RESEARCH ARTICLE

Residual biomass potential in olive tree cultivation and olive oil industry in Spain: valorization proposal in a biorefinery context

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Abstract

Olive crop and olive oil industry generates several residues, *i.e.*, olive tree pruning biomass (OTPB), extracted olive pomace (EOP) and olive leaves (OL) that could be used to produce high-added value products in an integrated biorefinery. OTPB is generated in the field as a result of pruning operation to remove old branches; EOP is the main residue of the pomace olive oil extracting industry after extraction with hexane of residual oil contained in olive pomace; and OL comes from the olive cleaning process carried out at olive mills, where small branches and leaves are separated by density. In this work, an analysis of the potential of OTPB, EOP and OL residues was addressed by estimating the production volumes at national level and the spatial distribution of these residues using geographic information system software. Information provided by public institutions and personal surveys to the industries was evaluated. Moreover, chemical analysis of the residues was undertaken and the results used to make a first assessment of valorization into biofuels such as bioethanol and bio based chemicals. Results show that close to 4.2 million tons/year of EOP, OL and OTPB derived from olive oil industry and olive tree cultivation in Spain could be available as a raw material for biorefineries in Spain. The analysis of the chemical characteristics indicates the relevant potential of these feedstocks for the production of bioethanol and other compounds such as phenols based on suitable processing and conversion routes, although techno-economic evaluations must be tackled to refine this approach.

Authors' contributions: Conception and design, and wrote the paper: PM and ER; Acquisition, analysis, or interpretation of data: PM, MJN, FJG, JCL and ER; Critical revision of the manuscript: MB and EC.

Competing interests: authors have declared that no competing interests exist.

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Introduction

Olive (*Olea europaea* L.) oil production has a significant importance in the agroindustry of Mediterranean countries due to the large extension in the growing area of olive tree crop and the number and capacity of olive processing facilities. Particularly in Spain, and according to the recent estimations from FAOSTAT (http://faostat3.fao.org), 2.5 Mha of olive crop were cultivated in 2014, representing 24.4% of total worldwide production and positioning the country as the leader in olive tree cultivation. Regarding olive fruit production in the EU, which was 9.43 Mtons in 2014, the major producer was Spain with 4.58 Mt, close to 50% of the total EU yield. In Spain, olive oil production represents the major part of the olive agroindustry, with close to 1,800 operating olive mills that process more than 3 million tons per year of olives for virgin olive oil production.

Olive tree cultivation generates a large amount of biomass from the olive tree pruning practice that is needed to remove old branches and increase crop productivity. The olive tree pruning biomass (OTPB) comprises leaves (~ 25% dry weight basis, dwb), thin branches (~ 50% dwb) and wood of different thickness (~ 25% dwb) (Romero-García *et al.*, 2014). Nowadays, this residual biomass has no specific use except for the higher size wood that is often used in domestic fire. Only a small amount of OTPB is used as a raw material in power generation plants due to the low density of this biomass, which also involves a high transportation cost. About a half of farmers eliminate OTPB by controlled burning in the field that produces CO_2, particulates emissions and poses a potential fire risk. A potential and important use of the pruning is to protect the soil and improve soil quality. According to Calatrava & Franco (2011), farmers are increasingly adopting chopped pruning as mulch. The chopping of pruning residues is important because this mulch can protect the soil for long time periods than cover crops, helping farm workers to prevent land degradation, as found by Rodríguez-Lizana *et al.* (2017) in olive groves.

Olive oil industry generates several residues or by-products, *i.e.*, olive pomace, extracted olive pomace (EOP), olive stones and olive leaves (OL) from olive cleaning operations at olive mills. Olive pomace is the main residue of the oil extraction process currently used in practically all the olive mills in Spain, the so-called two-phase system. This residue represents ~ 80% by olive weight and consists of olive skin, pulp, seed and fragments of stones, as well as a small amount of residual oil, between 1% and 3%, depending on the process conditions and olive variety. It is a highly contaminating residue due to the elevated organic matter and phenolics content, as well as difficult to dispose of, since it has high moisture content from 60-80% (Borja *et al.*, 2006). Currently the most widely used practice for olive pomace is to treat the residue in extracting industries where it is dried and extracted with hexane to recover any residual oil that is commercialized as pomace olive oil after chemical refining.

The final solid residue generated in pomace olive oil extracting industries after pomace oil recovery, EOP, usually has ~ 10% moisture and contains residues of pulp, seeds, skins and stones (Cruz-Peragón *et al.*, 2006). The proportion of stone in EOP depends on the upstream extraction processes, since frequently part of the stones are removed either in the mill, or in the pomace olive oil extracting industry itself. Due to its high-calorific value, the coproduct is usually burned in domestic heating systems or in industrial boilers in small industries. However, although EOP can be also used in industrial combustion equipment, it is a less valuable material as it contains some impurities that decrease its value as a fuel. During the initial olive cleaning process carried out in olive mills, small branches and leaves from harvest are separated by density. This residue is named in this work as OL.

