Biorefinery based on olive biomass. State of the art and future trends

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Abstract

With currently more than nine million hectares, olive tree cultivation has spread worldwide, table olives and olive oil as the main products. Moreover, a number of by-products and residues derived from both tree cultivation and the process of industrial olive oil production, most having no practical applications, are obtained yearly. This paper reviews the research regarding these by-products, namely biomass from olive tree pruning, olive stones, olive pomace and wastewaters obtained from the process of olive oil production. Furthermore, a wide range of compounds has been identified and can be produced using a broad definition of the term biorefinery based on olive tree biomass. As an example, this paper reviews ethanol production as one of the main proposed applications, as well as research on other value-added products. Finally, this paper also assesses recent technological advances, future perspectives and challenges in each stage of the process.

Keywords: Biorefinery, Olive, Oligosaccharides, Antioxidants, Ethanol

1. Introduction

The production of renewable fuels, especially ethanol, proves to be one of the most promising alternatives to fossil energy sources. Biofuels are classified usually as either first or second-generation. First generation biofuels are those based mainly on sugars, grains, or seeds, and generally require relatively simple processing to produce the fuel. Currently, all commercial production of bioethanol uses only this first-generation technology with corn (United States), sugarcane (Brazil), wheat and barley (Europe). In contrast, second generation biofuels are generally made from lignocellulosic biomass, including residues of forestry or crops production and whole plant biomass (e.g., energy crops). Lignocellulosic materials are of great interest as feedstocks for second generation ethanol production due to their large availability, high carbohydrate content, and mainly because they do not affect the food provision. However, while technologies to produce ethanol from sugar or starch are well established, the technology to produce bioethanol from lignocellulosic biomass is still under development.

Within the last two decades, plant material components such as lignocellulosic residues and their potential biofuel production have increasingly received more attention in the science community, as well as their new value-added compounds and biomaterials utilizing a “biorefinery” approach. This concept is comprised of a wide range of technologies able to separate biomass components into their building blocks (carbohydrates, proteins, fats, etc.), which can be converted to value-added products, biofuels, and chemicals. Separation takes place in a facility, or network of facilities, that integrates biomass conversion processes and equipment to produce transportation biofuels, power, and chemicals from biomass (Cherubini, 2010). Thus, the biorefinery concept tries to integrate all these productions in a single installation in an analogous way to today’s petroleum refinery, where multiple fuels and products are obtained from crude petroleum. Moreover, biorefinery industries are expected to develop as dispersed industrial complexes able to revitalize rural areas. Unlike oil an refinery, which typically refers to very large plants, biorefineries will most probably cover a whole range of different sized installations. With this in mind, several bio-industries can combine their material flows in order to reach a complete utilization of all biomass components; the residue from one bio-industry becomes an input for other industries, giving rise to integrated bio-industrial systems. Furthermore, biomass resources are locally available in many countries and their use may contribute to reduce national dependence on imported fossil fuels (Cherubini, 2010).

Olive trees are usually native to the Mediterranean countries, but cultivation has spread globally during the past two decades due to healthy benefits attributed to olive oil consumption. In 2013, production of olive oil accounted for 2.67 million tons with human consumption being its main destination. In addition to olive oil, olive trees are also cultivated for table olive production. Currently, olive trees are cultivated in more than forty countries, and the total dedicated surface is 9.98 million ha (Faostat, 2012). As depicted in Fig. 1, an olive tree field is not only the source of olive oil, its main product, but also of a number of other by-products or residues, e.g., biomass from pruning, olive stones, pomace oil and pomace residues, and wastewater, and whose use can be the focus of a biorefinery based on olive trees. Fig. 2 summarizes the simplified process for olive oil production, indicating the points at which the above-mentioned by-products or residues are obtained.

Figure 1

Figure 2

While excellent reviews dealing with the use of olive stones (Rodríguez et al., 2008) or olive mill wastes (Dermeche et al., 2013) are available, the objective of this work is to present an updated revision of the main research regarding different kinds of biomasses derived from the olive tree cultivation and olive oil production process, specifically including olive tree pruning biomass.

2. Characterization of different biomasses from olive

2.1. Olive tree biomass from pruning

Olive tree pruning (OTP) is an essential operation performed every two years after fruit harvesting. A typical OTP lot includes leaves (approximately 25% by weight), thin branches (approximately 50% by weight), and thick branches or wood (approximately 25% by weight), although the proportions may vary depending on culture conditions, tree age, production and/or local pruning practice. In the Mediterranean region, residual biomass from OTP yield ranges from 1 to 5 and from 4 to 11 t/ha, respectively for Spanish and Italian orchards (Spinelli and Picchi, 2010).

OTP biomass, like other biomasses of lignocellulosic composition, is a complex mixture of cellulose, hemicelluloses and lignin, the three main components, as well as a significant amount of soluble compounds (extractives) and ash. The overall chemical composition of OTP biomass may differ slightly depending on tree age, soil makeup, and climate conditions. Cellulose, hemicellulose, lignin content and extractive content from OTP biomass are in the range of 26.1–36.6; 20.0–25.0; 17.9–27.7 and 14.1–31.4 (% w/w), respectively (Ballesteros et al., 2011, Cara et al., 2012, Cuevas et al., 2010, Requejo et al., 2012a, Romero et al., 2007, Toledano et al., 2013). Such differences can be mainly ascribed to the heterogeneity of this biomass, potentially presenting a variable proportion of leaves as well as different branch diameters. One special feature of this biomass is the relative high-derived glucose content in the extractives due to the presence of non-structural glucans present in olive leaves. This composition allows for the development of a multiproduct industry that utilizes various components in biomass and their intermediates thus maximizing the value derived from biomass feedstock.

2.2. Olive stones

As shown in Fig. 2 olive stones are recovered in the olive oil extraction process after oil separation. The table olive industry can also provide for a substantial a source of olive stones, as whole pits are regularly removed before further processing. However, in the case of olive stones obtained from olive oil production processes, they are usually crushed and retrieved as small particles. According to several reports (Matos et al., 2010, Rodríguez et al., 2008) the main components of olive stones are cellulose (28.1–40.4%), hemicelluloses (18.5–32.2%) and lignin (25.3–27.2%), while olive stones represent approximately ten percent by weight of the olive fruit.

2.3. Olive oil pomace

Crushed olive stones, together with vegetation water, process water, and all materials coming from the fruit except olive oil, make up olive pomace, which represents the main residue of the olive oil extraction process by weight. It is important to note that the composition of olive pomace may differ depending on the production process. The two-phase separation mode (Fig. 2), the most usual olive oil production method in Spain, produces a pomace with higher moisture content (55–70%) than that which is obtained in the three-phase operation (40–45%) (Borja et al., 2006). Besides water, olive pomace contains carbohydrates, lipids (remaining oil), polyphenols, and a number of metals and salts with a 4.8–5.2 pH average. Furthermore, it possesses a high chemical and biological oxygen demand due to its high organic charge.

2.4. Olive mill wastewater (OMWW)

According to the general scheme depicted in Fig. 2, OMWW is generated at three different points: during olive fruits cleaning; from the horizontal centrifuge (decanter) during the three-phase separation step; and during the washing process from the secondary centrifuge of virgin olive oil. However, standard practice dictates the disposal of these three types wastewater by pouring them into an open-air pond for evaporation. OMWW contains sugars (1.6–4%), and phenolic compounds responsible for the difficulty of proper treatment. This poses environmental concerns as OMWW has a high biological and chemical oxygen demand, namely in the range of 35–110 and 45–170 g/L (Borja et al., 2006).

