependent on external supply of fossil resources for energy and chemicals.
In this context, the extraction of olive oil and the olive table market represent an economic and social industrial activity that is very relevant in Mediterranean countries, such as Spain, Greece, Italy and Tunisia, being olive stones one of main waste obtained. The annual production of olives in the Mediterranean basin is estimated about 19 million tons, according to the Corporate Statistical Database of the United Nations Food and Agriculture Organization (FAOSTAT, 2016), generating 3 million tons of olive stones, as it represents between 10-30% by weight of the fruit (Garrido-Fernández et al., 1997). Spain, considered as the main world producer of olive-derived products, produces approximately 30000 tons per year of olive oil and 400000-600000 tons per year of olive stones (International Olive Oil Council, 2007; Manzanares et al. 2017).

Currently, the main use of olive stones and its derivatives is as solid fuel, or renewable source of energy due to its heat of combustion and good physico-chemical properties (Romero-García et al., 2014). Olive stones also find applications as plastic filler for thermoplastic polymer (Siracusa et al., 2001), abrasive (Dawson, 2006), in cosmetic (Cosmoliva Road, 2007; Korres, 2007), binder metal (Calero et al., 2006), source of phenols to obtain phenol-formaldehyde resins (Tejeda-Ricardez et al., 2003) and for electrochemical applications (Theodoropoulou et al., 2004). Likewise, olive stones have also been employed as raw material to produce high value-added chemicals, such as furfural and 5-hydroxymethylfurfural (HMF). Furfural is considered one of the most promising chemicals with an annual world production about 430000 tons, whose industry is growing due to green chemical initiatives (Werpy and Petersen, 2004; Yebo, 2014; Raman and Gnansounou, 2015). This compound can be employed for the production of fungicides, nematicides, specialized adhesives, flavoring compounds and recovery of refinery lubricants, in addition to being an important precursor of other chemicals, such as 5-methyl furfural, furfuryl alcohol, tetrahydrofururyl alcohol and
tetrahydrofuran (Win, 2005; Raman and Gnansounou, 2015). Furfural is obtained by acid hydrolysis of hemicellulose and subsequent dehydration of the resulting C5 monomers, mostly xylose and arabinose, although some hexoses and uronic acids are also present after hydrolysis (Filiciotto et al., 2018; Gómez-Millán et al., 2019). The pentosan content varies between 6-32%, depending on the kind of biomass, being olive stones one of the lignocellulosic biomass with higher hemicellulose content (21-28 wt%) (Zeitsch, 2000; Cuevas et al., 2015a). On the other hand, cellulose and lignin can be employed as fuel or to efficiently produce other chemicals, such as ethanol and lignin derivatives (Vázquez et al., 2007). Therefore, the fractionation of biomass is required for total exploitation of their main components (cellulose, hemicellulose and lignin). Thus, hemicellulose can be separated as a liquid fraction by means of a hydrolysis stage, obtaining a solid which contains cellulose and lignin that can subsequently be valorized (Cai et al., 2014; Cuevas et al., 2015b; Raman and Gnansounou, 2015). In the literature, there are numerous studies dealing with the production of furfural from agricultural biomass, in single (Fernández-Bolaños et al., 2001; Lama-Muñoz et al., 2014; Saleh et al., 2014; Cuevas et al., 2015a), two-steps (Riansa-Ngawong and Prasertsan, 201; Raman and Gnansounou, 2015) or continuous (You et al., 2015) processes. However, cellulose and lignin can also be degraded, leading to side reactions that decrease furfural yield and generate more wastes (Zhang et al., 2014). It has been reported that the side reactions are limited when furfural production is carried out in two steps, obtaining higher furfural yields (Mansilla et al., 1998; Punsvon et al., 2008).

On the other hand, although the use of liquid mineral acids, such as H$_2$SO$_4$ or HCl, has been widely studied for the hydrolysis of polysaccharides (Fernández-Bolaños et al., 2001; Montané et al., 2002; Hernández et al., 2014; Padilla-Rascón et al., 2020), much attention is being paid to the development of autohydrolysis processes in the
presence of only water, since the presence of acids coming from hemicellulose degradation, such as acetic or formic acids, as well as hydronium ions produced by autoionization of water, provide low pH values that allow autohydrolysis reaction (Cuevas et al., 2015b). Thus, autohydrolysis of olive stones has been studied in the literature. Nabarlatz et al. (2007) compared different agricultural wastes, being olive stones between them, carrying out hydrolysis in deionized water at 179 °C for 23 min. They found that hemicellulose can be easily depolymerized, whereas cellulose and lignin mostly remained in the hydrolysis solid residue. Moreover, the xylo-oligosaccharides yield depended on both the xylan content and the amount of acetyl groups of these raw materials, due to these groups liberated acetic acid, which was able to depolymerize xylans. Cuevas et al. (2009) realized autohydrolysis of olive stones between 175 and 225 °C, with severity factors between 2.73 and 4.39, in order to employ these liquors for ethanol production. In the autohydrolysis step, they found that the maximum content of oligosaccharides was attained for a severity factor of 3.67, since higher values promoted degradation processes, decreasing the oligosaccharide yield. Likewise, Cardador dos Santos et al. (2011) confirmed that the composition of liquors depended on the severity factor employed for autohydrolysis of olive stones. They also demonstrated that higher hydrolysis rates, observed under harder hydrolysis conditions, led to higher concentrations of monosaccharides and aliphatic acids, such as formic and acetic acids. On the other hand, Cuevas et al. (2015b) studied autohydrolysis of olive stones with hot water between 150-225 °C for 0–10 min, concluding that complete hemicellulose solubilization took place with a severity factor near of 3.7, obtaining high oligosaccaride yield and a low amount of acetic acid. Borrero-López et al. (2017) evaluated autohydrolysis of olive stones between 160-240 °C at different reaction times (1-8 h), showing that pH values and the severity factor influenced the
Furfural production and degradation, achieving the highest furfural yield after 4 h at 190 °C.

Once that depolymerization of hemicellulose has occurred by autohydrolysis, furfural production is carried out in the presence of acid catalysts. Traditionally, conventional liquid mineral acids are reported as catalysts in the literature (Riansa-Ngawong and Prasertsan, 2011; Raman and Gnansounou, 2015), but the use of solid acid catalysts is more convenient due to they, unlike mineral acids, are environmentally friendly and can be reused. Recently, our research group reported that the combined use of γ-Al₂O₃ and CaCl₂ allows successfully to carry out the xylose dehydration in a water:toluene biphasic system, attaining a furfural yield of 55% after 50 min at 150°C (Fúnez-Núñez et al., 2019). In this previous work, a synergistic effect between alumina and inorganic salt was found due to CaCl₂ favored the formation of α xylose anomer and γ-Al₂O₃ promoted the furfural production. Thus, this fact was studied by ¹H-NMR spectroscopy, showing that CaCl₂ increased the α-xylopyranose/β-xylopyranose ratio, whereas signals associated to the furan ring of furfural were observed after addition of γ-Al₂O₃. Considering these aspects, the main goal of the present work was to obtain furfural from liquors made by autohydrolysis of olive stones. For this purpose, this process was carried out in two steps in order to decrease the side reactions: (1) the autohydrolysis of olive stones in hot water, optimizing reaction temperature and time, aiming at maximum recovery of carbohydrates present in the hemicellulose and (2) the furfural production from liquors produced in the first stage, as xylose source, in the presence of γ-Al₂O₃ and CaCl₂. Likewise, characterization of both olive stones and liquors was carried out in order to know how their properties and composition influence furfural production in the dehydration stage. The use of other solid acid catalysts, such as mesoporous Nb₂O₅, Nb-doped SBA-15 and Zr-doped HMS silicas which previously
demonstrated to be active for dehydration of carbohydrates (García-Sancho et al., 2014a; García-Sancho et al., 2014b; Mérida-Morales et al., 2020), was also evaluated for furfural production by using hemicellulosic liquors obtained from olive stones.