Thus, from the viewpoint of an integrated biorefinery in olive oil production zones to produce biofuels and other compounds of interest (hydroxytyrosol, tyrosol, oleouropein, mannitol, xylitol, flavonoids, etc.), the olive oil derived residues with better perspectives to be used as feedstocks would be OL and EOP, as olive stones are already considered a suitable solid biofuel. Such a biorefinery would include OTPB that has already been explored as a raw material for biofuels and other products with promising results (Conde *et al.*, 2009; Cara *et al.*, 2012; Díaz *et al.*, 2012). The extraction of a wide range of bioactive compounds from OL has been also investigated (Rahmaniana *et al.*, 2015; Romero-García *et al.*, 2016). As lignocellulose-derived biomass materials, OTPB, OL and EOP residues contain a certain proportion of carbohydrate polymers and lignin that could be converted into fermentable sugars and other valuable molecules, which in turn would work as precursors for high added value products such as biofuels, antioxidant compounds and sweeteners. Thus, the selected residues have the potential to be used in a biorefinery to provide a range of bulk and speciality chemicals that serve as the basis for producing valuable compounds in both the existing petrochemical-dominated market and the future bio-based product markets (FitzPatrick *et al.*, 2010; González-García *et al.*, 2016). However, for lignocellulosic biomass materials to become a feasible feedstock in a biorefinery, it is necessary to improve the pre-treatment process that fractionates biomass into its

constituents and the efficiency of the enzymatic hydrolysis step that results in the hexose and pentose sugars being released from polysaccharides (Huang *et al.*, 2016). The conversion of the released sugars into bioethanol and building blocks chemicals by biological processes, such as fermentation, is in the core of many current biorefinery schemes (Alexandri *et al.*, 2016; Huang *et al.*, 2016). In the same way, Cai *et al.* (2016) have recently reported on a biorefinery process based on corn cob for microbial lipid and bioethanol production, highlighting the necessity of using all biomass components for the production of value-added products to get a proper lignocellulosic biomass use in a biorefinery.

On the other hand, the development of an economic approach to convert these residues into valuable products requires, in parallel to the development of adequate and efficient conversion processes, an assessment of the volumes generated and the regional distribution, to define the scale of transformation technology that optimizes collection and transportation costs (Estornel *et al.*, 2015). To date, although there is some information on the production yield of these residues in Andalusia (Junta de Andalucía 2010, 2015), there are no published data of production volumes at a national level.

Thus, the overall objective of the present work was to estimate and locate the production potential of OL, EOP and OTPB in Spain, as a first approach to their use in a multi-feedstock biorefinery that would include residues from olive tree crop and olive oil industry. In addition, based on the chemical composition of the feedstocks, a preliminary estimate of the production yield of a main product in the biorefinery, such as bioethanol, was carried out. The implementation of such a biorefinery would transform gricultural areas traditionally directed to food production into new providers of biofuels and bioproducts, that would be a clear incentive for employment generation and technology development in rural zones. Specific objectives to achieve the above mentioned main goal were to (i) develop a methodology to estimate the production of the targeted residues; (ii) calculate the amount of residues generated in the main olive oil production areas in Spain; (iii) locate geographically the production poles; (iv) evaluate the valorization potential of these residues in a biorefinery context based on their chemical characteristics.

Material and methods

Estimation of olive tree pruning biomass (OTPB) generation

The information about olive tree cultivation surface was provided by the Spanish Agricultural Guarantee Fund (FEGA) from the Spanish Ministry of Agricul-

ture, Food and Environment of Spain (MAPAMA), according to data from the Spanish Agricultural Plot Geographic Information System (SIGPAC). This is the most accurate source of geo-referenced information available at national level and allows mapping of all existing olive orchard parcels and their specific characteristics. Given the perennial character of olive tree cultivation, the area dedicated to this crop is quite constant. This fact is reflected in the data provided by MAPAMA for the last five years in Spain, with olive tree crop area (in thousands hectares) of 2,503.7 in 2011, 2,504.3 in 2012, 2,507.0 in 2013, 2,515.8 in 2014 and 2,526.5 in 2015. Consequently, the OTPB biomass potential assessment was based on the year with the most recent planning area data available, which is 2015. Neither abandoned olive groves nor the plots where olive trees are associated with other crops were taken into account. In addition, olive areas with terrain slope over 20% have been also discarded, due to difficulties in the mechanization of biomass collection (Terrados *et al.*, 2011). On the other hand, olive land parcels from the Spanish Autonomous Regions (AR) with extremely low olive crop surface were not considered, *i.e.* Galicia (3 ha), Asturias (0 ha), Cantabria (0 ha), País Vasco (31 ha) and Canarias (43 ha).

The evaluation of the availability of residual biomass from pruning olive trees was undertaken taking into account the following indexes that had been applied to previous research works at regional level (Terrados *et al*., 2011):
— 1.4 tons OTPB/year ha: OTPB production index for dry crops with terrain slope > 10%,
— 1.6 tons OTPB/year ha: OTPB production index for dry crops with terrain slope < 10%, and for irrigated crops with terrain slope > 10%,
— 1.7 tons OTPB/year ha: OTPB production irrigated crops with terrain slope < 10%.

Evaluation of the production of residual biomass derived from olive oil industry

To evaluate OL and EOP production, data on processing volumes and technical characteristics of all olive mills and pomace olive oil extraction industries operative in Spain were obtained from the Spanish Agency of Information and Food Control (AICA) of MAPAMA. These data were provided only for the purpose of this research. In the case of olive mills, data used to estimate OL residues were the tons of olive processed in each facility, while in pomace olive oil industries the input value used to estimate EOP refers to the quantity of olive pomace (wet or already dried in specific dryers) processed. In contrast to the olive tree cultivation area (section above), olive production shows

a wide variability among different years (Aparicio *et al.*, 2016). Because of this, data from the three consecutive campaigns available were analyzed, *i.e.*, 2012-2013, 2013-2014 and 2014-2015. Average values of the three campaigns were calculated and used as initial values for calculation of residues.