2.5. Olive leaves

Olive leaves are lignocellulosic residues mainly found in two different points during the process of olive oil production (Fig. 2). They are fist found during OTP, in which they constitute twenty-five percent of the pruning, but are usually burned or ground together with the remainder of the OTP by-products, i.e., branches. The second point is in the olive oil production facility, where leaves are separated from the fruits using a blower machine in the early steps of olive cleaning. Olive leaf composition includes as a percentage of fresh material 51% moisture, 26.9% carbohydrates, 3.2% oil, 7.2% crude protein, 6.9% crude fiber, 2.5% total polyphenols, and 2.4% ash (Aydinoglu and Sargin, 2013). According to García-Maraver et al. (2013) a high percentage of extractives was found in olive leaf samples (36.52%), as well as cellulose, hemicelluloses and lignin, accounting for 5.7%, 3.8% and 39.6%, respectively.

3. Olive tree biomass from pruning as a feedstock in a biorefinery concept

OTP takes place immediately after fruit collection. Older branches are cut down, gathered into to the center of each row of trees, and further treated. These trimmings must be promptly eliminated from the cultivation fields; otherwise a risk for vegetal diseases may arise. Currently, there exist two different applications for this pruned biomass, either by grinding it and scattering the chips over the field or by direct burning, which can cause economic costs and environmental concerns. Therefore, as an alternative, olive tree biomass has been proposed as feedstock for ethanol and production of other chemicals. The following sections review the main results published on these issues.

3.1. Ethanol production

A cost-effective conversion of carbohydrates contained in lignocellulosic material into fermentable sugars remains a key issue for biorefineries, which attempt to provide a viable route to biofuels or bioproducts. In general, schemes for lignocellulosic biomass conversion include a pretreatment step followed by enzymatic hydrolysis and the subsequent fermentation by microorganism of the carbohydrates contained in biomass.

3.1.1. Pretreatment

After collecting and comminuting, the first stage in any lignocellulose-based biorefinery process is pretreatment. It represents a crucial step in the production of biofuels from lignocellulosic biomass. In addition to enhancing the enzyme's accessibility to cellulose, an ideal pretreatment aids in the ready fractionation of the biomass into its key constituents, cellulose, hemicelluloses and lignin, while facilitating its subsequent conversion into fuels and high value co-products in high yield. Pretreatments for lignocellulosic biomass include biological, mechanical, chemical methods and various combinations thereof (Alvira et al., 2010).

3.1.1.1. Hydrothermal pretreatments

Hydrothermal pretreatments utilize water at elevated temperatures to improve the lignocellulose conversion. Several pretreatment technologies are included in this category including liquid hot water (LHW) and steam explosion (SE).

LHW pretreatment uses a pressurized reactor to keep water in its liquid state. Biomass undergoes high temperature cooking in water with high pressure, and under these conditions ionization of water make protons appear and act as catalysts for autohydrolysis process by breaking up acetyl groups present in ester form in hemicellulose, releasing acetic acid to the medium. LHW pretreatment for enzymatic hydrolysis presents favorable characteristics, including limited corrosion effects, recovery of valuable hemicellulose-derived compounds, and high cellulose digestibility of treated solid (Alvira et al., 2010).

Effects due to temperature (range 170–230 °C) and to residence time (10 and 60 min) on OTP biomass have been studied by Cara et al. (2007) and showed the most significant effect on the recovery of hemicellulose sugar. In contrast to hardwood and herbaceous biomass, the glucose was the most abundant sugar in the liquid fraction under any conditions. In fact, the highest glucose content (10.1/100 g raw material, equivalent to a concentration of 22.2 g/L) was found in the liquid fraction obtained under softest conditions (170 °C for 10 min). The glucose found in the liquid fraction is attributed to compounds present in the extractive non-structural glucose derivatives. Glucose recovery yields ranged from 63% to 76% in the solid fraction, and 30% in the liquid fraction in pretreatment performed below 200 °C (Cara et al., 2007). In addition, the aqueous fraction also contains soluble oligosaccharides (OS). A maximum xylooligosaccharides (XOS) yield was reported at 180 °C and glucooligosaccharides (GlcOS) at 170 °C. Temperatures above 200 °C produce more degradation of solubilized sugars than are usually associated with more severe autohydrolysis conditions (Cara et al., 2012). In a separate study, Requejo et al. (2012b) obtained yields of 29.5 g saccharides/100 g of OTP biomass in the liquid fraction after LHW treatment at 197 °C. The XOS were the most abundant-derived saccharides, reaching their maximum concentration (16 g/L) followed by GlcOS (8 g/L).

SE is pretreatment subjecting the biomass to pressurized steam for a period of time ranging from seconds to several minutes, and then suddenly depressurized. As a physic-chemical pretreatment, it combines mechanical forces and chemical effects due to the hydrolysis (autohydrolysis) of acetyl groups present in hemicellulose. Cara et al. (2006) reported the effect of SE pretreatment of olive tree wood by testing a range of 190–240 °C for 5 min. They noted that glucose recovery in the solid fraction increased with temperature, from 79.6% (equivalent to 27.4/100 g raw material) at 190 °C to 82.8% (equivalent to 28.5/100 g raw material) at 230 °C. Nevertheless, they found that xylose recovery in the solid fraction reduces as temperature increases, from 39.3% at 190 °C to 5% at 230 °C, due to complete solubilization of hemicellulose. Furthermore, alkali peroxide treatment has been traditionally used to remove residual lignin from post-treated samples, and combining this treatment with SE allows for the removal of hemicellulose and lignin, respectively. The cellulose content of the olive tree was effectively increased from 34.4% (expressed as glucose) in raw material to 64–85.8% (expressed as glucose) following SE and alkaline peroxide pretreatments, when applied in that order (Cara et al., 2006).

In another study, (Cara et al., 2008a) pretreated OTP biomass instead of olive wood by SE at a temperature range of 190–240 °C with and without impregnation by water or sulphuric acid solutions. They found cellulose recovery values ranged from 60% to 96%, indicating that some partial cellulose solubilization occurred at every pretreatment condition. Cellulose solubilization was higher when acid was used for impregnation and when the temperature was above 210 °C. Specifically, hemicellulose sugar recovery in the prehydrolysates ranged from 65–75% when acid was used as an impregnation agent (Cara et al., 2008a). In general, prehydrolysate obtained from water impregnated material exhibited lower contents of potential inhibitory compounds (acetic acid and furans).

3.1.1.2. Acid pretreatment

The main objective of acid pretreatments is to solubilize the hemicellulosic fraction of the biomass and make the cellulose more accessible to enzymes. Diluted acid pretreatment appears as a favorable method for industrial applications and has been widely studied for pretreating a wide array of lignocellulosic biomass. Sulphuric acid is the most commonly used pretreatment in olive tree residues (Cara et al., 2008b, Díaz-Villanueva et al., 2012), although other mineral acids such as phosphoric acid (Romero et al., 2007) have also been assayed. (Cara et al., 2008b) evaluated the effect of both temperature and sulphuric acid concentration on OTP biomass obtaining a maximum value of 83% of hemicellulosic-sugars at 170 °C (using 1% sulphuric acid for 10 min) in the prehydrolysate. Moreover, they found complete glucose recovery (~100%) taking into account the liquid and solid fractions.