2. Experimental

2.1. Synthesis of catalysts

A commercial γ-alumina (Alfa-Aesar, Brockmann Grade I, 58 Å) was employed as solid acid catalyst.

A zirconium-doped mesoporous HMS silica with a Si/Zr molar ratio of 5 was prepared following the method proposed by Cecilia et al. (2016). For this, 3.1 g of dodecylamine (Merck, 98%) were dissolved in 21.5 mL of water and 17.9 mL of ethanol (VWR), under stirring. A solution composed of 14.8 mL of tetraethyl orthosilicate (TEOS) (98%, Aldrich) and 5.78 mL of zirconium n-propoxide (70 wt.% in 1-propanol, Aldrich) was added dropwise, keeping stirring for 24 h. The solid was recovered by filtration, washed with deionized water, dried and calcined at 550 ºC for 6 h (1ºC min⁻¹). This catalyst was denominated as Zr-HMS.

A niobium-doped mesoporous SBA-15 silica with a Si/Nb molar ratio of 16 was synthesized modifying the procedure described by Trejda et al. (2008). Thus, an aqueous solution of 4 g of Pluronic P123 (Sigma-Aldrich) was added to a solution of NbCl₅ (Sigma-Aldrich, 99%) previously dissolved in water. Then, 9.1 mL of TEOS were incorporated to the mixture, which was aged at room temperature for 7 days. Finally, the solid was filtered, washed with deionized water, dried and calcined at 550 ºC for 6 h (1ºC min⁻¹). This catalyst was denoted as Nb-SBA.

A mesoporous niobium oxide was synthesized following the route previously reported by Lee et al. (2002). Thus, 0.22 mmol of Pluronic L121 (Sigma-Aldrich) were
dissolved in 10 g of n-propanol (VWR), and, after complete dissolution, 7 mmol of NbCl₅ were added, and, after 5 min of vigorous stirring, 1.0 mL of a 0.05 M NaCl aqueous solution was also incorporated, under inert atmosphere. This mixture was stirred at room temperature for 30 min and subsequently aged at 40 ºC for 10 days. Finally, the solid was recovered and calcined at 450 ºC for 4 h (1 ºC min⁻¹). This material was called as Nb₂O₅.

The textural and acidic properties of these catalysts were evaluated by N₂ adsorption-desorption isotherms at -196 ºC and NH₃-TPD respectively (see analysis conditions in Supplementary Information).

2.2. Synthesis of hemicellulosic liquors by autohydrolysis

Olive stones used as the starting biomass in the liquor manufacturing process were supplied by Orujera Interprovincial de Fuente de Piedra (Málaga, Spain) and were characterized by using NREL, TAPPI standards and bibliographic methods (Scheme 1 and Supplementary Information). Olive stones were milled, sieved and dried under air conditions until equilibrium in relative humidity (less than 10%) was reached. After that, they were employed to obtain hemicellulosic liquors rich in xylose by autohydrolysis (Scheme 2).

In this autohydrolysis stage, 100 g of olive stones were put in contact with water by using a solid:liquid weight ratio of 1:10, taking into account the humidity degree of the raw material. This step was carried out in a 2 L stainless steel pressure reactor with temperature–pressure control and mechanical stirring (Parr, Moline, IL, USA). In order to optimize the autohydrolysis conditions, this stage was studied under different hydrolysis temperature and time (160, 180, 190, 200 ºC and 30, 45, 60, 75 min) to maximize the hydrolysis of pentosans and the concentration of pentoses, mainly xylose.
The mixture of olive stones and water was heated at 10 °C-min⁻¹ and time zero was set when the reactor reached the study temperature. After autohydrolysis, the liquid and solid fraction were separated by filtration and characterized according to the corresponding standardized methods, giving rise to 16 liquors obtained at different experimental conditions, which were denoted as LX.1 where X indicates values between 1-16 attributed to given experimental conditions and 1 means first autohydrolysis step (Table 1). Likewise, other two liquors (L17.1 and L18.1) were prepared by using CaCl₂ (0.65 gCaCl₂·gaqueous solution⁻¹) in the autohydrolysis step in order to evaluate its effect.

2.3. Characterization of hemicellulosic liquors

The liquid fraction recovered after autohydrolysis stage (L1.1-1.18) was analyzed by high performance liquid chromatography (HPLC) to determine its composition, trying to recover the maximum possible xylose concentration, being the main detected products: xylose, arabinose, glucose, furfural, HMF, acetic acid (AA), formic acid (FA) and lactic acid (LA). Post-hydrolysis process was used for complete hemicellulose oligosaccharides depolymerisation for L1.1-L16.1 liquors. This process allows the conversion of oligosaccharides into their respective monomeric sugars. For this purpose, 100 mL of each liquor was subjected to a post-hydrolysis process with 4% H₂SO₄ (w/w) at 100 °C for 1 h, extracting small aliquots of post-hydrolysis liquor every 15 min, which were analyzed by HPLC. The potential xylose for furfural production present in these LX.1 liquors was determined by this post-hydrolysis process, giving rise to LX.2 liquors (Scheme 2). In all cases, a JASCO instrument equipped with two detectors, multiple wavelength detector (MD-2015) and refractive index (RI-2031), a quaternary gradient pump (PU-2089), automatic injector (AS-2055), an oven (co-2065) and a column (Phenomenex Rezex ROA-Organic Acid H⁺ (8%) (300 mm×7.8 mm, 5
μm) was employed to determine the composition of liquors. All chemicals were analyzed by means of a refractive index detector, while the production of furfural was controlled using a multiple wavelength detector (278 nm). The mobile phase consisted of aqueous H$_2$SO$_4$ solution 0.005M (flow rate 0.35 mL·min$^{-1}$) for Rezex ROA-organic acid H$^+$, being the column at 40 °C.

On the other hand, 10 mL of each liquor (LX.1) was also characterized in terms of density, pH and percentage of total dissolved solids (oven at 105 °C for 24h). Likewise, the percentage of organic matter (mainly lignin and cellulose) was obtained by calcination of the sample in an oven at 525 °C for 3 h, after calculating the total matter, and, finally, the percentage of inorganic matter (silicates and salts) was determined by difference.

2.4. Catalytic test for furfural production

The catalytic dehydration reaction of xylose to produce furfural was performed by using the hemicellulosic liquors obtained after autohydrolysis (LX.1). Catalytic tests were carried out in batch conditions, under magnetic stirring (Scheme 2), using a glass pressure bushing reactor (Ace, 15 ml). In a typical experiment, 1.5 mL of LX.1 liquor were poured into the reactor (aqueous phase), to which were added 0.05 g catalyst, 0.65 g CaCl$_2$·g$_{\text{aqueous solution}}$ as inorganic salt, and 3.5 mL of toluene, as organic co-solvent. To minimize side reactions, the reactor was purged with N$_2$ before catalytic experiments. Likewise, reactors were introduced in an aluminum block, whose temperature was controlled by a thermocouple. The reaction was quenched by immersing the reactor in a cold water bath. Both the organic and aqueous phases were separated and filtered to be analyzed by HPLC, being xylose, arabinose, glucose, AA, FA, LA, HMF and furfural the main detected products. The aqueous phase was analyzed under similar experimental conditions than liquors (see section 2.3). In the
case of the organic phase, a reverse phase Phenomenex Luna C18 column (250 mm×4.6 mm, 5 μm) was employed, determining the furfural concentration by the multiple wavelength detector (285 nm). The mobile phase consisted of pure methanol (flow rate 0.5 mL·min⁻¹), being the column at room temperature.