Surveys of the industrial sector were used as the main instrument to determinate the production residue index (RI) that correlates the amount of raw material processed by the industry with the quantity of residue generated. Only the four major productive regions were considered for the surveys, *i.e.*, Andalusia, Castile-La Mancha (CLM), Extremadura and Catalonia, as they account for the 90.7% of total cultivation area in Spain, with 59.9%, 15.8%, 10.5% and 4.5% of contribution, respectively (MAPAMA, 2014). Thus, they were considered to be representative of the whole production and the rest of regions were not taken into account in this study. In the case of pomace olive oil extraction industries, all the facilities that produce EOP have been considered. However, in the case of olive mills, the large number of existing operational facilities in the four AR selected (close to 1,400) made it necessary to establish a selection of target mills to survey, as explained below.

Several variables (Table 1) were determined to select the most representative olive mills to be surveyed. First, the average quantity of olive processed by mill (in tons) in each province (PR) was calculated (AV_{PR}, Eq. [1]), using the input data of the three campaigns provided by AICA. Then, the relative weight of each province in terms of the total quantity of olives processed by AR (RW_{PR}) was calculated by Eq. [2]. Finally, a weighted average of olives processed by mill in each AR (AV_{AR}) was calculated (Eq. [3],) taking into account the average processing index by mill in each province and the relative importance of each province in the total.

$$AV_{PR} \text{ (tons)} = \frac{\text{Sum of olives processed in each province (tons)}}{\text{Number of mills in each province}} \quad [1]$$

$$RW_{PR} = \frac{\text{Total olives processed in each province (tons)}}{\text{Total olives processed in RC (tons)}} \quad [2]$$

$$AV_{RC} \text{ (tons)} = \text{sum of } (AV_{PR} \cdot RW_{PR}) \quad [3]$$

To select target mills, only those processing the quantity of olives above AV_{AR} value were taken into account in each AR. The final selection (230 industries) represents those larger industries that process 75% of the total production of those facilities above AV_{AR}. The number of mills surveyed in each province is shown in the last column of Table 1. The procurement of quantitative information about olives leaves and

EOP residues produced in the sample of the selected industries was addressed through surveys made by e-mail and/or telephone call, prepared to obtain actual data about the quantity of residues generated/campaign in relation to the input of feedstock and also know aspects related to the current use, if any, of these residues. Table S1 [suppl] shows the main questions considered in the surveys. The aim was to calculate an average residue production index (RI), both for leaves generated in the olive mill, RI_{OL} (Eq. [4]), and for EOP generated from pomace olive oil extraction, RI_{EOP} (Eq. [5]) that could be averaged by region and applied to all processing facilities, using the input data provided by AICA.

$$RI_{OL} = \frac{\text{Volume of collected OL (tons)}}{\text{Volume of processed olives (tons)}} \times 100 \quad [4]$$

$$RI_{EOP} = \frac{\text{Volume of EOP generated (tons)}}{\text{Volume of processed olive pomace (tons)}} \times 100 \quad [5]$$

Spatial representation of residues distribution

Geographical distribution of olive tree cultivation and production volumes of EOP and OL in Spain was conducted using the Geographic Information System (GIS) mapping software ArcGIS 10.2.1 (ESRI, Inc., Redlands, USA).

Chemical characterization of biomass

The composition of the residual biomasses OTPB, OL and EOP, was carried out following the analytical methods for biomass described by Slutier *et al.* (2010). The procedure includes a previous two extraction step with water and ethanol consecutively. Soluble sugars in the aqueous extraction liquid were analyzed by high performance liquid chromatography (HPLC) as described elsewhere (Martínez-Patiño *et al.*, 2015). The total phenolic content in the aqueous extract was determined using the Folin-Ciocalteu reagent (Singleton & Rossi, 1965). The quantity of structural sugars, cellulose and hemicellulose, was obtained by taking into account the amount of monomers solubilized after acid hydrolysis stage in two steps, first with 72% (w/w) sulfuphic acid (30 ºC, 60 min) and then at 4% (w/w) sulphuric acid (121 ºC, 60 min). The HPLC method mentioned above was employed to determine the sugar content of the hydrolysis liquors. The insoluble solid remaining unaltered after acid hydrolysis corresponds to acid-insoluble lignin, whereas the acid-soluble lignin content was evaluated by ultraviolet–visible spectroscopy. The ash content was also determined as the solid remaining

Table 1. Data of number of operative mills by Spanish Autonomous Region (AR)/Province (PR) and values of indexes used to determine the sample size of mills to be surveyed.

AR/PR	Nº. of mills	AV_{PR}	RW_{PR}	AV_{AR}	Nº. surveyed mills
Andalusia	819	-	-	5,637	146
Almería	25	2,114	0.01	-	1
Cádiz	19	2,377	0.01		2
Granada	109	4,219	0.10	-	10
Córdoba	180	6,492	0.27	-	49
Huelva	18	1,921	0.01	-	0
Jaén	321	5,628	0.41		61
Málaga	66	4,800	0.07		7
Sevilla	81	6,289	0.12		16
Castile-La Mancha	254	-	-	1,828	41
Albacete	36	1,437	0.13	-	4
Ciudad Real	76	2,449	0.45	-	23
Cuenca	25	925	0.055	-	1
Guadalajara	7	280	0.005	-	0
Toledo	110	1,353	0.36	-	14
Extremadura	122	-	-	2,350	18
Caceres	43	1,160	0.19	-	2
Badajoz	79	2,629	0.81	-	16
Catalonia	194	-	-	871	25
Barcelona	13	316	0.03	-	0
Gerona	10	389	0.02	-	0
Lérida	58	769	0.28	-	9
Tarragona	113	953	0.67	-	16
Total	1,389				230

AV_{PR} = average value of olive processed by mill (in tons) in each PR. RW_{PR} = relative weight of each province in the total of olives processed by AR (on a per unit basis). AV_{AR} = weighted average of olive processed (in tons) by mill in each AR.

after combustion at 550 ºC. Elemental analysis (C, H, N) and the sulphur content of selected residues were carried out following European Norms EN 15104 and EN 15289, respectively.