3.1.1.3. $FeCl_3$ pretreatment

Inorganic salts have been studied as catalysts for hemicellulose solubilization in different biomasses. Pretreatment with $FeCl_3$ could disrupt most ether linkages and some ester linkages between lignin and carbohydrates while having no effect on delignification (Liu et al., 2009). $FeCl_3$ pretreatment removes the hemicellulose, enhances the accessibility of cellulose to cellulase, and moreover, high temperatures facilitates hydrolysis by increasing surface area and widening pores (Liu et al., 2009). López-Linares et al. (2013) obtained a maximum glucose recovery of 96% for pretreatment at 140 °C, 0.125 M $FeCl_3$ for 15 min. Under such conditions, they recovered 84% of hemicellulose-derived sugars in both the solid and the liquid fraction. Although high-temperature treatment of biomass with inorganic salt solutions can enhance glucose conversion yields, high temperature rapidly depolymerizes the structure of lignocellulose, resulting in some sugar degradation and increases utility costs.

3.1.1.4. Organosolvents

The organosolv pretreatment uses organic or aqueous solvents (ethanol, methanol, ethylene glycol, acetone, glycerol, etc.) to extract lignin and provide more accessible cellulose. Díaz et al. (2011) carried out OTP pretreatment of biomass with organosolvents. They noted a higher pretreatment severity, and ethanol content of the solvent increased delignification (up to 64% at 210 °C for 60 min and 66% w/w aqueous ethanol). In contrast, they found that xylan hydrolysis was promoted by lower ethanol content (maximum 92%). Organosolvent pretreatment was also explored by Toledano et al. (2011). They noted that the maximization of lignin concentration in the liquid fraction required using high temperatures and low ethanol concentration, resulting in solid fraction with low lignin content and high cellulose content. Reaction temperature and ethanol concentration were the most significant variables for organosolv extraction process, while reaction time was less important for the delignification process.

3.1.2. Enzymatic hydrolysis

The goal of the enzymatic hydrolysis (EH) process is to depolymerize the polysaccharides contained in the pretreated lignocellulosic substrates. Due to the complex structure and composition of lignocelluloses, different enzymes are involved and an appropriate combination of different activities is required for complete hydrolysis. Several pretreatment methods have been evaluated jointly with enzymatic hydrolysis (i.e., LHW, SE, diluted acid, mineral salts and organosolv) and commercial enzymes have frequently been used to convert OTP to fermentable sugars (Table 1).

Table 1

Cara et al. (2008b) evaluated the effect of diluted acid pretreatment on fractionation and enzymatic convertibility of OTP. They noted that diluted acid pretreatment improved the enzymatic convertibility of cellulose and achieved the highest enzymatic yield (76.5%) in the hydrolysis of the material obtained by pretreatment at 210 °C, 1.4% sulphuric acid concentration and 5 min. However, low severity pretreatment conditions (180 °C and 1% acid concentration) produced the maximum overall sugar yield (36.3 g sugar/100 g raw material), representing 75% of all sugars in olive tree biomass. These results compared favorably with those obtained using LHW pretreatment, which reported a maximum overall yield of 57.5% (Cara et al., 2007). The enhancement detected in overall sugar yield is mainly associated with a significant increase of hemicellulose-derived sugars in prehydrolysates when using diluted sulphuric acid.
Cara et al. (2008a) achieved relatively low yields (approx. 60%) using steam exploded OTP as substrate for enzymatic hydrolysis. The high extractive content in the OTP biomass is due to its large amount of leaves (approx. 30% by weight of dry matter basis) and the fact that during the steam explosion process lignin, is left with the substrate, which seems to be responsible for the relatively low glucose production in the enzymatic step from steam exploded olive tree biomass.
According to Ballesteros et al. (2011), a water extraction stage before SE pretreatment resulted in a high overall sugar recovery. They obtained an overall xylose yield of 13.7 g xylose/100 g raw material and an overall glucose yield of 31.4 g glucose/100 g raw

material in optima conditions (187 °C for 30 min), and recovered more than 90% of total glucose and approx. 80% of xylose present in the OTP. This process resulted in an improvement of more than 20% of sugars recovery (both glucose and xylose) when compared to previous works (Cara et al., 2008a) in which OTP was not subjected to water extraction before pretreatment.

López-Linares et al. (2013) reported improved results when using inorganic salts ($FeCl_3$) to pretreat olive tree biomass. They reported a maximum glucose yield of 39% (referring to the raw material) when pretreatment conditions were at 160 °C, 0.275 M FeCl3 for 30 min, corresponding to an efficiency value of 88.7%. Organosolv pretreatment produces a highly digestible cellulose substrate from OTP (87.2% EH yield), and lignin with the potential of high-value utilization can be recovered after pretreatment (Toledano et al., 2013).

As seen from above studies, it is important to note that OTP-EH experiments were typically conducted at 2–5% total solid substrate to ensure proper mixture enzyme and substrate. Operating at a high solid content during the EH process is crucial for large-scale development of bioproduct and biofuel production processes. The concentration of glucose increases as a function of substrate concentration, and the highest glucose concentration (64 g/L, 53.4 g/L and 52 g/L for LHW, diluted and steam explosion substrates, respectively at 23% (w/w) solid concentration and 72 h hydrolysis). However, the hydrolysis efficiency using commercial cellulases at 17% (w/w) total solid concentration is about 9% lower than that obtained at 5% WIS and ultimately up to 30% lower when total solid was 23% (Cara et al., 2007, Manzanares et al., 2011). Moreover, the use of cellulose enzyme supplemented with other enzymes can raise the EH rate. Toledano et al. (2013) reported EH yields above 80% when using organosolv pretreated OTP biomass at 15% substrate consistency. In this study, a mixture of cellulase and xylanases enzymes was employed.

Table 1 depicted results obtained for pretreatment OTP biomass. No current treatment technology produces a 100% conversion of biomass into fermentable sugars. A loss of biomass is inevitable; hence it affects the final yield and increases the cost of the finished product, i.e., biofuel. OTP biomass pretreatment of with combination of two or more process could improve results. There is need for extensive research in this area, so that either a new efficient treatment process should be developed.

3.1.3. Fermentation

Sugars fermentation into ethanol, either from enzymatic hydrolysis of cellulose or hemicellulosic-derived sugars from prehydrolyzates, is commonly carried out by using yeast. In the first case, strains of Saccharomyces are used, while for the second option microorganisms that are able to ferment C5 sugars such as Pachysolen tannophilus, Candida shehatae and Pichia stipitis are utilized. OTP sugars from cellulose and hemicellulose fraction can be converted to ethanol by either a simultaneous saccharification or fermentation (SSF) process or by a separated enzymatic hydrolysis and fermentation (SHF) process.

Cuevas et al. (2010) evaluated the influence of pretreatment conditions (temperature and acid concentration) on SSF of olive-pruning debris (OPD) using response-surface methodology and the fermenting yeast Saccharomyces cerevisiae. They found that using SSF for washed pretreated solids produced ethanol percentages higher than 80% of the theoretical (based on the cellulose content in the pre-treated solids) but low SSF ethanol yields (based on the weight of the raw material) because of the existence of a cellulose fraction for mild pre-treatments that is transferred to hydrolysate. Moreover, Manzanares et al. (2011) studied the effect of pretreated (LHW and diluted-acid) OTP at different substrate loadings on ethanol production in different process configurations, SHF, presaccharification and simultaneous saccharification (PSSF) and SSF. The study showed an overall ethanol yield (based on the amount of cellulose in the raw material) of 38.7 g ethanol per 100 g cellulose (8.8 g ethanol per 100 g raw material) by SSF process. However, they only obtained 26.7 g ethanol per 100 g cellulose (6.1 g ethanol per 100 g raw material) when using dilute-acid pretreated olive pruning. They also noted that high ethanol concentration of about 3.7% (v/v) could be obtained by SHF or PSSF of LHW-pretreated olive pruning at 23% (w/w) substrate loading. Similar ethanol concentration was reported by Toledano et al. (2013) when using organosolv pretreated OTP. In addition, these authors reported the highest overall ethanol yield (17.1 g ethanol/100 g OTP biomass) found in the literature.