2.4.1. Xylose and furfural quantification

Through HPLC analysis, all chemicals, mainly xylose and furfural, were quantified in the liquors obtained after the both stages, LX.1 and LX.2 (X = 1-18). From these data, the recovery of pentoses was calculated considering the pentoses detected (xylose and arabinose) with respect to hemicellulose determined for olive stones and these pentoses together with the mass of xylose required to obtain the amount observed of furfural, according to these two expressions (eq. 1 and 2):

\[
y_{\text{pentoses}}(\%) = \frac{\text{Xylose Mass} + \text{Arabinose Mass}}{\text{Hemicellulose Mass of Olive Stones}} \cdot 100 \quad (1)
\]

\[
y_{\text{pentoses+furfural}}(\%) = \frac{\text{Xylose Mass} + \text{Arabinose Mass} + \text{Xylose Mass} \cdot \text{Furfural}}{\text{Hemicellulose Mass of Olive Stones}} \cdot 100 \quad (2)
\]

Likewise, the LX.1 liquors were synthesized under different severity factors (log (R0)) in order to summarize in one variable the harshness of different autohydrolysis treatment conditions. Thus, it was calculated as defined by Overend and Chornet, (1987) (eq. 3), where t is the reaction time in minutes, T_H represented the process temperature and T_ref is a reference temperature (100 ºC):

\[
\log R_0 = \left(\frac{T_H - T_{\text{ref}}}{14.75}\right) \times \log t \quad (3)
\]
On the other hand, regarding furfural produced, the results of the present study were expressed as a function of furfural yield and furfural efficiency, in which furfural produced was expressed with respect to the total mass of olive stones and the highest mass of pentoses detected in our liquors (23.6 wt% obtained from L5.2), respectively (eq. 4 and 5):

\[ y_{Furfural} (%) = \frac{\text{Furfural Mass Obtained}}{\text{Total Mass of Olive Stones}} \cdot 100 \quad (4) \]

\[ E_{Furfural} (%) = \frac{\text{Furfural Mass Obtained}}{\text{Maximum mass of Pentoses}} \cdot 100 \quad (5) \]

In both cases, the actual total mass of furfural obtained in each experiment was calculated taking into account both the furfural formed in the aqueous and organic phases after the dehydration process, and removing the amount of initial furfural present in the liquor after the stage of autohydrolysis.

3. Results and discussion

3.1. Characterization of olive stones

The characterization of olive stones, used as starting biomass in the liquor production process, by standardized methods (Scheme 1) provided the following composition: lignin (37.9 wt%), holocellulose (64.0 wt%), α-cellulose (33.7 wt%), hemicellulose (30.3 wt%), extractives (2.7 wt%) and ashes (0.8 wt%). In general, these results were similar to those obtained by Álvarez et al. (2018) by using the same methods. It can be shown that hemicellulose was the minor of three main components for lignocellulosic biomass (cellulose, hemicellulose and lignin) in our case, accounting about 30 wt% of olive stones, similarly to the value deduced by Álvarez et al. (2018) by using a novel method, and slightly lower than that obtained by Montané et al. (2002) by
using different methods for the analysis of olive stones. Therefore, this hemicellulose content was close to those reported for other olive stones in the literature. A key factor was the calculation of holocellulose since a value of 80.9% was attained in our case following the method proposed by Wise et al. (1946). For this reason, it was decided to employ the novel method proposed by Álvarez et al. (2018) for some types of lignocellulosic biomass, such as olive stones, since they decreased from 95% of holocellulose determined by the standard method until 54% with the novel method. This latter was applied as an alternative in the present study, thus obtaining a 64% of holocellulose content of olive stones. Therefore, it could be affirmed that this method was more suitable to determine the holocellulose content. Regarding extractives (non-structural components of lignocellulose, including phenolics, resin acids, waxes, fats, and inorganics), 2.7 wt% was found in our case, similarly to that obtained by Álvarez et al. (2018) (2.3 wt%) and higher than that reported by Montané et al. (2002) (1.5 wt%) (Montané et al., 2002; Álvarez et al., 2018). Considering that these latter authors employed an ethanol-toluene mixture instead of ethanol-benzene, it is inferred that this latter could be more effective. In addition, the percentages of humidity, ash, and solubility in hot water and in NaOH were also determined, attaining 9.0%, 0.8%, 1.1%, and 12.4%, respectively.

3.2. Characterization of hemicellulosic liquors

3.2.1. Autohydrolysis process

Firstly, the autohydrolysis of olive stones, under different experimental conditions, was carried out to produce pentose-rich liquors, mainly xylose, which was subsequently dehydrated to produce furfural in a second stage. Therefore, it was relevant to optimize the autohydrolysis conditions to obtain the maximum pentose concentration. In addition, the solid waste mainly composed by cellulose and lignin
could also be valorized, although this fact was not objective for this work. The influence of severity factors associated to different autohydrolysis temperatures (160-200 ºC) and times (30-75 min) was evaluated, giving rise to 16 liquors (L1.1-L16.1). Prior to the compositional analysis, some physico-chemical properties were determined, such as density, pH and the contents of organic and inorganic matter (Table 1). All the liquors showed acid pH values after the autohydrolysis stage, finding the lowest ones for liquors with the highest severity factor values. This fact could be probably due to more drastic temperature and time conditions led to the formation of higher amounts of organic acids such as acetic acid (AA) produced by the presence of acetyl groups in the lignocellulosic biomass, which decreased the final pH of these liquors to pH= 3-4, as had previously found by other authors in the autohydrolysis of olive stones (Nabarlatz et al., 2007; Cuevas et al., 2015a). Regarding density, values close to water density were found in all cases for L1.1-16.1 liquors, being slightly lower for those liquors with the highest severity factor values, although a trend was not found. On the other hand, the inorganic matter content (IM) was very low in all cases and the organic matter content (OM) increased for higher autohydrolysis times at 160 ºC, but it was lower when the autohydrolysis took more time at higher temperatures.

Afterwards, the composition of these liquors was analyzed, being xylose, arabinose, glucose, furfural, acetic acid and formic acid the main constituents detected (Figure 1 and Table 1S). It is well known that hemicellulose is mainly formed for pentosans, mostly xylans, whose hydrolysis reaction gives rise to the corresponding monomers. Therefore, one of more abundant chemicals found for these liquors after depolymerization of hemicellulose present in olive stones was xylose, whose concentration varied in the range of 0.13-16.76 g xylose·L⁻¹, depending on temperature and time of autohydrolysis (Table 1S). Hence, the xylose concentration enhanced with
the time at 160 ºC (L1.1-4.1), although, at higher temperatures (180 and 190 ºC), the xylose concentration also increased initially, but it started to decrease from 60 and 45 min, respectively, in such a way that the maximum values were obtained for L7.1 and L10.1 (16.76 and 16.48 gxylose·L⁻¹ respectively). These hydrolysis conditions correspond to severity factor of 4.13 and 4.30 respectively. Thus, lower xylose concentrations were found for more drastic conditions (log R₀ > 4.3), since degradation of some monosaccharides could take place, as previously noted by Cuevas et al. (2009). Therefore, it could be inferred that the production of xylose monomers due to hydrolysis of polysaccharides prevailed over the degradation reactions for L7.1 and L10.1 liquors, although total hydrolysis of xylans could not have took place in these conditions, since the recovery of pentoses was lower, as will be commented later.