OL were obtained from the olive mill 'S.C.A. Unión Oleícola Cambil' in November 2015 and EOP was collected from the olive pomace extracting industry 'Oleocastellar S.A' in January 2016. Both facilities are located in the province of Jaén. The biomass samples were air-dried at room temperature and then chipped up to 1 mm before characterization. Triplicate analyses of OL and EOP samples were performed simultaneously and separately by the two laboratories participating in the research, CIEMAT and University of Jaén. The overall mean and standard deviations were calculated using the results from both laboratories. In the case of OTPB, chemical characterization was performed by Universidad de Jaén laboratory in a sample of material collected in March 2016. Results of elemental analysis of OTPB come from La Cal *et al.* (2012).

Results and discussion

Olive tree pruning biomass production

Fig. S1 [suppl] is a map showing the olive tree cultivation areas potentially available for OTPB generation in Spain. Colours used on the map help discern the different orchard types, depending on the slope and whether irrigated or not. Some restrictions were applied to the total surface area provided by the SIGPAC database from MAPAMA, in order to evaluate the actual cultivation area that could facilitate biomass logistics. Only olive tree parcels of up to 20% terrain slope were considered. Associated crops and abandoned plots were also discarded. Despite this, the percentage of surface available after restriction criteria represents about 80% of the total surface area of olive orchards in Spain. Fig. S1 [suppl] shows that the most concentrated productive areas are located around the Guadalquivir river valley, mainly in the provinces of Jaén and Córdoba, in Andalusia. The

Table 2. Surface area (ha) of several types[1] of olive tree cultivation (in ha) available for residual biomass supply in the different productive regions (AR) of Spain.

AR	Type 1	Type 2	Type 3	Type 4	Total	OTPB[2]
Andalusia	484,071	429,761	75,543	150,392	1,139,767	**1,741,852**
Navarra	1,208	1,537	322	3,565	6,632	**10,726**
La Rioja	723	2,065	270	1,688	4,746	**7,618**
Baleares	1,646	1,148	4	53	2,851	**4,238**
Castile-Leon	1,166	986	39	407	2,598	**3,964**
Castile-La Mancha	67,281	260,149	1,162	12,364	340,956	**533,310**
Catalonia	31,457	52,890	5,709	12,045	102,101	**158,275**
Valencia	26,045	55,096	364	1,940	83,445	**128,497**
Murcia	3,223	15,034	221	3,418	21,896	**34,731**
Extremadura	51,012	147,572	923	15,107	214,614	**334,691**
Madrid	6,335	16,839	93	344	23,611	**36,545**
Aragon	16,955	23,990	1,849	11,364	54,158	**84,398**
Total (Spain)	**691,122**	**1,007,067**	**86,499**	**212,687**	**1,997,375**	**3,078,844**

[1] Type 1: Non-irrigated land with terrain slope > 10%. Type 2: Non-irrigated land with terrain slope < 10%. Type 3: Irrigated land with terrain slope > 10%. Type 4: Irrigated land with terrain slope < 10%. [2] Estimation of olive tree pruning biomass (OTPB) production (tons/year). The production indexes (tons OTPB/year ha) applied were 1.4 for olive cultivars type 1; 1.6 for types 2 and 3; 1.7 for type 4.

presence of such important areas with a high density of olive tree cultivation could be a significant positive factor for the development of biorefineries based of this biomass, as transport costs to the plant is an important factor that should be reduced by limiting the distance from the available biomass to the refinery (Searcy *et al.*, 2007).

The quantitative data on the area of olive tree cultivation available for biomass production in the different ARs (Table 2), shows that Andalusia has the most important contribution (57%), followed by CLM, Extremadura and Catalonia. Thus, these four regions have a 90% of the total olive cultivation area available for biomass generation in Spain (1,997,375 ha). Non-irrigated lands predominate at national level, with more than 80% of the contribution in the main productive regions. Only two less productive regions in the North (Navarra and La Rioja) have a higher percentage of irrigated orchards. Concerning the land slope, in the most productive region (Andalusia), half of the olive cultivation area has medium slopes, between 10% and 20%. Plain lands predominate in the next productive AR, *e.g.* CLM and Extremadura with 79.9% and 75.8% of the olive orchard with less than 10% of terrain slope.

As explained in the Material and Methods section, estimation of the OTPB generated in the field has been performed by applying different indexes that correlate the production of residual biomass with the surface area of olive tree cultivation. These indexes have slight variations (from 1.4 to 1.7 t/ha) depending on the terrain slope and the water cultivation conditions, and were applied in previous works (Terrados *et al.*, 2011) at a regional level in the framework of a local research project focused on the province of Jaén, the most important productive region in the world. The indexes were verified experimentally in the field in the local research project with good results and consequently were considered as representative indexes to be applied at national level in this work. The total amount of OTPB obtained was slightly higher than 3 million tons in Spain, with close to 1,750,000 tons potentially generated in Andalusia.