Glucose and xylose are two dominating sugars in lignocellulosic hydrolysates. The main difficulty in using two microorganisms for the co-fermentation of these sugars is the inability to provide optimal environmental conditions for the two strains simultaneously. In general, a detoxification treatment of the hydrolysates is required for reducing the inhibitory effect of compounds present in the hydrolysate obtained after pretreatment. Different detoxification methods of hemicelluloses hydrolyzates from acid pretreated OTP have been reported (Díaz et al., 2009, Negro et al., 2014). Specifically, Romero et al. (2007) carried out the fermentation of olive tree biomass hydrolysates (obtained after phosphoric acid pretreatment) using *P. tannophilus* as fermenting microorganism. The ethanolic fermentation of liquid fractions from pretreated olive tree biomass utilizing *P. stipitis* and *P. tannophilus* have been studied by Díaz-Villanueva et al. (2012) and Romero et al. (2007). Results reported show that ethanol yields obtained from hydrolysates using *P. stipitis* as the fermenting microorganism, ranging from 0.35 to 0.42 g/g although the process proceeds at lower rates. Moreover, inhibiting compounds affect the performance in a synergistic way. Ethanol production from both sugars (xylose and glucose) after steam explosion pretreatment and enzymatic hydrolysis using *S. cerevisiae* and *S. stipitis* was recently evaluated (Negro et al., 2014). Ethanol yields in an SSF process were close to 80% of theoretical when using 15% (w/w) solid consistency. However, a detoxification treatment was required for reducing the inhibitory effect of compounds present in the hydrolysate.

3.2. Xylitol

Xylose and arabinose are the main pentoses or C5-carbohydrates in hemicellulose; hydrogenation of these carbohydrates yields the isomers xylitol and arabitol. Of these, xylitol remains the most widely produced xylan derived product with substantial marketability (Deutschmann and Dekker, 2012). Xylitol may be also produced by xylose fermentation present in hemicellulosic hydrolysates generated after acid and autohydrolysis pretreatment. Moreover, many microorganisms are able to produce xylitol from xylose, namely different yeast species, e.g., *Candida*, *Pichia* and *Pachysolen*.

García et al. (2011) evaluated the uses of different sulphuric acid hydrolysis techniques to achieve maximum d-xylose yield and subsequent fermentation of the olive debris hydrolysates with *Candida tropicalis*. Under optima conditions (pretreatment in a extruder at 70 °C with 1 N sulphuric acid followed by acid hydrolysis with 1 N sulphuric acid at 90 °C for 2.5 h), xylitol production accounted for 53 g xylitol per kg of dry olive debris.

3.3. Lignin

Lignin present in OTP biomass is in the range of 14.1–31.4% (w/w). Lignin offers a significant opportunity for enhancing the operation of a lignocellulosic biorefinery. Organosolvent pretreatments have been applied to OTP biomass for lignin production. Toledano et al. (2012) studied not only operational conditions (temperature, time and ethanol concentration) but also the characteristics of lignin obtained from OTP after organosolv treatment. Optimal organosolv conditions (200 °C, 70% ethanol and 90 min.) allowed for the production of high quality lignin, high acid insoluble lignin content (71.90%) and low contamination (sugars 2.94% and ash 0.39%). Interestingly, lignin seemed to be highly reactive due to its high functionality (Toledano et al., 2012). The production of bioethanol from lignocellulosic feedstocks could result in the availability of a new form of higher quality lignin for chemical applications. The production of more valuable chemicals from lignin (e.g., resins, composites and polymers, aromatic compounds, or carbon fibers) is viewed as a medium to long-term opportunity depending on the quality and functionality of the lignin that can be obtained.

3.4. Oligosaccharides (OS)

OS are small carbohydrate compounds that belong to an extensive and heterogeneous family. Traditionally, OS are defined as polymers of monosaccharides with degrees of polymerization (DP) between 2 and 10 (3 and 10 according to the IUB-IUPAC nomenclature) (Mussatto and Mancilha, 2007). Non-digestible oligosaccharides (NDO) are low molecular weight carbohydrates consisting of sugars moieties that resist hydrolysis in the gastrointestinal tract by virtue of the β-configuration their glycosidic bond. The human body lacks the enzymes required to hydrolyze the β-links, and therefore are considered prebiotics and soluble fibers because they are not digested in the stomach and thus reach the large intestine intact. Moreover, NDO could be fermented by the intestinal microflora, stimulating selectively the growth and/or activity bacterial associated with health and wellbeing (Gibson et al., 2004).

Reis et al. (2003) studied the characterization of olive XOS obtained by partial acid hydrolysis olive pulp and olive seed hull. The acidic XOS from olive pulp were found predominantly substituted with 4-O-methyl glucuronic acid residues, while those from olive seed hull were found predominately substituted with glucuronic acid residues. Lama-Muñoz et al. (2012) further identified some bioactive phenol glucosides and poly- and oligosaccharides from thermally treated olive oil by-products.

Regarding commercial production, NDOs, such as galactooligosaccharides, XOS and fructooligosaccharides, can be extracted from lignocellulosic materials; however, OS production from lignocellulosic materials is neither simple nor economical because it needs to complete two treatment steps. The first is xylan extraction from lignocellulosic materials, which includes a chemical treatment. Various pretreatment have been used for the complete extraction of hemicellulose to make xylan for hydrolysis reaction (Alvira et al., 2010). The second step includes a xylan enzymatic reaction or xylan acid hydrolysis (Mussatto and Mancilha, 2007).

Hydrothermal methods for lignocellulosic residues fractionation are an economically attractive and environmentally friendly alternative to obtain OS from sugars rich materials. According to Cara et al. (2012), the most appropriate autohydrolysis temperature for oligosaccharide production from OTP raw material is 180 °C for 10 min, resulting in a maximum yield of oligosaccharides together with a low amount of by-products. They found that the total concentration of oligosaccharides was 37.5 g/L mainly consisting by glucooligosaccharides (GLcO) and XOS. Moreover, they subjected OTP hydrolysate to fractionation by preparative gel filtration chromatography. After purification, a range of OS fractions with an average degree of polymerisation (DP) from 3 to 25 was selected for further characterization. GLcO and XOS were the predominant OS in these fractions. OS yields ranging 80–90% were obtained for fractions with an average DP between 7 and 25, and were practically free of low molecular compounds (Cara et al., 2012). Mateo et al. (2013) further studied the effect of temperature (ranging from 180 °C to 230 °C) with diluted acid or LHW pretreatment under pressure on oligosaccharides production from OTP biomass. They generated maximum concentration of oligosaccharides as well as monosaccharides with the lowest possible severity.

Obtaining valuable co-products coupled with the ethanol production process is a characteristic feature of the biorefinery concept. Industrial scale biorefineries can contribute greatly to make second generation ethanol economically feasible due to the simultaneous production of oligosaccharides.