In addition, it should be noted that another pentose, arabinose, was also detected for L1.1-4.1 liquors prepared at 160 ºC and traces for L5.1, obtained at 180 ºC and 30 min. However, its concentration (0.09-0.58 garabinose·L⁻¹) was much lower than those of xylose (Figure 1 and Table 1S). As previously Cuevas et al. (2015b) confirmed, the hydrolysis of arabinose chains would require lower severity factor than the xylose ones, attaining its maximum concentration after autohydrolysis at 160 ºC for 75 min. Moreover, glucose monomers were only detected for L12.1-L16.1 liquors, being necessary at least 190 ºC and long reaction times (> 75 min), or higher than 200 ºC for its production, although a very low glucose concentration was detected for L1.1 (160 ºC and 30 min) (Figure 1 and Table 1S). This result agrees with those obtained by Gao et al. (2012), who affirmed that cellulose degradation takes place above 200 ºC because of its crystallinity. The low glucose concentration observed for L1.1 could be due to glucose present in hemicellulose, thus demonstrating that its content is very low. These monomers would disappear for L2.1-L11.1, since they were converted into other
chemicals, as, for example, 5-hydroxymethylfurfural (HMF), which was detected by HPLC, but its concentration was negligible (not included).

On the other hand, aliphatic acids, such as acetic (AA) and formic (FA) acids had been reported after hydrolysis of olive stones in the literature (Cardador-Santos et al., 2011; Padilla-Rascón et al., 2020). In our case, AA was detected in all cases, whereas a low concentration of FA was found for more severe conditions (Figure 1 and Table 1S). Another self-produced organic acid coming from the hydrolysis of lignocellulosic biomass is lactic acid (LA) (Lyu et al., 2019), which was not detected in any case for L1.1-16.1 liquors. The presence of these organic acids explains the acid pH of these liquors. Regarding the AA concentration, it enhanced with the treatment severity, attaining a maximum concentration for L10.1. Nevertheless, the AA content decreased for more drastic conditions, that is, for severity factor above 4.4. This result agrees with that found by Cuevas et al. (2015b), who observed the highest AA formation for log R₀ values of 3.5-4.5. It is noteworthy that the xylose concentration grew in parallel with the AA increment, following these chemicals a similar trend for similar autohydrolysis conditions (Figure 1). Only in the case of autohydrolysis at 200 °C (L13.1-16.1), a decrease in xylose concentration was observed, whereas the amount of AA was almost unchanged. Therefore, a higher AA concentration could provide a more acidic environment, promoting autohydrolysis reactions and consequently a positive effect of the pretreatment (Lu et al., 2016). However, high AA concentrations exert a negative effect on the recovery of xylose monomers, due to their degradation could also have been promoted, as was previously suggested by Padilla-Rascón et al. (2020). These authors affirmed that xylose degradation reactions led to the formation of furfural for high AA concentrations. In our case, this relationship between furfural and AA concentration was also observed, in such a way that they followed similar trends
(Figure 1), obtaining the greatest furfural concentration at high temperatures and short times, as previously observed by Montané et al. (2002) for acid-diluted hydrolysis of olive stones. Recently, Lyu et al. (2019) studied the hemicellulose depolymerization by using sweet sorghum bagasse as biomass source, confirming that self-produced organic acids accelerated its hydrolysis, but high acid concentrations, mainly, of AA and LA, promoted the conversion of xylose to furfural and other small degradation products under severe conditions. Nonetheless, the combined use of AA and LA accelerated the production of xylose, but hindering the formation of furfural. As the inhibition of furfural formation was not displayed in the presence of AA for our liquors (L1.1-16.1), it could be thought that the absence of LA in these liquors could avoid the degradation of xylose. This fact could be related to LA possesses lower pKₐ (3.86) than AA (4.76) in such a way that its higher acid strength could favor these degradation reactions.

Likewise, the recovery of pentoses-containing olive stones with respect to its hemicellulose content (30.3 wt%) was calculated in order to know autohydrolysis conditions that provide a greater degree of C5 carbohydrate recovery. On the one hand, the content of C5 sugars in liquors was considered as the sum of xylose and arabinose monomers with respect to hemicellulose content (ypentoses). It can be observed that the highest pentose concentrations were found for L7.1 and L10.1 liquors in such a way that the recovery of pentoses was equal to 55.3 and 54.4% respectively (Figure 2). In the case of autohydrolysis carried out at 180 °C, shorter times than 60 min (L7.1) were not enough to make accessible all pentose monomers, as occurred for L5.1 and L6.1. However, it is feasible that polysaccharides had been partially depolymerized and shorter oligosaccharide chains were obtained, which were not identified by HPLC. Indeed, Cuevas et al. (2009) previously affirmed that the maximum oligosaccharide content was attained for a severity factor of 3.67, being this value between L4.1 (log R₀
= 3.64) and L5.1 (log \( R_0 \) = 3.83), so it is probably that one of these liquors present the highest concentration of oligosaccharides. However, the recovery of pentoses was maximum after 45 min when autohydrolysis was carried out at 190 °C (L10.1), and then it considerably decreased probably due to side reactions promoted at higher temperatures and/or times. This fact was corroborated by the recovery of pentoses after autohydrolysis at 200 °C (L13.1-16.1), where the concentration of pentoses (xylose+arabinose) was low, even at short reaction times. On the other hand, the amount of furfural produced comes from pentoses, so it could be considered inside the recovery of C5 carbohydrates in liquors (\( y_{\text{pentoses+furfural}} \)). These values were also included in Figure 2, and it can be observed that, although higher values were found, the trend was similar to that detected for \( y_{\text{pentoses}} \), being maximum for L7.1 and L10.1 liquors, with values of 70 and 73%, respectively.

Finally, it had been previously reported that calcium cations can interact with carbohydrates, even improving the production of high value-added chemicals, such as furfural and HMF (Yang et al., 2006; García-Sancho et al., 2017; Fúnez-Núñez et al., 2019). Ca\(^{2+}\) ions exhibit the ability to form complexes with carbohydrates, facilitating their subsequent transformation. In this sense, it was considered convenient to ascertain the influence of calcium ions on the autohydrolysis process due to it is likely that these cations can also interact with carbohydrate-containing hemicellulose. Moreover, if Ca\(^{2+}\) promoted autohydrolysis, this reaction could be carried out under milder conditions in the presence of these cations. Thus, the optimal concentration found in a previous work, which considerably enhanced the xylose dehydration to furfural (0.65 g\( \text{CaCl}_2 \cdot \text{aqueous solution} \)^{-1}), was employed to perform the autohydrolysis of olive stones (Fúnez-Núñez et al., 2019). Since the presence of this salt could favour hydrolysis, two liquors (L17.1 and L18.1) were prepared under similar conditions as L1.1 and L2.1, respectively,
because those conditions yielded a very low pentose concentration. As expected (Table 1), these liquors, L17.1 and L18.1, exhibited the lowest pH values and the highest densities. In addition, their appearance was darker and a higher amount of solid waste was found after autohydrolysis stage. It can be observed (Figure 1 and Table 1S) that the presence of this salt increased the hydrolysis rate, increasing xylose and furfural concentration values with respect to L1.1 and L2.1. However, the recovery of C5 carbohydrates, taking into account only xylose and furfural concentrations since arabinose was not detected, was lower than those found for liquors obtained at higher temperatures, being slightly lower than that achieved for L5.1 (Figure 2). It should also be noted that lactic acid (LA) was only detected for liquors obtained by using CaCl\(_2\) in the autohydrolysis stage, obtaining 0.88 and 0.44 g·L\(^{-1}\) for L17.1 and L18.1, respectively (Table 1S). It has been reported that LA is produced by the degradation of xylose and its combined use with AA accelerates the hydrolysis process (Lyu et al., 2018). However, LA could avoid the furfural formation in the pretreatment. Moreover, these liquors (L17.1 and L18.1) showed similar recovery of C5 sugars than L5.1, in spite of the concentration of both organic acids, LA and AA, was higher for the former. Considering that the presence of LA would come from xylose degradation, it looks like that the use of CaCl\(_2\) favored this reaction and subsequently other degradation reactions, hindering the furfural production. Therefore, it could be affirmed that the presence of AA was beneficial for both hydrolysis and dehydration processes, but LA enhanced the side reactions giving rise to the formation of solid waste.