Olive oil industry derived residues production

Sample size and quantitative survey outcome

To determine the size of olive mill sample to be submitted to survey, data of the volume of olives processed in the three campaigns were analysed, averaged and the indexes AV_{PR}, RW_{PR} and AV_{AR} explained above calculated according to these mean values. The criterion was that only those mills processing an amount of olives above the AV_{AR} value were taken into account in each AR and the total amount of olives processed in that interval was calculated. Finally, mills that processed 75% of that total value were selected as representative samples in each AR. Table 1 shows the values of the indexes mentioned above, as well as the number of existing and surveyed mills in each province. As can be seen, close to 59% of olive mills were located

in Andalusia, followed by CLM with 18.3% of the total and Catalonia and Extremadura, representing 13.9 and 8.8% respectively. Expectedly, the highest average value of olive processing volume/mill was found in Andalusia, reaching 5,637 tons/campaign. Analysis of the relative weighting of each province shows that Cordoba reached the maximum average volume/mill, ~ 6,500 tons/campaign, while Jaén, with only a slightly lower average processing capacity, had the peak number of olive mills in Spain (321), thus yielding the top processing capacity in the national territory. CLM was the second AR in number of olive mills (254) and in total processing capacity, with Ciudad Real province representing 41% of total production (data not shown). However, the average value by AR (AV_{AR}) in CLM was lower than in Extremadura, which shows a concentration of high-volume processing facilities in the province of Badajoz. Catalonia has substantial amount of olive mills compared to CLM and Extremadura, but the small size of the facilities between 316 and 953 tons/campaign results in the lowest mean processing size.

Totally, 230 mills were surveyed, distributed as shown in Table 1. They represent 16.6% of olive mills in the four selected ARs. The percentage of reply to the e-mail survey in olive mills was very low, 10-25%, so it was necessary to conduct it by telephone call.

Regarding pomace olive oil extracting industries, all of them (69) were interviewed. Of the total, 62.3% were located in Andalusia (43), 14.5% in CLM (10), 10.1% in Extremadura (7), 8.7% in Catalonia (6) and the rest in Aragon, Murcia and Navarra with only one facility by province.

In relation to these industries, it is relevant to point out that in Spain not all of the facilities generate EOP, as a significant number only carry out the process of extracting pomace oil by a physical process similar to that of the virgin olive oil, thus generating exhausted olive pomace residue, or by drying of the latter residue that is then submitted to chemical extraction, generating the EOP residue. The scheme in Fig. S2 [suppl] is provided to help understanding of the different processing strategies used in the pomace olive oil extracting industry in Spain and to specify that only industries carrying out step 3 generate EOP as a residue. The mills can receive feedstock either wet olive pomace and perform steps 1 to 3, or the residue of step 1, then performing only process steps 2 and 3, or the dried olive pomace from step 2, being only necessary to carry out the final chemical extraction step 3. Based on the interview outcomes and the analysis of the different processing systems in the 69 extracting industries in Spain, it could be stated that only 28 facilities generated EOP, of which 71.4% were located in Andalusia.

The percentage of reply to the e-mail survey was quite low in extracting pomace olive oil industries, around 20%, and thus, as with olive mills, it was necessary to complete the survey by telephone call.

Information on current uses of EOP and OL from surveys

As can be seen in Table S1 [suppl] the surveys included questions on the current uses of the residues EOP and OL, aimed at estimating the actual availability of these feedstocks. Regarding EOP, most of the companies consider using a part of this residue for power generation in the facility, mostly for drying wet pomace. The proportion of internal consumption varies from 25 to 50%, although about half of the companies responding to the survey advised about 40-50% was used. The remainder is usually sold to other small industries, olive mills or power generation plants using biomass as fuel. However, all the companies surveyed agreed on the problems arising in the last years around EOP trading, due to the price reduction of fossil fuel that has led to a surplus of EOP. This fact supports the research on alternative transformation routes for this residue as those envisaged in the biorefinery concept.

The survey enabled obtaining concrete aspects of the process generating EOP that influence its composition. Of particular interest was the removal or not of the residual stone fraction that still contains the wet pomace entering the pomace olive oil extracting industry (1-5%, depending on the particular facility and the campaign). About 75% of the industries surveyed stated stone removal before pomace drying and pomace oil extraction, with the EOP thus containing only a minor residual quantity of stone. On the other hand, 25% of the industries did not undertake stone removal and the initial content present in wet pomace remains in the EOP. This different processing pattern affects the chemical composition of the residue as feedstock in a biorefinery, as well as its performance as solid fuel.

In relation to OL generated in olive mills, current practices varied among the ARs, although a common pattern of use was identified. In a part of the mills, traditionally OL is given to the farmers in the area as an animal feed, free of charge. A few mills sell the residue or even have to pay for the collection. The use of the OL for animal feeding is common in the case of clean leaves obtained from air-collected olives at the beginning of the collection campaign. However, when olives are collected from the ground, animals usually refuse this feed because of the presence of soil. Some of the farmers interviewed even declared some cases of interference with the milk quality produced by animals that feed with OL. However, ~ 50% of the interviewed

mills stated that the main part of OL currently generated was still used as animal feed. This percentage rises up to nearly 100% in the case of the mills that produce organic olive oil from olive orchards ecologically cultivated where chemical fertilizers are not employed.