3.5. Antioxidants

Antioxidants are defined as a kind of additive, which prolong the shelf-life of foods by protecting them against oxidation deterioration. In recent years, there is a great interest in the food industry on substitution of artificial antioxidants by natural antioxidants. Moreover, it is important to note that olive trees are a great sources of natural antioxidants because they exist in fruit, pulp (Nadour et al., 2012), pomace (Cardoso et al., 2005) and leaves (Lee et al., 2009, Lee and Lee, 2010). Hence, olive trees and OTP biomass serve as a viable alternative in the quest for natural antioxidants.

Studies have shown that phenolic compounds are present in several parts of the olive tree, such as, in case of the fruit where hydroxytyrosol, tyrosol and oleuropein are present at high levels. Active compounds such as hydroxytyrosol, tyrosol, cycloolivil, 7-deoxyloganic acid, oleuropein were detected in olive wood extracts (Pérez-Bonilla et al., 2011).

Castro et al. (2008) studied the evaluation of phenolic content and antioxidant activity of the ethyl acetate soluble present in the liquors from olive wood by SE. They noted that the most active radical scavenger was obtained at 210 °C, showing antioxidant activity comparable to those of a synthetic antioxidant. Conde et al. (2009) also studied the effect on extraction of antioxidants compounds after LHW and SE pretreatment. They concluded that compounds with more activity were extracted in the LHW at low temperature.

3.6. An integrated biorefinery based on olive tree pruning biomass

Considering that olive tree pruning biomass can be used as raw material for the production of a number of different products, a biorefinery scheme is depicted in Fig. 3, identifying the main process routes as well as final/potential products. The proposed operation sequence is based on previous research results with aqueous extraction as the first step. This operation has been determined to be necessary because of interferences and side reactions between the extractive fraction of the olive tree biomass and lignin (Ballesteros et al., 2011). The extracted stream can be further processed to take advantage of the soluble sugars and other special features, such as antioxidant capacity. On the other hand, the extracted biomass proceeds to the pretreatment step (see previous section for details) and upon completion of this step, the liquid fraction or prehydrolyzate and the solid fraction can be separated by filtration. Depending on the pretreatment conditions, the liquid fraction represents a potential source for oligosaccharides, sugars and antioxidants, while the pretreated solids constitute a mixture of mainly lignin and cellulose. The enzymatic hydrolysis of this fraction yields a glucose solution, which can be fermented into ethanol; a variety of process configurations are possible at this stage, including separate hydrolysis and fermentation, simultaneous saccharification and fermentation, with or without a presaccharification step. The lignin-rich residue after fermentation is also a valuable material that can be used as biofuel for energy supply or can be directed to chemical processing for a wide range of final compounds.

Figure 3

Alternatively, Toledano et al. (2013) propose a different scheme for a biorefinery based on olive tree pruning according to which biofuels are produced from the solid fraction of pretreated materials, following enzymatic hydrolysis and fermentation, while liquid fractions issued from pretreatment are used as starting point for biochemicals production by means of lignin precipitation. Yet in a dissimilar approach, Requejo et al. (2012a) propose the use of the main fraction of olive pruning as a sugar source by means of hydrothermal treatment, then producing either paper pulp or ethanol from the pretreated solid, and finally using the residual fraction of olive pruning, e.g., leaves and thin stems, to provide heat.

4. Olive stones

Rodríguez et al. (2008) reviewed olive stones' main and potential uses. Moreover, Pattara et al. (2010) noted that olive stone are still being used primarily for their heating capacity as a fuel, namely in domestic boilers or in large industrial plants for cogeneration. However, López et al. (2010) suggest that it can serve as a substitute for fossil fuels especially in public heating systems where the fuel change may have a demonstration effect. Lastly, (Vera et al., 2013) consider it as a raw material for gasification processes.

Other recent applications of olive stones, still in the research phase, are briefly described below and subsequently summarized in Table 2. Furthermore, several researches have focused on activated carbon prepared from olive stones. Plaza et al. (2009) found the stones to be versatile precursors to the preparation of adsorbent materials. Specifically, one of the main advantages is the low cost of the raw material together with the high CO_2 adsorbent capacity of the materials prepared using olive stones. Some of the cations assayed for removal with activated carbon produced from olive stones include Cr^{3+} and Cr^{6+} (Blázquez et al., 2009), Fe^{2+} (on crude stones, Martínez-Nieto et al., 2010). Microwave assisted olive stone activated carbon was also used for the successful removal of heavy metals from contaminated wastewater (Alslaibi et al., 2013). Olive stones, together with other agroindustrial lignocellulosic residues, were used as a source for biopolyols (Matos et al., 2010) exhibited attractive properties for polyurethanes and other industrial sectors (Briones et al., 2012).

Table 2

5. Olive mill wastewater

Olive mill wastewater (OMWW) constitutes a major concern for olive oil production industry due to its pollutant charge, expensive disposal treatments, and the large amounts annually generated. Nevertheless, several research groups around the world have studied a number of possible applications (Table 3); using OMWW as an inexpensive raw material for recovering phenolic compounds is one of the commonly addressed objectives. Concerning the specific phenolic compounds, hydroxytyrosol, verbascoside, and isoverbascoside are some of the ones being studied as possible food antioxidants. As an example, Cardinali et al. (2012) are currently developing a diversified technology set of procedures including membrane technology coupled with low-pressure gel filtration chromatography. Moreover, various groups are studying different membrane extraction techniques (Cassano et al., 2013). Klen and Vodopivec (2011) are working on filtration, liquid–liquid and ultrasonic-assisted extraction of liquid and solid (freeze-dried) OMWW and others on solid phase extraction (Scoma et al., 2011).

Table 3

OMWW has also been assayed as a culture medium for producing enzymes, especially lipases (Brozzoli et al., 2009). Bioplastics (polyhydroxyalkanoates) have also been produced using OMWW as a starting medium (Cerrone et al., 2010). Removal of the phenolic compounds from OMWW is standard practice before trying to take advantage of its carbohydrate content. Some have proposed a number of different biofuels including biogas, ethanol, methane, and hydrogen to be produced from OMWW using different techniques. For example, the capability of *Pleurotus sajorcaju* to degrade phenols of OMWW was confirmed on a number of pretreatment conditions, and the resulting substrate was diluted to 50% as a culture broth for ethanol fermentation by *S. cerevisiae* (Massadeh and Modallal, 2008). Using media enriched with glucose, with sugar concentrations up to 115 g/L, a maximum ethanol concentration of 52 g/L was obtained in a batch reactor system (Sarris et al., 2013).

Hydrogen photo-production is another objective that has been studied based on OMWW as a low-cost feedstock (Eroglu et al., 2011). A typical process includes the pretreatment of OMWW to eliminate the polyphenols and then the use of a microorganism

(*Rhodopseudomonas palustris sp.*) to produce hydrogen (Padovani et al., 2013). Different adsorbent matrices including granular active carbon, resin, and zeolite were used to dephenolize stored-OMW (Scoma et al., 2013).

Methane production has also been the focus of several research groups. For this application they have identified high chemical oxygen demand concentrations (54–55 kg COD/m^3), acid pH (5.0) and lack of alkalinity and nitrogen as adverse characteristics of OMWW (Sampaio et al., 2011). One of the study's approaches consisted in combining progressive increases of OMWW volumes with a complementary effluent (piggery effluent). Furthermore, OMWW could be used to replace fresh water in clay brick manufacturing; the wastewater came out either the oil-washing stage (OWW) in the two-phase olive oil extraction method (de la Casa et al., 2009) or from the decanter in the three-phase separation system (Mekki et al., 2008). In both cases, a double benefit could be reached; on the one hand, they reduced or eliminated the environmental problem related to OMWW disposal and on the other hand, they noted potential savings in the fire clay industry because of the partial substitution of tap water and, more interestingly, the reduction in fuel need in the brick kiln as the heat requirements are partially covered by the organic matter fraction present in OMWW.