### 3.2.2. Post-hydrolysis process

Finally, a second acid hydrolysis stage was carried out by using L1.1-16.1 liquors as feedstocks, in order to know the evolution of xylose concentration in the presence of acid homogeneous catalyst and calculate the potential xylose for olive
stones by total hydrolysis. For this, the pertinent liquors were put in contact with 4 wt% H$_2$SO$_4$ aqueous solution, in a reflux system at 100 ºC for 1 h, and different aliquots were extracted every 15 minutes (Scheme 2). It can be observed that xylose concentrations slightly grew at short hydrolysis times and then this value was maintained during the reaction (Figure 3); indeed, this increase did not take place in all cases. Moreover, the recovery of xylose in this post-hydrolysis process enhanced for those liquors obtained at longer autohydrolysis times in the 1st step carried out at 160 ºC. In the case of autohydrolysis at 180 ºC, the xylose concentration increased for L5.2 (obtained from L5.1) with post-hydrolysis treatment, attaining the highest values of recovered xylose (23.6 g$_{\text{xylose}}$·L$^{-1}$) which was considered as the potential xylose of olive stones. This value was the highest reached by acid post-hydrolysis from L5.1, compared to the rest of liquors (Table 1S). It should be taken into account that this liquor had a severity factor for autohydrolysis stage (log R$_0$ = 3.83) which could maximize the oligosaccharide content, as was previously mentioned, being likely a higher recovery of pentoses in the following steps. Nonetheless, the xylose concentration decreased for post-hydrolysis of liquors obtained at longer autohydrolysis times (L6.2-8.2), which showed higher severity factor in the autohydrolysis step. Likewise, lower values of xylose concentration were found for higher autohydrolysis temperatures (190 and 200 ºC). This fact could be due to the presence of sulphuric acid together with different composition of each liquor caused by its different autohydrolysis conditions led to degradation of these xylose monomers. Regarding furfural concentration obtained after post-hydrolysis process, in most of cases, it was maintained along post-hydrolysis time reaction. Only in the case of acid post-hydrolysis for L7.1 and L10.1 liquors, an increase was found at short times, but it decreased along acid hydrolysis reaction, which had shown the highest xylose and AA concentrations after autohydrolysis (Figure 1S). Likewise, very
low values of furfural concentration for post-hydrolysis process from liquors whose autohydrolysis had been carried out at 190 °C and long autohydrolysis times (L11.2-12.2) or 200 °C (L13.2-16.2). Moreover, these liquors had shown high AA concentrations after autohydrolysis (Table 1S and Figure 1). Therefore, it is feasible that more severe autohydrolysis conditions led to a high aliphatic acid concentration, which had a relevant role in the following stages, demonstrating that the composition of liquors by autohydrolysis was a key factor for subsequent steps and it could have a relevant role in furfural production.

3.3. Catalytic tests

Considering that L7.1 and L10.1 liquors showed the highest xylose concentration (16.759 and 16.476 g\textsubscript{xylose}·L\textsuperscript{-1}, respectively, Figure 1 and Table 1S) after the autohydrolysis step, these liquors were selected to evaluate the furfural production. One of the main problems for furfural production is associated to undesired reactions, such as condensation and resinification, leading to the formation of soluble and insoluble products (humins), which decrease furfural yield (Gómez-Millán et al., 2019). Although several alternatives have been proposed in the literature, the use of organic co-solvent to extract furfural instantaneously from the aqueous solution, avoiding these undesired processes, is frequently used, being toluene the most employed solvent due to its effectiveness (Mittal et al., 2017). On the other hand, it has been previously reported that the use of γ-Al\textsubscript{2}O\textsubscript{3}, as solid acid catalyst, and CaCl\textsubscript{2} improves furfural yield due to a synergistic effect. Thus, the inorganic salt favored the formation of α anomer of xylose and alumina promoted its dehydration, thus accelerating the dehydration process to furfural (Fúnez-Núñez et al., 2019). Consequently, the effect of γ-Al\textsubscript{2}O\textsubscript{3} and CaCl\textsubscript{2} was firstly evaluated for furfural production from these hemicellulosic liquors (Figure 4). Nevertheless, it must be noted that these liquors had a lower xylose concentration than
those solutions used in previous works (10 wt%) (Fúnez-Núñez et al., 2019), even if the potential xylose is considered (2.36 wt%) (Table 1S). The catalytic data reveal that alumina was not able to improve itself the conversion reached in the non-catalytic process. However, furfural yield and efficiency improved in the presence of CaCl$_2$ from both liquors, which were considerably higher when salt and alumina were jointly used. This would also corroborate the synergistic effect between $\gamma$-Al$_2$O$_3$ and CaCl$_2$ by using hemicellulosic liquors as source of xylans and xylose. On the other hand, a better catalytic performance was observed by using L7.1 rather than L10.1, attaining maximum furfural yield and efficiency (11 and 46%, respectively) in the former case, with only 6 and 24% in the latter case, in spite of both liquors exhibited similar xylose concentration after the autohydrolysis stage. It should be noted that L10.1 liquor also displayed the highest concentration of AA (Table 1S and Figure 1). Although it has been reported that the presence of acetic acid due to the cleavage of the acetyl groups catalyzed the depolymerization of hemicelluloses (Nabarlatz et al., 2007), it would also be possible that organic acids, such as formic and acetic acids, promoted the formation of insoluble humins, as was proposed by Fu et al. (2019). This fact could be minimized in the first stage, but the use of liquors with high AA concentration for furfural production in the presence of $\gamma$-Al$_2$O$_3$ and CaCl$_2$ could enhance undesired reactions. Therefore, the highest organic acid concentration (formic and acetic acids) for L10.1, produced by more severe autohydrolysis conditions, could have led to losses of furfural due to the side reactions catalyzed by these acids in the second stage.