Surveys returned by the olive oil producers also revealed a rise in the amount of OL return to the olive farms from the mill, especially in the case where the residues were separated from olives collected from the ground that have some soil and small stones. According to the opinion of the producers surveyed, the residues may have a positive effect in some locations leading to better water retention and erosion control. In the case of the Andalusian mills surveyed, we estimated that up to 40% of the OL might end up being spread on the field.

On the other hand, only a few mills declared applications such as composting, sometimes in mixtures with other kind of residues, with the organic part of the domestic wastes. In Andalusia, where the largest size mills were located, other minor specific uses were found. For example, a small number of mills in Córdoba

and Jaén provinces sell the residual leaves to power generation plants.

Calculation of residues production yield

Based on the quantitative data reported in the surveys, average RI indexes were calculated both for OL and EOP in the four main productive AR. Regarding OL, it is important to mention that most of the olive mills surveyed lack of precise quantitative data on OL generation and thus, the values provided refer to estimations of the volumes produced. In the case of the value of RI_{OL} calculated for Andalusia, it was checked by performing in-situ measurements of OL generated in an olive mill located in Jaén (SCA Unión Oleícola Cambil). Table 3 shows the results for the average RI_{OL} and estimated values for leaves generated by volume by each AR. Of a total of 5,227,770 tons of olives processed in Spain, 329,233 tons of OL from the cleaning operation of olives was obtained, with the major production found in Andalusia (87.8% of total).
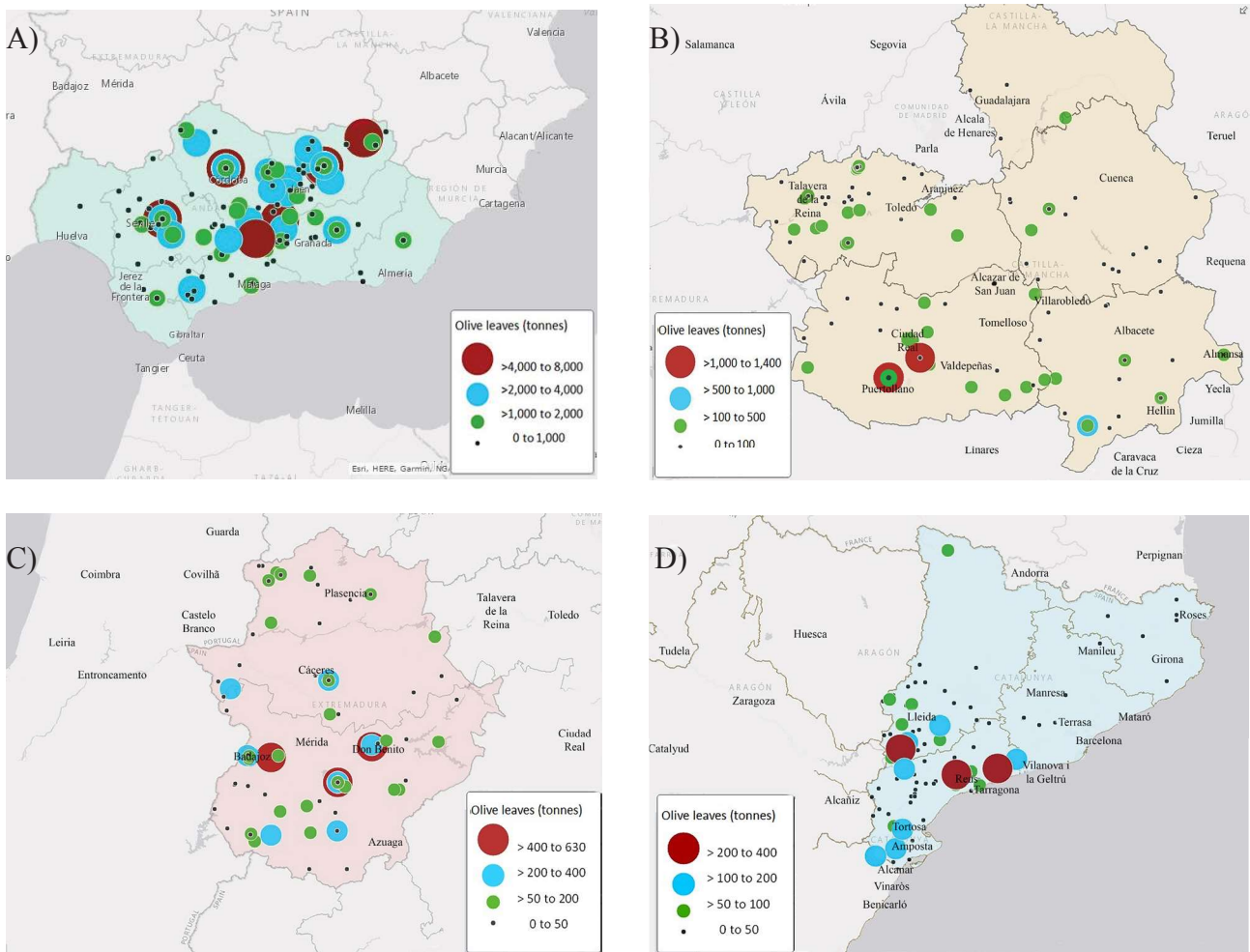

Figure 1. Maps of spatial regional distribution of olive leaves (OL) generated in olive mills in the four Spanish Autonomous Regions studied. A) Andalusia, B) Castile-La Mancha, C) Extremadura, D) Catalonia.