6. Olive oil pomace

Olive oil pomace is the main residue resulting from olive oil production process in quantitative terms. Currently, olive oil pomace is treated to recover any residual oil (approx. 2% by weight) by solid-liquid extraction with hexane, followed by distillation and solvent recycling. Moreover, it is usually taken out for free by extraction facility owners or, depending on oil prices, a minimal amount can be paid. As olive oil is produced in a short period of time, olive oil pomace is stored in large open-air ponds, waiting to be processed in the extraction plants. This storage can be the origin of different environmental problems; hence, much research has been devoted to this residue and recent achievements, mainly at the laboratory scale, are described below. Most of the available reports deal with the use of pomace as a source of valuable compounds recovery, aiming at the same time to help solve the environmental problem caused by pomace disposal.

Aliakbarian et al. (2011) studied phenolics recovery using a high-temperature high-pressure reactor with oleuropein and tyrosol being identified as predominant phenolics in the extracts, while the environmental impact derived from solid residues after phenolics extraction were considered low. Moreover, Coimbra et al. (2010), based on the polysaccharide composition of dry olive pomace, almost the same proportions of cellulose, glucuronoxylans, and arabinan-rich pectic polysaccharides, propose that olive pomace can be a potential source of gelling pectic material. Several particular features, including a higher temperature resistance than other gels, make those derived from olive pomace beneficial for particular applications.

Furthermore, Tayeh et al. (2014) estudied bioethanol production from olive mill solid wastes. Biogas production has also been reported with olive pomace as a starting material. Rincón et al. (2013) studied the methane potential of two-phase olive mill solid waste by means of a thermal pretreatment. Composting is another typical application for olive oil pomace (Federici et al., 2011).

7. Olive leaves

Olive leaves are cut down at the same time as olive fruit during harvesting and are usually separated in the early steps of olive processing (Fig. 2). Occasionally, this residue finds an application as animal feed or is directly discarded in the olive oil producing facility. Research efforts based on olive leaves focus mainly on the phenolic content. Among them, oleuropein is widely considered to be a potential health benefit (Bulotta et al., 2011). Antibacterial and antioxidant activity have also been described in phenolic extracts from olive leaves and could be applicable both in the health and medical food (Lee and Lee, 2010). Besides health related issues, olive leaves have also been studied for a variety of applications. For example, as a substrate for composting and assessing the degradation capacity of a mixture of pesticides (Karanasios et al., 2010) has been studied. The phenolics extracts from olive leaves and olive pomace have also been used as an ingredient for enriching oils, converting them in supplemented foods or even nutraceuticals (Sánchez-Medina et al., 2011).

8. Final remarks

Olive trees should be considered a valuable source of renewable biomass in two ways. On the one side, tree pruning causes a substantial amount of lignocellulosic residues generated annually, that must be eliminated from the fields. On the other side, once the olive fruits are in the factory, the olive oil extraction process also produces a series of biomass residues, including leaves, stones, olive pomace, and olive wastewater, all of can be used as raw material for a number of value-added compounds.

Regarding olive-pruning residues, pretreatment must be advanced and appropriately integrated with the rest of the processes to achieve a more complete and sustainable utilization of the OTP biomass for fuel and chemicals by advanced and updated conversion technologies. Therefore, an increase in pretreatment effectiveness in terms of hemicellulosic sugar recovery is needed. Moreover, more studies need to be carried out to verify if efficient biological conversion of lignocellulosic biomass to ethanol can render lignocellulosic economically competitive.

In relation to enzymatic hydrolysis process, the challenge is to achieve an efficient process to produce high concentration fermentable monomers; enhance ethanol production especially from hemicellulosic sugars, simplify process flow, e.g., reducing process steps, and increase scale (more articles on OTP biomass are based on laboratory scale). Besides, the integration of the overall steps is a future challenge that should be overcome.

In fermentation configuration, the challenges are to improve the xylose and glucose co-fermentation. Due to the presence of toxic compounds (generated in pretreatment step) in the fermentation broth, genetic modification, evolutionary engineering or adaptive strategies are promising alternatives to obtain more tolerant microorganisms. The use of robust and efficient recombinant microorganism could contribute to increase ethanol yield.

Economically speaking, obtaining antioxidants, oligosaccharides, lignin-derived chemicals, and energy may improve the economy of the global conversion process. The separation and purifications of valuable compounds from process streams present also a technical and economic challenge. Future efforts will focus on process integration, and the development of the biorefinery concept based on olive tree pruning biomass.

Concerning olive oil extraction-derived residues, the great advantage of having them already in the oil factory can facilitate their integration into valorization schemes, one again under the biorefinery concept. In that way, olive oil will continue to be the main product, but a wide range of value-added compounds.

9. Conclusions

Olive biomass is not only the source of olive oil but also of a number of other by-products and residues, e.g., biomass from pruning, olive stones, pomace oil and pomace residues and wastewater, all of which can be the focus of a biorefinery. The integration of the different processes outlined in this review will certainly have a positive effect on the scientific, technological, economic, environmental, and social points of view, not only for olive oil production but also for a wide range of co-products including biofuels, chemicals, sorption matrices, materials, polyphenols, and other compounds.

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Figure caption

Fig. 1. Average mass balance derived from 1 hectare of olive trees corresponding to Spanish typical cultivation procedure.

Fig. 2. Simplified process of olive processing for olive oil production. Bold names correspond to the different feedstocks reported in this investigation.

Fig. 3. Simplified flow diagram for a biorefinery based on olive tree pruning biomass. Product definition based on works by Requejo et al., 2012a, Toledano et al., 2013 and Cara et al. (2008b).

Figure 1

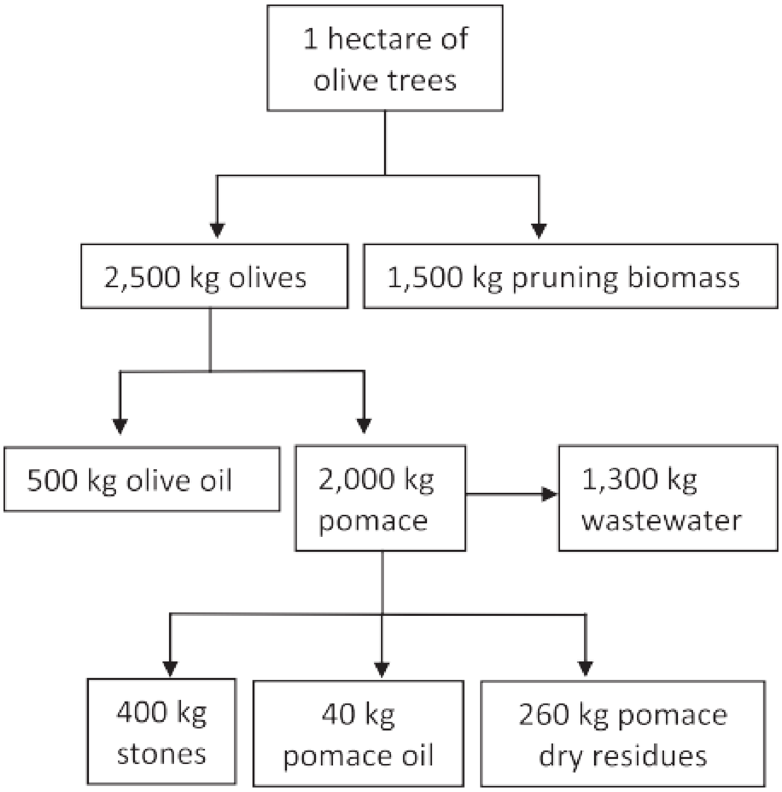
1 hectare of olive trees
2,500 kg olives
1,500 kg pruning biomass
500 kg olive oil
2,000 kg pomace
1,300 kg wastewater
400 kg stones
40 kg pomace oil
260 kg pomace dry residues