Considering that the highest xylose concentration after acid hydrolysis was achieved for L5.2 liquor (23.6 g$_{\text{xylose}}$·L$^{-1}$), the concentration of organic acids for L5.1 was lower than those obtained for L7.1 and the severity factor for L5.1 was suitable to recover the highest amount of oligosaccharides, the catalytic performance of $\gamma$-Al$_2$O$_3$
and CaCl$_2$ was evaluated by using L5.1 and L7.1 liquors. First, the effect of reaction temperature for furfural production was studied (Figure 5), since it is one of the reaction parameters that exerts a great influence on both xylose conversion and furfural yield (Raman and Gnansounou, 2015; Gómez-Millán et al., 2019). Before analyzing the catalytic results, we must stress that both liquors were prepared at the same temperature, but different hydrolysis times (30 and 60 min, respectively), and hemicellulose may not be completely depolymerized for L5.1 conditions. Therefore, furfural production could take place from depolymerization of pentosans which had not been depolymerized in the first stage and subsequent dehydration of pentoses, mainly xylose. So, the catalytic behaviour of alumina-calcium chloride system was evaluated at 125 ºC (Figure 5A). Both furfural yield and efficiency enhanced with the reaction time in the case of L7.1, achieving maximum values of 10 and 42%, respectively, after 60 minutes. Then, these values started to decrease for longer reaction times, obtaining values of 3 and 15% after 120 min, respectively. In the case of L5.1, a different trend can be observed, since so high values were not attained along the reaction ($y_{L5,6}$=6% and $E_{L5,6}$=27%), but these values were maintained along 120 min. Thus, it could be affirmed that the undesired reactions of furfural were less relevant for L5.1 than L7.1 at this reaction temperature. This fact could be due to L5.1 exhibited considerably lower organic acid concentration (AA and FA) than L7.1. Then, the furfural production was tested at 150 ºC (Figure 5B), attaining better catalytic performance by using L5.1, reaching values of furfural yield and efficiency of 23 and 96%, respectively, after only 60 min, which were maintained after 120 min. In the case of L7.1, lower values were achieved at this reaction temperature, but they were very similar within 120 min. Therefore, the presence of a higher acid concentration had certainly influence on the side reactions, but not all furfural produced was degraded. In order to know if it was possible to attain a high
furfural efficiency for lower reaction times, favoring the depolymerization of pentosans and dehydration of pentoses, the furfural production was also studied at 175 °C (Figure 5C). Thus, lower values were found at this temperature from both liquors. However, the furfural efficiency was again higher for L5.1 than L7.1, but both liquors showed their maximum values (E\text{L5}=49\% and E\text{L7}=24\%) after 15 min of reaction and then they decreased until E\text{L5}=35\% and E\text{L7}=17\% after 30 min, being maintained after 120 min. Thus, it can be affirmed that L5.1 liquor provided better catalytic results than L7.1, probably due to this liquor had a lower organic acid concentration, which has shown to favor the undesired reactions of furfural in this second stage. The furfural production was lower for L5.1 when the reaction was carried out at 125 °C because the initial xylose concentration was also lower for this liquor, since the depolymerization in the first stage was not complete in its hydrolysis conditions. Therefore, the depolymerization of pentosans would require a higher temperature than 125 °C. However, the furfural production considerably enhanced when the reaction was carried out at 150 °C from this liquor, being the optimal temperature for this process carried out in two steps, since the catalytic performance was worse at 175 °C, probably due to the undesired reactions were promoted at higher reaction temperature, as previously reported (Gómez-Millán et al., 2020). In the case of L7.1, these undesired reactions took place even at low reaction temperatures, since the deactivation was observed even at 125 °C, which could be due to the presence of higher amounts of formic and acetic acids. Therefore, both organic acid concentration and reaction temperature would have influence on the decrease of furfural efficiency provoked by these undesired reactions, obtaining the best results at 150 °C by using L5.1 as feedstock for furfural production.

On the other hand, the furfural production was also studied from L17.1 and L18.1 at 150 °C, in spite of these liquors had shown lower xylose concentration, due to
the use of CaCl₂ could accelerate its depolymerization (Figure 2S). In this case, additional salt was not added to the reaction medium, since the liquors should have the same concentration which was employed for their preparation. It can be checked that both furfural yield and efficiency were much lower when these liquors were used as feedstocks, being lower than 5 and 20 %, respectively, in both cases. Therefore, it could be affirmed that the presence of CaCl₂ for the production of liquors decreased the effectiveness to recover carbohydrates present in olive stones and consequently hinder their transformation into furfural. This fact is probably due to this salt could promote, in the autohydrolysis stage, the formation of LA by degradation of xylose. Thus, the presence of LA considerably favored undesired reactions leading to high humin concentration and decreasing the furfural efficiency.

Although the interesting effect of γ-Al₂O₃ and CaCl₂ on the catalytic performance has been demonstrated, other solid acid catalysts should also be evaluated for furfural production from these hemicellulosic liquors. Thus, mesoporous silica doped with heteroatoms such as Al, Zr or Nb, have demonstrated to be active for dehydration of xylose to furfural (Lima et al., 2010; García-Sancho et al., 2013; García-Sancho et al., 2014; Sánchez-Bastardo and Alonso, 2017). In particular, García-Sancho et al. (2014b) incorporated Nb₂O₅ on different supports (commercial, MCM-41 and SBA-15 silicas and γ-Al₂O₃) for their use as acid catalysts for xylose dehydration. Thus, the best catalytic performance was found for a catalyst with 12 wt% of Nb₂O₅ supported on mesoporous SBA-15 support, attaining high xylose conversion and furfural selectivity (84 and 93%, respectively) after 24 h at 160 °C, in a biphasic water/toluene system. Recently, Zr-doped mesoporous HMS silica showed better catalytic results for glucose dehydration to 5-hydroxymethylfurfural (HMF) compared to other Zr-doped mesoporous silica, such as MCM-41, SBA-15 and KIT-6 (Mérida-Morales et al., 2020).
This fact was explained by the easy access of glucose molecules to acid sites by its morphology, besides a high surface Zr concentration which accelerated the transformation glucose into HMF. On the other hand, a mesoporous niobium oxide displayed a high xylose conversion and furfural yield (90 and 50%, respectively) after 90 min at 170 ºC, in a biphasic water:toluene system (García-Sancho et al., 2014a). Therefore, it was decided to compare the activity of γ-Al₂O₃ with other solid acid catalysts based on mesoporous Nb₂O₅, Nb-doped mesoporous SBA-15 and Zr-doped mesoporous HMS silicas. In all cases, CaCl₂ was employed to enhance the furfural yield. Although furfural efficiency was similar at the beginning of reaction (about 15 min), γ-Al₂O₃ was much more active than other catalysts under these experimental conditions (Figure 6). Thus, furfural efficiency did not exceed 45% for Nb-SBA, Zr-HMS and Nb₂O₅ catalysts, whereas γ-Al₂O₃ provided values close to 100%, after only 60 minutes at 150 ºC. It should be mentioned that γ-Al₂O₃, in spite of its total acidity was lower than those observed for Zr-HMS and Nb-SBA catalysts, exhibited the highest density of acid sites (Table 2), considerably higher than those obtained for the rest of catalysts. Thus, a correlation between acid and textural properties could be proposed to play an important role in this catalytic process. Moreover, the synergistic effect between CaCl₂ and Al₂O₃ previously reported (Fúnez-Núñez et al., 2019) was corroborated, since the use of this salt was not so beneficial when other catalysts were employed. Although calcium chloride would promote the formation of α anomer for xylose, other acid catalysts such as Nb-SBA, Zr-HMS and Nb₂Os showed a lower density of acid sites, and consequently furfural production was lower. Indeed, mesoporous Nb₂O₅, with the second highest acid density, provided higher furfural efficiency than those observed for Nb-SBA and Zr-HMS, after 30 min at 150 ºC. However, similar values were found for longer reaction time. Finally, the behavior of Nb-SBA and Zr-HMS was very similar
in spite of the former showed a higher density of acid sites (1.09 versus 0.55 μmoles NH₃·m⁻²). This fact is probably due to their morphologies, in such a way that the hexagonally packed cylindrical pores of SBA-15 hindered the access of xylose molecules and the globular structure of HMS facilitated it, as was found for dehydration of glucose into HMF (Mérida-Morales et al., 2020). Therefore, the combined use of CaCl₂ and Al₂O₃ provided the highest values of furfural efficiency (almost 100%), being able to hydrolyze pentosans and dehydrate pentoses contained in L5.1 liquor obtained by autohydrolysis of olive stones at 180 °C for 30 minutes.