Table 3. Total volume of olives processed, average residue production index for olive leaves (RI_{OL}) and olive leaves (OL) production yield in the four selected Spanish Autonomous Regions (AR). Input data of olive processing were mean value of campaigns 2102-2013, 2013-2014 and 2014-2015.

AR	Total olives processed (t)	RI_{OL} (%)	Total leaves (t)
Andalusía	4,393,656	6.59	289,542
Castile-La Mancha	416,223	5.52	22,975
Extremadura	257,568	4.00	10,303
Cataluña	160,323	4.00	6,413
TOTAL	5,227,770		329,233

In this AR the highest value of RI_{OL} found was 6.6%, which could be related to the higher productivity of olive trees in this region that might involve increased amounts of leaves being collected together with the olives. Results obtained from in-situ weighing of mill leaves confirmed the estimated RI_{OL} value in Andalusia. Thus, with several olive samples ranging from 390 to 970 kg, the percentages of OL fluctuated between 3.3% and 9.5%, leading to an average RI_{OL} index of 7%, very close to the value estimated from the surveys (6.6%).

Concerning RI_{EP}, minor variation was found among the industries surveyed that generate EOP, with an average value for all AR of 0.25 tons of EOP/tons of fresh olive pomace entering the pomace olive oil extracting industry. This value was used to estimate the amount of EOP generated in in Spain, which accounts for 1,181,274 tons/campaign, as an average of the three campaigns studied. As expected, Andalusia concentrates major generation of EOP, with almost 89% of the national production.

Spatial distribution of residues

Fig. 1 illustrates the regional distribution and intensity of production of OL generated in olive mills in the selected AR. The peak production is found in Andalusia (Fig. 1A) and particularly in Jaén province, where in numerous municipalities significant volumes of OL, from 4,000 to 7,500 tons/campaign, are generated. In Jaén a total of 118,000 tons are generated, while the region with the second highest production volume, Córdoba, gave olive mill production of 76,000 tons/ campaign (data not shown). Fig. 1B shows the maximum OL production in CLM was located in Ciudad Real province, with a total yield of 10,000 tons/ campaign (data not shown). Extremadura and Catalonia

olive mills generated significantly lower volumes of OL ranging 400-600 t/mill and 200-400 t/mill, concentrated in Badajoz and Tarragona provinces, respectively.

From these results, it can be stated that in Jaén and Córdoba provinces, important production of residual OL can be identified, sufficient to design the supply of material to a biorefinery for processing of such residues. Likewise, in Ciudad Real province, concentrated production sites could be selected, with the final choice being determined by the size of the future transformation plant.

In relation to EOP generation in Spain, Fig. 2 illustrates the spatial distribution and intensity of production, specifically for each AR. In Andalusia, that produces the maximum EOP production (~ one million tons), extracting industries in Córdoba account for about 50% of total production, followed by Jaén (~ 32%). Important EOP production locations were located in the region around the municipalities of Baena and Lucena in Córdoba, with extracting facilities generating volumes of EOP over 150,000 tons/campaign.

Biomass composition and biorefinery valorization proposal

With the viewpoint of making a first approach to the valorization of the selected residues as feedstocks

Table 4. Chemical characterization of olive tree pruning bio-mass (OTPB), olive leaves (OL) and extracted olive pomace (EOP). Results are expressed as g/100 g raw material oven dry weight.

Composition (%, dry matter)	OTPB	OL	EOP
Cellulose	21.6 ± 0.2	9.3 ± 0.4	10.1 ± 0.5
Hemicellulose	14.5 ± 0.2	9.5 ± 0.2	11.3 ± 0.8
Xylose	10.2 ± 0.0	4.5 ± 0.1	10.3 ± 0.6
Galactose	2.2 ± 0.0	2.0 ± 0.1	1.0 ± 0.1
Arabinose	3.2 ± 0.2	4.0 ± 0.4	1.1 ± 0.2
Mannose	0.6 ± 0.1	0.3 ± 0.0	0.3 ± 0.1
Acid-insoluble lignin	15.4 ± 0.4	15.1 ± 0.5	20.1 ± 1.5
Acid-soluble lignin	2.3 ± 0.1	2.6 ± 0.2	1.8 ± 0.2
Extractives	28.6 ± 1.3	45.2 ± 1.5	48.8 ± 1.2
Glucose	7.3 ± 0.1	7.1 ± 0.1	8.0 ± 0.5
Phenolics[1]	2.9 ± 0.0	4.4 ± 0.2	6.1 ± 0.1
Ash	3.9 ± 0.6	8.3 ± 0.2	9.1 ± 0.5
Elemental			
Nitrogen	0.5 ± 0.1	1.3 ± 0.1	1.7 ± 0.1
Carbon	45.9 ± 0.3	49.4 ± 0.3	48.3 ± 0.4
Hydrogen	6.3 ± 0.1	6.8 ± 0.2	6.1 ± 0.0
Sulfur	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0