Figure 2

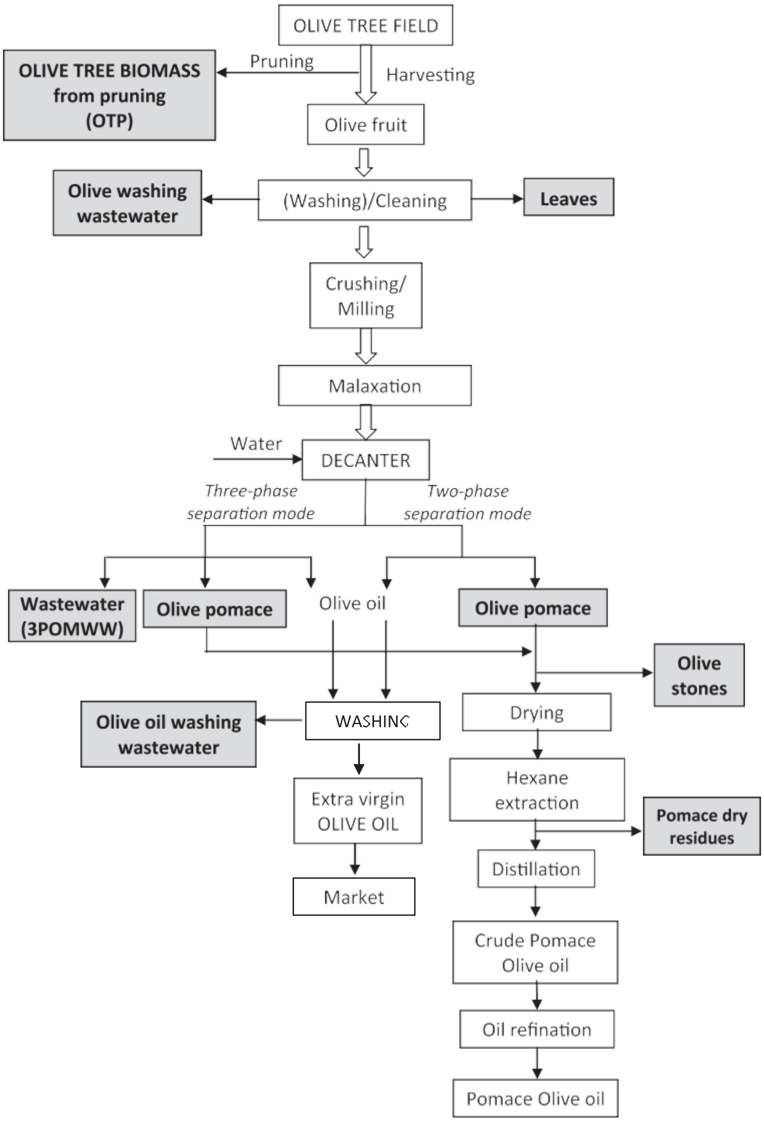
OLIVE TREE FIELD
Pruning
Harvesting
OLIVE TREE BIOMASS from pruning (OTP)
Olive fruit
Olive washing wastewater
(Washing)/Cleaning
Leaves
Crushing/ Milling
Malaxation
Water
DECANTER
Three-phase separation mode
Two-phase separation mode
Wastewater (3POMWW)
Olive pomace
Olive oil
Olive pomace
Olive stones
Olive oil washing wastewater
WASHING
Drying
Hexane extraction
Pomace dry residues
Extra virgin OLIVE OIL
Distillation
Market
Crude Pomace Olive oil
Oil refination
Pomace Olive oil

Figure 3

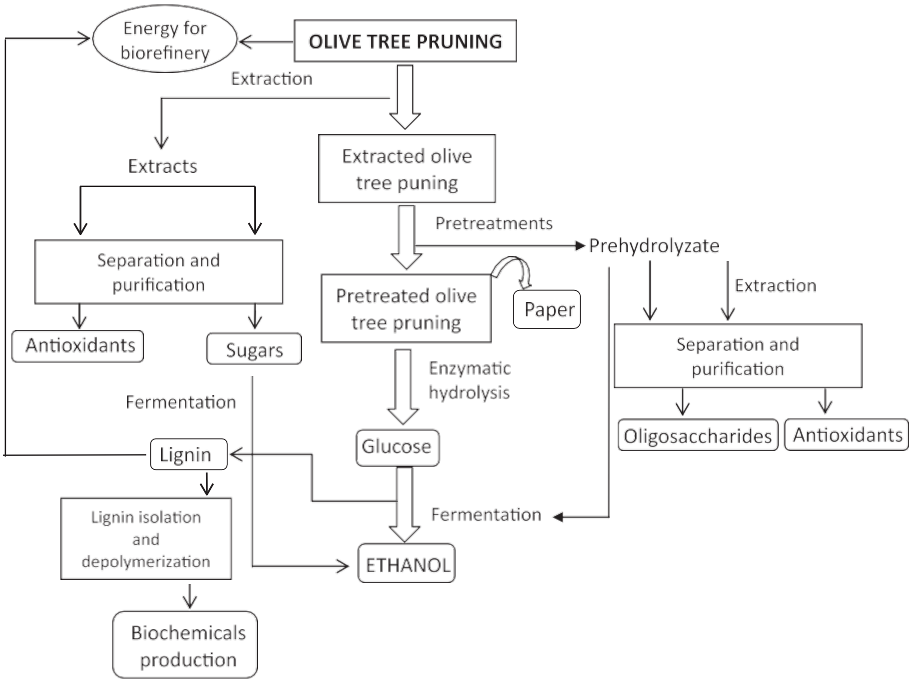
Energy for biorefinery
OLIVE TREE PRUNING
Extraction
Extracts
Extracted olive tree puning
Separation and purification
Pretreatments
Prehydrolyzate
Pretreated olive tree pruning
Paper
Extraction
Antioxidants
Sugars
Enzymatic hydrolysis
Separation and purification
Fermentation
Oligosaccharides
Antioxidants
Lignin
Glucose
Lignin isolation and depolymerization
Fermentation
ETHANOL
Biochemicals production

Table 1

Table 1. Different pretreatment employed on OTP and their results reported in literature.