Finally, the stability of alumina for several catalytic runs to obtain furfural in the presence of CaCl₂ by using L5.1, as source of pentoses, has been evaluated. Fúnez-Núñez et al. (2019) had demonstrated that alumina could be reused for ten catalytic runs in the presence of calcium chloride when furfural production was carried out by using a commercial xylose as feedstock. However, the presence of other chemicals in liquors obtained from olive stones, like organic acids, could hinder its reusing. Thus, the reuse of γ-Al₂O₃ was carried out in the presence of CaCl₂ by using L5.1 at 150 °C for 15 min to avoid that side reactions influenced on the catalytic activity (Figure 7). The catalyst remained inside the reactor and, after each catalytic cycle, a new mixture (L5.1, CaCl₂, water and toluene) was incorporated to the reactor without any catalyst pretreatment. It can be observed that alumina maintained its furfural yield and efficiency around 8.1-8.2 and 34.5-35.0%, respectively, for five catalytic runs without any treatment between cycles, demonstrating its stability and relevance to produce furfural from liquors obtained by autohydrolysis of olive stones.

**Conclusions**

Olive stones is an interesting sustainable feedstock for furfural production because of its high pentose content, mainly xylose, which can be recovered by
autohydrolysis reaction in the absence of mineral acids. Thus, the autohydrolysis under different experimental conditions led to hemicellulosic liquors whose xylose concentrations varied as a function of treatment temperature and time, in such a way that the maximum values were found for L7.1 (180 ºC and 60 min) and L10.1 (190 ºC and 45 min) liquors, with 16.76 and 16.48 g_{xylose}\cdot L^{-1}, respectively. Moreover, the acid hydrolysis with sulphuric acid of these liquors obtained by autohydrolysis was carried out for their characterization in order to determine the potential xylose of olive stones, obtaining the highest concentration (23.6 g_{xylose}\cdot L^{-1}) when L5.1 was completely hydrolysed. It has been demonstrated that the use of L5.1 as feedstock for furfural production, obtained under less severe autohydrolysis conditions than L7.1 and L10.1, provided higher furfural yield and efficiency, 23 and 96%, respectively, after only 60 minutes at 150 ºC, by using a commercial $\gamma$-Al$_2$O$_3$ and CaCl$_2$. Although autohydrolysis of L5.1 was not complete, the combined use of alumina and this salt catalysed hydrolysis and subsequent dehydration, giving rise to high furfural efficiency, close to 100 %, after only 60 min at 150 ºC. Thus, a better catalytic performance was achieved by using L5.1 as source of pentoses rather than L7.1 and L10.1, in spite of these latter had shown higher xylose concentration after the autohydrolysis step. Thus, their higher organic acid concentration, mainly acetic acid, could promote undesired reactions, consequently decreasing furfural efficiency. Likewise, the use of CaCl$_2$ for autohydrolysis step was evaluated in order to carry out this stage at lower temperature and time, giving rise to L17.1 and L18.1 liquors. However, the presence of this salt promoted the formation of lactic acid by degradation of xylose, avoiding the furfural production and favoring other undesired reactions. Therefore, the composition of liquors obtained by autohydrolysis was a key factor for the subsequent furfural production in such a way that high concentrations of acetic acid and, especially, lactic
acid hindered furfural production from these liquors. Finally, the combined use of a commercial $\gamma$-Al$_2$O$_3$ and CaCl$_2$ provided better catalytic performance than other solid acid catalysts, such as mesoporous Nb$_2$O$_5$ and Nb-doped SBA-15 and Zr-doped HMS silicas, because alumina displayed a higher density of acid sites which facilitated the access of pentoses to active sites for their transformation into furfural. $\gamma$-Al$_2$O$_3$ can also be reused in the presence of CaCl$_2$ for the production of furfural from hemicellulosic liquors, obtained from olive stones, at least for five catalytic runs without any pretreatment, thus demonstrating its stability.

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Conversion of xylose and xylan into fufural in biorenewable choline chloride-oxalic acid deep eutectic solvent with the addition of metal chloride
<table>
<thead>
<tr>
<th>Sample</th>
<th>$S_{\text{BET}}$ (m$^2$·g$^{-1}$)</th>
<th>$V_p$ (cm$^3$·g$^{-1}$)</th>
<th>$S^a$ (m$^2$·g$^{-1}$)</th>
<th>$V_p^a$ (cm$^3$·g$^{-1}$)</th>
<th>μmoles NH$<em>3$·g$</em>{\text{cat}}^{-1}$</th>
<th>μmoles NH$_3$·m$^{-2}$</th>
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<td>1149</td>
<td>1.147</td>
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<td>Zr-KIT(30)</td>
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<td>1.328</td>
<td>1010</td>
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<td>833</td>
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<td>Zr-KIT(5)</td>
<td>701</td>
<td>0.540</td>
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<td>0.606</td>
<td>817</td>
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<tr>
<td>Zr-HMS(5)</td>
<td>909</td>
<td>0.528</td>
<td>733</td>
<td>0.582</td>
<td>501</td>
<td>0.551</td>
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<tr>
<td>Zr-SBA-HT(5)</td>
<td>462</td>
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<td>494</td>
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<td>746</td>
<td>1.615</td>
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<td>Zr-SBA(5)</td>
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<td>0.346</td>
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<tr>
<td>Zr-MCM(5)</td>
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<td>396</td>
<td>0.214</td>
<td>495</td>
<td>0.878</td>
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$^a$: determined by MP method; n.d.: not detected
Table 2. XPS data of Zr-X(y) catalysts.

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<th>Catalyst</th>
<th>Binding Energy (eV)</th>
<th>Atomic ratio</th>
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<tr>
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<td>Si 2p</td>
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<tr>
<td>Zr-KIT(30)</td>
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<tr>
<td>Zr-KIT(14)</td>
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<td>103.3</td>
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<td></td>
<td>532.7 (94.9%)</td>
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<td>532.8 (92.2%)</td>
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<td></td>
<td>532.9 (95.5%)</td>
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<td>533.0 (95.3%)</td>
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<td>Catalyst</td>
<td>Binding Energy (eV)</td>
<td>Atomic ratio</td>
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<td>---------------</td>
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<tr>
<td></td>
<td>533.0 (95.3%)</td>
<td></td>
</tr>
</tbody>
</table>
PREPARING THE SAMPLE
250-500 mm
(T 204 cm-97, 1997)

HUMIDITY
105 ºC, 24h
(T 257 cm-12, 2012)

ASH
525 ºC, 3h
(T 211 cm-02, 2002)

NaOH SOLUBILITY
100 mL NaOH 1%
100 ºC, 1h
(T 212 cm-02, 2002)

H2O SOLUBILITY
100 mL H2O
100 ºC, 3h
(T 207 cm-99, 1999)

EXTRACTIVES
150 mL ET-B, 6h
(T 204 cm-97, 2007)

150 mL H2O + 1.08 mL CH3COOH + 6.25g NaClO2
96 ºC, 90 min
(Novel method based on ASTM-D-1104 (Álvarez et al., 2018))

HEMICELULLOSE= HOLOCELLULOSE - CELLULOSE

LIGNIN - 1° STEP
3 mL H2SO4 72% 30 ºC, 1h
(Sluiter et al., 2012)

LIGNIN - 2° STEP
84 mL H2SO4 4% 121 ºC, 1h
(Sluiter et al., 2012)

HEMICELULLOSE= HOLOCELLULOSE - CELLULOSE

Scheme 1. Chemical extraction procedure to determine the composition of olive stones.
Scheme 2. Experimental process for furfural production from olive stones in two steps and estimation of potential xylose by acid hydrolysis.
List of captions.

**Figure 1.** Distribution of products detected for LX.1 liquors as function of their autohydrolysis temperature and time (water:olive stones weight ratio of 10:1).