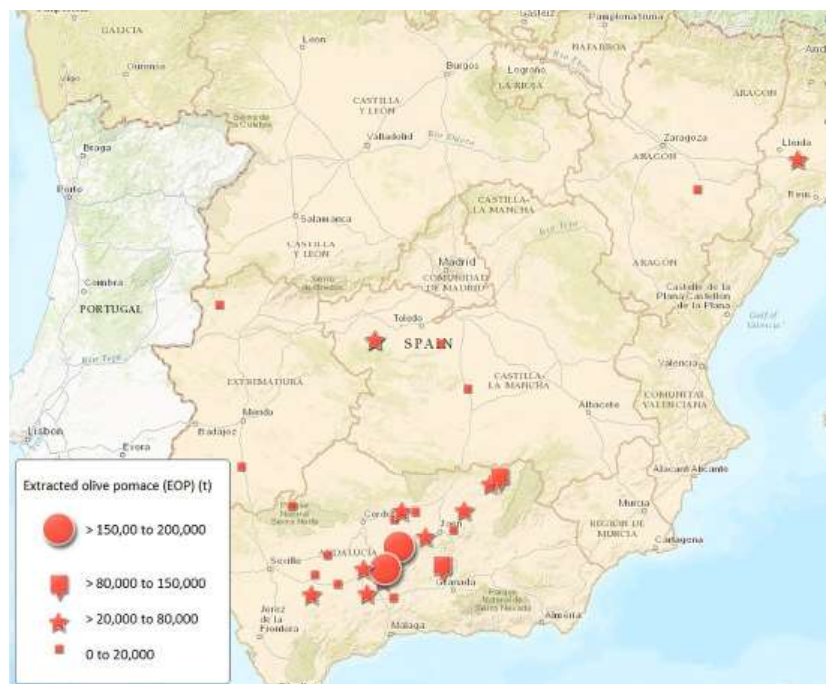[1] Expressed as gallic acid equivalents (GAE).

Figure 2. Map of spatial regional distribution of extracted olive pomace (EOP) production in Spain.

of biofuels and bioproducts, the chemical composition of the three targeted residues was determined and the results shown in Table 4. Structural carbohydrates were the main components in the case of OTPB, with 21.6% of cellulose and 14.5% of hemicellulose. Taking also into account the glucose present in the extractives fraction, total sugars accounted for ~ 50% of the OTPB. Sugars contained in OTPB could potentially be transformed into bioethanol to be used as an advanced biofuel. The conversion of OTPB into bioethanol by a biochemical process involving pretreatment, enzymatic hydrolysis and fermentation has been successfully carried out by Martínez-Patiño *et al*. (2015). Considering the production yields estimated for OTPB, EOP and OL, carbohydrate composition (Table 4) and theoretical, stoichiometric maximum ethanol yield of 0.51 g ethanol/g sugar, potential production of bioethanol from the three residues was assessed. Potentially up to $500 \cdot 10^6$ L of bioethanol could be obtained from the availability $3 \cdot 10^6$ tons/year OTPB estimated as availabile at a national level (Table 2). Smaller amounts of structural carbohydrates were detected in the case of OL and EOP (18.8% and 21.4%, respectively), whereas the glucose content in the extractive fraction of both residues was slightly higher than in the case of OTPB. Following the same calculations above, if all sugars coming from the structural carbohydrates present in OL and EOP could be used for ethanol production, potentially up to $30 \cdot 10^6$ L and $160 \cdot 10^6$ L of bioethanol, respectively, could be

also obtained in Spain, according to the production values determined in this work. These figures, although indicating a high potential for production of high added value products such as fuel ethanol based on the selected residues, must be considered only as a theoretical estimation and techno economic and energy balances are required to refine the significance of this approach.

Furthermore, the high proportion of extractives that these residues contain, especially in the case of OL (45.2% dwb) and EOP (48.8% dwb) was noted. In a biorefinery, valorization of this fraction could be very important. A significant amount of soluble glucose and phenolic compounds were found in the OTPB, OL and EOP extractives (Table 4) and the presence of phenolic compounds with antioxidant activity in these materials has also been reported elsewhere (Conde *et al.*, 2009; Romero-García *et al.*, 2014, 2016). Other interesting compounds *i.e.* mannitol, have been detected in this fraction (Martínez-Patiño *et al.*, 2015; Romero-García *et al.*, 2016). The separation and purification of these added-value compounds (Fernandez Bolaños *et al.*, 2000, 2013) could be an interesting option to explore further. In addition, given the inhibitory effect that phenolic compounds can exert on sugar fermentation, removal of these compounds from the aqueous extract could also favour production of ethanol from the glucose present in the extractive fraction.

On the other hand the amount of lignin present in OPTB, OL and EOP was also significant (18-22%)

and valorisation strategies could be developed to obtain high value products from the lignin (Toledano *et al.*, 2011). Another way to take advantage of this fraction could be energy production using self-consumption in the biorefinery facility, given the high calorific value of lignin (Negro *et al.*, 2016) and the fact that the lignin appears to be concentrated in the final solid remaining after bioethanol production from the lignocellulosic biomass. However, other uses with higher added value than energetic applications would be desirable from an economic point of view. As the lignin is the main byproduct of the ethanol production process, its transformation into chemical compounds of interest is a key factor for future development of this type of biorefineries (Fernández Rodríguez *et al.*, 2017).

In summary, the results of this study showed that substantial quantities of OTPB, OL and EOP are produced in Spain and could be considered as promising feedstocks for conversion to biofuels and bioproducts, based on their chemical composition and the existing background on suitable conversion routes. Although potential production yields of OL and EOP are considerably lower than that for OTPB (~ 322,000 and 1,182,000 *vs* > 3 million tons/campaign, respectively) the former may provide an advantage, as they are generated in the olive oil factories, while OTPB is scattered in the field. Logistics aspects should be also investigated to ensure the optimum strategy for biomass supply to the bio-refineries and the best location for these facilities should be evaluated in regions with a high concentration of olive cultivation and olive oil industry derived residues. Indeed, a challenging research is necessary to develop suitable valorisation strategies including the three residues.

Acknowledgements

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