Pretreatment	Pretreatment condition	Optima conditions	Sugars recovery % w/ w OTP	EH yields (%)	EH conditions	Overall yield (g/100 g OTP)	Remarks	References
Liquid hot water	170–230 ºC; 10–60 min; solid/liquid ratio 1:5 (w/v) batch, volume reactor: 2 L particle size <10 mm	210 ºC–10 min	94% Glucan	62.7	15 FPU and 15 CBU/g substrate 50 ºC, 72 h 5% solid consistency	18.8 g Glucose/100 g 20.2 g Sugars/100 g	Hemicellulose solubilization: 96%. Oligosaccharides in liquid fraction	Cara et al. (2007)
	175–215 ºC liquid/solid ratio 8:1 (w/w) batch, volume working: 0.5 L particle size <8 mm	210 ºC	73% Glucan 94% hemicellulose	83.5	10 FPU/g and 50 CBU/g substrate 48.5 ºC, 96 h 5% solid consistency	43 g Sugars/100 g	Liquid phase containing hemicellulose-derived compounds (29.5 g saccharides per 100 g OTP), 68% as oligomers	Requejo et al. (2012b)
Steam explosion	190–240 ºC; 5 min batch, volume reactor: 2 L particle size <10 mm	240 ºC–10 min water	66% Glucan 40% hemicellulose	60	15 FPU and 15 CBU/g substrate 50 ºC, 72 h 5% solid consistency	17 g Glucose/100 g 21 g Sugars/100 g	High production of ''lignin-like'' products in which the extractives could be involved	Cara et al. (2008a)
	175–204 ºC; 4–46 min batch, volume reactor: 2 L particle size <10 mm	187 ºC–30 min uncatalyzed	100% Glucan 86.5% hemicellulose	70	15 FPU and 15 CBU/g substrate 50 ºC, 72 h 5% solid consistency	31.4 g Glucose/100 g 13.7 g xylose/100 g	Extractive removal previous to steam explosion resulted in 20% more total sugars recovery in comparison to a material without water extraction stage	Ballesteros et al. (2011)
	170–230 ºC acid catalyst 10 min batch, volume reactor: 2 L	230 ºC–1% H_2SO_4	69.2% Glucan 80% hemicellulose	57.7	15 FPU and 15 CBU/g substrate 50 ºC, 72 h 5% solid consistency	19.4 g Glucose/100 g 31.1 g sugars/100 g	Complete hemicellulose solubilization	Cara et al. (2008a)
Diluted acid	170–210 ºC; 10 min solid/liquid ratio 1:5 (w/v) batch, volume reactor: 2 L particle size <10 mm	180 ºC, 1% H_2SO_4	92.8% Glucan 83.9% hemicellulose	66	15 FPU and 15 CBU/g substrate 50 ºC, 72 h 5% solid consistency	36.3 g Sugars/100 g	78.5% sugars are recovery in liquid fraction	Cara et al. (2008b)
Salts	120–180 ºC 0–30 min 0.05–0.275 M $FeCl_3$ batch, volume reactor: 1 L solid/liquid ratio 1:5 (w/v) particle size <1 cm	160 ºC 30 min, 0.275 M $FeCl_3$	85.0% Glucose 40.6% hemicellulose	88.7	45 FPU and 15 CBU/g substrate 50 ºC, 72 h 5% solid consistency	14.3 g Glucose/100 g 11.3 g hemicellulosic sugars/100 g	40.6% hemisugars presents in the liquid fraction	López-Linares et al. (2013)
Organosolvents	190–210 ºC;15–60 min ethanol:water 43–66% w/w batch solid/liquid ratio 1:5 (w/v) particle size <10 mm	210 ºC–15 min ethanol:water 43% (w/w)	60% Glucan (in solid fraction) 16.9% xylan (in solid fraction)	89.6	15 FPU and 15 CBU/g substrate 50 ºC, 72 h 5% solid consistency	Non-data available		Díaz et al. (2011)
	160–200 ºC ethanol (60–80%) 60–120 min batch solid/liquid ratio: 6 (w/v)	200 ºC-90 min-ethanol–water (with a mass fraction of 70%)	Non-data available	87.2	Cellic Ctec2 and Htec2 (with a doses of 9% and 0.9%). 50 ºC, 72 h 15% solid consistency	Non-data available	17.1 g ethanol/100 g OTP lignin was depolymerized into interesting compounds	Toledano et al. (2011, 2013)

Table 2

Table 2. Recent advances in olive stone research and potential applications.

Application	Methodology	Main results	Reference
Preparation of CO_2 adsorbents	Activation with CO_2, heat treatment with gaseous ammonia	Activated carbons from olive stones with a CO_2 capture capacity exceeding those of commercial activated carbons	Plaza et al. (2009)
Removal of metal cations	Preparation of microwave assisted potassium hydroxide activated carbon from olive stones	Removal of >95% of Cu^{2+}, Cd^{2+} Ni^{2+}, Pb^{2+}, Fe^{2+}, and Zn^{2+}	Alslaibi et al. (2013)
Source of polyols	Mild liquefaction using polyhydric alcohols to obtain biopolyols	The multifunctional liquids derived from several residues including olive stones could be used as precursor in polyurethane production and also for replacement of a certain amount of the polyhydroxy alcohol in polyester synthesis	Briones et al. (2012)
Adsorption of iron from olive oil wastewater	Iron solutions were mixed at different concentrations with olive stones of different particle size	The adsorption process was highly dependent on the particle size	Martínez-Nieto et al. (2010)
Electricity production by means of gasification	Modeling of a small-scale plant based on a downdraft gasifier and a gas engine connected to the grid	The gasification process results in a gas with of 5.1 MJ/kg calorific value and 14% electric efficiency	Vera et al. (2013)

Table 3

Table 3. Recent advances in olive mill wastewater research and applications.

Application	Methodology	Main results	Reference
Polyphenols and reusable water	Integration of a membrane system including ultra and nanofiltration in OMWW treatment	A concentrated solution containing organic substances at high molecular weight; a concentrated solution enriched in polyphenolic compounds suitable for cosmetic, food and pharmaceutical industries; a water stream reusable in the process	Cassano et al. (2013)
Production of biohydrogen	Packed bed biofilm reactors were used to develop anaerobic processes with dephenolized OMWW	Production of hydrogen and volatile fatty acid, that can be used as PHAs production is possible by parameter adjustment	Scoma et al. (2013)
	Dephenolization of OMWW using different matrices resulting in a suitable feedstock for biohydrogen production	Granular active carbon was the best matrix, yielding a maximum hydrogen production rate of 14.31 mL/L/h, when using 25% of the effluent from the pre-treatment of stored-OMWW	Padovani et al. (2013)
Enzyme production	Use of OMWW as ingredient in culture media for three yeast species	OMWW can be used as a valuable ingredient in media formulation for some lipase-producing yeasts. The fed batch strategy increased lipase production and favored waste degradation	Brozzoli et al. (2009)
Enzyme production	Use of OMWW as ingredient in culture media for three yeast species	OMWW can be used as a valuable ingredient in media formulation for some lipase-producing yeasts. The fed batch strategy increased lipase production and favored waste degradation	Brozzoli et al. (2009)
Ethanol production	Phenols removal by *Pleurotus sajor-caju* and fermentation by *S. cerevisiae*	Maximum ethanol production of 14.2 g/L after 48 h using 50% diluted OMWW	Massadeh and Modallal (2008)
	Batch bioreactor with OMWW-glucose enriched media	The maximum ethanol was 52 g/L from initial reducing sugars concentration at 115 g/L	Sarris et al. (2013)
Brick production	Tap water is partially replaced by OMWW	The final product is a brick similar to the conventional ones, but energy savings due to the organic material of OMWW are found in the brick oven	de la Casa et al. (2009)
Production of purified extracts with antioxidant potential	Adsorption of OMWW onto an amphoteric polymer resin was used to produce a purified olive extract rich in phenolic and oleosidic compounds	The purified extract obtained from OMWW can be used as preservative in the food or pharmaceutical industry with higher capacities compared to the raw extract	He et al. (2012)