**Figure 2.** Recovery of pentoses and pentoses+furfural yield for LX.1 liquors as function of their autohydrolysis temperature and time (water:olive stones weight ratio of 10:1).

**Figure 3.** Xylose concentration detected for LX.2 liquors as function of time for acid hydrolysis (100 °C and 4 wt% H2SO4).

**Figure 4.** Furfural yield and efficiency from L7.1 and L10.1 liquors for non–catalytic process and in the presence of γ-Al2O3, CaCl2 and both γ-Al2O3 and CaCl2 (150 °C, 50 min, 0.05 g of γ-Al2O3 and 0.65 g CaCl2·g_{aq.sol.}^{-1} in each case).

**Figure 5.** Furfural yield and efficiency as function of reaction time from L5.1 and L7.1 liquors in the presence of γ-Al2O3 and CaCl2 at A) 125 °C, B) 150 °C and C) 175 °C (0.05 g of γ-Al2O3 and 0.65 g CaCl2·g_{aq.sol.}^{-1}).

**Figure 6.** Furfural efficiency as function of reaction time from L5.1 liquor in the presence of γ-Al2O3, Nb-SBA, Zr-HMS or Nb2O5 as acid catalyst and CaCl2 (150 °C, 0.05 g of catalyst and 0.65 g CaCl2·g_{aq.sol.}^{-1}).

**Figure 7.** Reuse of γ-Al2O3 for furfural production from L5.1 (150 °C, 15 minutes 0.05 g of catalyst and 0.65 g CaCl2·g_{aq.sol.}^{-1}).
Figure 1
Figure 2
Figure 3
Figure 4
Figure 5

A

B

C

125 °C

150 °C

175 °C

Figure 5
Figure 6
Figure 7
Supplementary Information

Characterization of catalysts

Nitrogen adsorption-desorption isotherms at -196 °C were obtained to evaluate the textural properties of solid acid catalysts, by using an automatic gas adsorption ASAP 2420 surface area and porosity analyzer model from Micromeritics. Prior to the N$_2$ adsorption, catalysts were degassed at 200 °C and 10$^{-4}$ mbar for 10 h. Surface area values were calculated by using the Brunauer-Emmet-Teller (BET) method and assuming a nitrogen molecule cross section of 16.2 Å$^2$. Pore size distributions were calculated employing the BJH method.

The total acidity of catalysts was evaluated by ammonia temperature-programmed desorption (NH$_3$-TPD). Firstly, 0.08 g of sample was pretreated under a helium flow by heating up to 550 °C, and, after cooling, the adsorption of NH$_3$ was carried out at 100 °C. Right after this, the NH$_3$-TPD was conducted under a helium flow of 40 mL min$^{-1}$ by increasing the temperature from 100 °C to 550 °C (10 °C min$^{-1}$), maintaining this temperature for 15 minutes. The desorbed ammonia was quantified by employing a TCD detector.

Characterization of olive stones

Olive stones used as the starting biomass in the liquor manufacturing process were ground and sieved until achieving a particle size range of 250-500 μm, according to TAPPI, 2007. Olive stones were characterized by using different methods (Scheme 1). Thus, the chemical composition was determined according to the next methods: moisture (TAPPI, 2012), ashes (TAPPI, 2002a), H$_2$O (TAPPI, 1999) and 1% NaOH (TAPPI, 2002b) solubilities, ethanol–toluene extractives (TAPPI, 2007), lignin (Sluiter et al., 2012), holocellulose (ASTM D1104-56, 1978; Álvarez et al., 2018), α-cellulose
(TAPPI, 2002b) and hemicellulose by difference. The data shown in the present study are expressed on a dry, ash and extract-free basis, and each experiment was performed twice to obtain adequate reproducibility.
Table 1S. Composition of liquors after autohydrolysis step and potential xylose determined by acid post-hydrolysis

| LIQUOR | T (°C) | t (min) | g<sub>x</sub>·L<sup>-1</sup> | g<sub>arab</sub>·L<sup>-1</sup> | g<sub>gluc</sub>·L<sup>-1</sup> | g<sub>AA</sub>·L<sup>-1</sup> | g<sub>FA</sub>·L<sup>-1</sup> | g<sub>LA</sub>·L<sup>-1</sup> | g<sub>furfural</sub>·L<sup>-1</sup> | Potential xylose (g·L<sup>-1</sup>)<sup>**</sup> |
|--------|--------|---------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| L1.1   | 160    | 30      | 0.13           | 0.22           | 0.04           | 0.35           | 0              | 0              | 0.02           | 3.56           |
| L2.1   | 160    | 45      | 0.31           | 0.38           | 0              | 0.62           | 0              | 0              | 0.06           | 6.6            |
| L3.1   | 160    | 60      | 0.61           | 0.47           | 0              | 0.8            | 0              | 0              | 0.11           | 14.61          |
| L4.1   | 160    | 75      | 1.03           | 0.58           | 0              | 1.08           | 0              | 0              | 0.18           | 15.07          |
| L5.1   | 180    | 30      | 3.64           | 0.09           | 0              | 1.63           | 0              | 0              | 0.62           | 23.60          |
| L6.1   | 180    | 45      | 12.69          | 0              | 4.6            | 0              | 0              | 0              | 2.4            | 15.21          |
| L7.1   | 180    | 60      | 16.76          | 0              | 6.06           | 0.15           | 0              | 0              | 2.88           | 16.18          |
| L8.1   | 180    | 75      | 13.68          | 0              | 5.3            | 0.13           | 0              | 0              | 2.83           | 17.57          |
| L9.1   | 190    | 30      | 14.65          | 0              | 6.05           | 0.15           | 0              | 0              | 3.01           | 14.67          |
| L10.1  | 190    | 45      | 16.48          | 0              | 8.22           | 0.17           | 0              | 0              | 3.57           | 11.79          |
| L11.1  | 190    | 60      | 2.02           | 0              | 1.85           | 0.14           | 0              | 0              | 1.95           | 7.23           |
| L12.1  | 190    | 75      | 3.585          | 0              | 0.2            | 4.5            | 0.34           | 0              | 3.04           | 5.24           |
| L13.1  | 200    | 30      | 2.87           | 0              | 0.23           | 5.27           | 0.35           | 0              | 3.07           | 4.86           |
| L14.1  | 200    | 45      | 3.06           | 0              | 0.17           | 4.78           | 0.42           | 0              | 2.98           | 4.6            |
| L15.1  | 200    | 60      | 1.16           | 0              | 0.24           | 5.04           | 0.41           | 0              | 3.15           | 1.55           |
| L16.1  | 200    | 75      | 0.46           | 0              | 0.27           | 4.64           | 0.37           | 0              | 3.06           | 0.78           |
| L17.1<sup>*</sup> | 160 | 30      | 1.46           | 0              | 0              | 2.5            | 0.16           | 0.88           | 1.32           | –              |
| L18.1<sup>*</sup> | 160 | 45      | 2.24           | 0              | 0.07           | 2.04           | 0.14           | 0.43           | 1.01           | –              |

<sup>*</sup>These liquors were prepared in the presence of 0.65 g CaCl<sub>2</sub>·g<sub>aqueous solution</sub><sup>-1</sup>

<sup>**</sup>Maximum xylose concentration obtained for these liquors after acid post-hydrolysis.
List of captions.

**Figure 1S.** Furfural concentration detected for LX.2 liquors as function of time for acid hydrolysis (100 °C and 4 wt% H₂SO₄).

**Figure 2S.** Furfural yield and efficiency from L17.1 and L18.1 liquors as function reaction time in the presence of γ-Al₂O₃ (150 °C and 0.05 g of γ-Al₂O₃).
Figure 1S
Figure 2S