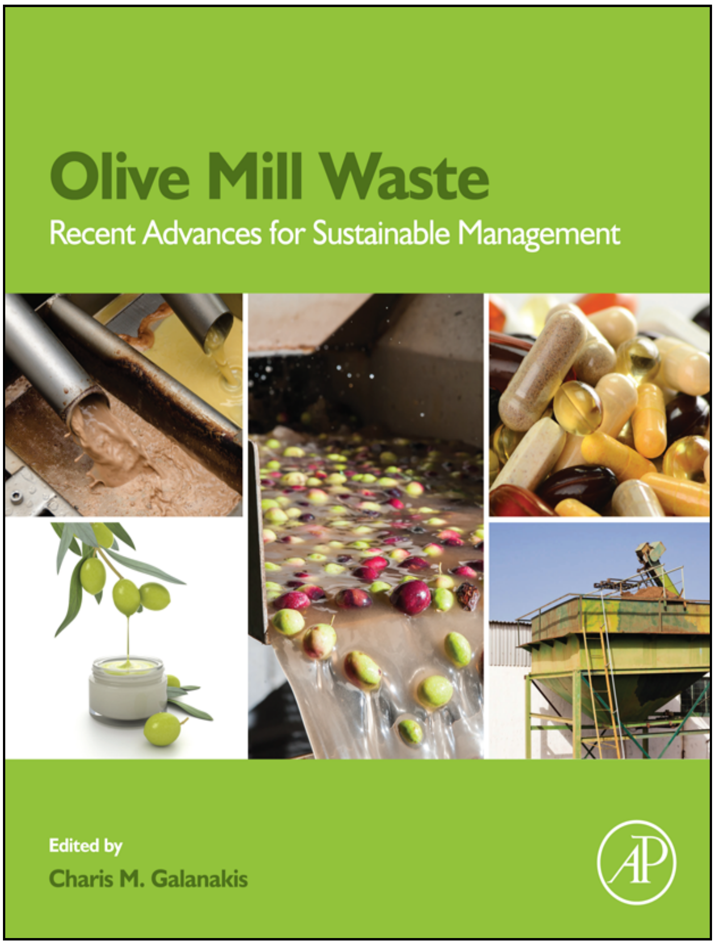

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CHAPTER

THE BIOREFINERY CONCEPT FOR THE INDUSTRIAL VALORIZATION OF RESIDUES FROM OLIVE OIL INDUSTRY

3

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3.1 INTRODUCTION

Nowadays, biorefineries include a wide range of technologies to separate main biomass components (carbohydrates, lignin, protein, etc.) and convert them into biofuels and chemicals. This approach has been applied to several biomasses and, currently, a broad spectrum of different large scale biorefineries, using a single feedstock, are under development (EBTP, 2016). On the other hand, the use of mixed biomass feedstocks in a single facility allows enlarging the view to a multi-feedstock biorefinery concept, wherein several materials are converted into a series of added-value products. In this context, agroindustrial and agrofood wastes, due to their high diversity of biomass derived products, offer a high potential of feedstocks to be processed in such a multifeedstock biorefinery plant.

This approach would be consistent with the development of small scale biorefineries better adapted to the rural areas where the wastes are generated, in contrast to the above mentioned large scale biorefineries that require high capital costs and face barriers for sustainable biomass supply and distribution. Conversely, small-scale biorefineries will require a significantly lower CAPEX, and solve several challenges facing their larger competitors. Nevertheless, despite their advantages, numerous technological and strategic challenges hamper commercial development. One of them is the inherent characteristic of heterogeneous biomasses that require complex technological transformation processes. A novel integrated self-sustainable biorefinery would be capable of transforming feedstocks by means of different process units and unit operations to produce a vast array of biomaterials and bioproducts, while maximizing the resources and energy efficiency.

Among main agroindustries worldwide, olive oil production is an economically important industry, especially in the Mediterranean countries. According to recent estimations from FAOSTAT (2015), close to 10.31 Mha of olive crop were cultivated in 2013 worldwide, with close to 50% corresponding to cultivation in nine countries of the EU, leaded by Spain (24.2%), Italy (11.1%), and Greece (9.0%). Total olive fruit production in the EU accounted for 13.24 Mt, the major producer being Spain with

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7.87 Mt, close to 60% of total EU yield. Regarding olive oil production in 2013, 1.11 Mt oil were produced in Spain, which accounted for close to 57 % of total EU yield (1.96 Mt).

Although olive tree is cultivated as a source of olives and olive oil, several by-products are generated from the cleaning operations of olive trees and the different steps of the olive processing to obtain olive oil. A detailed description of these residues, which can be in principle classified into the categories of low/medium-moisture (olive tree biomass residues, olive stones, and pomaces) and high-moisture residues (wastewaters) is given below. This chapter examines the utilization of the residues produced from start to finish in olive oil industry within an integrated biorefinery to obtain value-added products, such as antioxidants, biofuels, energy, etc. The technological processes to convert the solid and wet residues generated into different by-products are described in detail.

3.2 BIOMASS RESIDUES FROM OLIVE CROP AND OLIVE-OIL INDUSTRY

From olive tree cultivation and olive oil industry, a number of by-products are generated together with olive oil, that is, biomass residues from olive tree pruning operations (OTP), olive leaves, olive stones and pomace residues from olive oil extraction, and olive mill wastewaters (OMWW), which refers to all wastewater streams generated in washing steps and in the different stages of oil production (Fig. 3.1).

Tree pruning is an essential operation performed every two days after the fruit harvesting by cutting less productive branches for tree regeneration, thus improving fruit production. OTP includes a mixture of leaves, thin branches and wood, in variable proportions depending on culture conditions, tree age, and/or local pruning practice. OTP biomass contains a significant amount of cellulose, hemicelluloses, and lignin, 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, but as average carbohydrates may account from 46.1% to 61.6% (dwb) (Table 3.1). Extractives found in OTP, range from 14.1% to 31.4% (dwb), while an important part of them consists of nonstructural glucans. This composition allows considering OTP as an important energy and chemicals source that can be processed in a multiproduct industry.

Olive leaves come from the cleaning, and wastewater originate from the washing of the olives. Olive leaves are usually removed using a blower machine. They show a quite low carbohydrate content (close to 10%), but a high extractives content of around 40% (Table 3.1), that could be a source of polyphenols (Aydinoglu and Sargin, 2013) or other antioxidant compounds.

Regarding the process to extract oil from olives previously crushed, it can follow the two-phase and three-phase separation modes. In the three-phase system water is added to the paste, which is next separated into a solid (olive pomace), an oily phase and a water phase. The two-step mode is essentially the same process, but without adding water to the initial olive mash. In both separation systems, the resultant olive oil is washed to remove impurities and the wash water separated by centrifugation generating the "olive oil washing wastewater", which is normally processed together with other residual water streams generated. Olive pomace is the main residue after both types of separation systems and it is constituted by crushed olive stones, process water and all material coming from the olive fruits except the olive oil. It represents the main residue of the olive oil extraction process by weight and differs in composition depending on the production process (two- or three-phase). An example of a two-phase pomace composition is included in Table 3.1, showing a high content of extractives around 48% (dwb) and a carbohydrate content close to 20% (dwb). This residue contains some residual olive oil and also

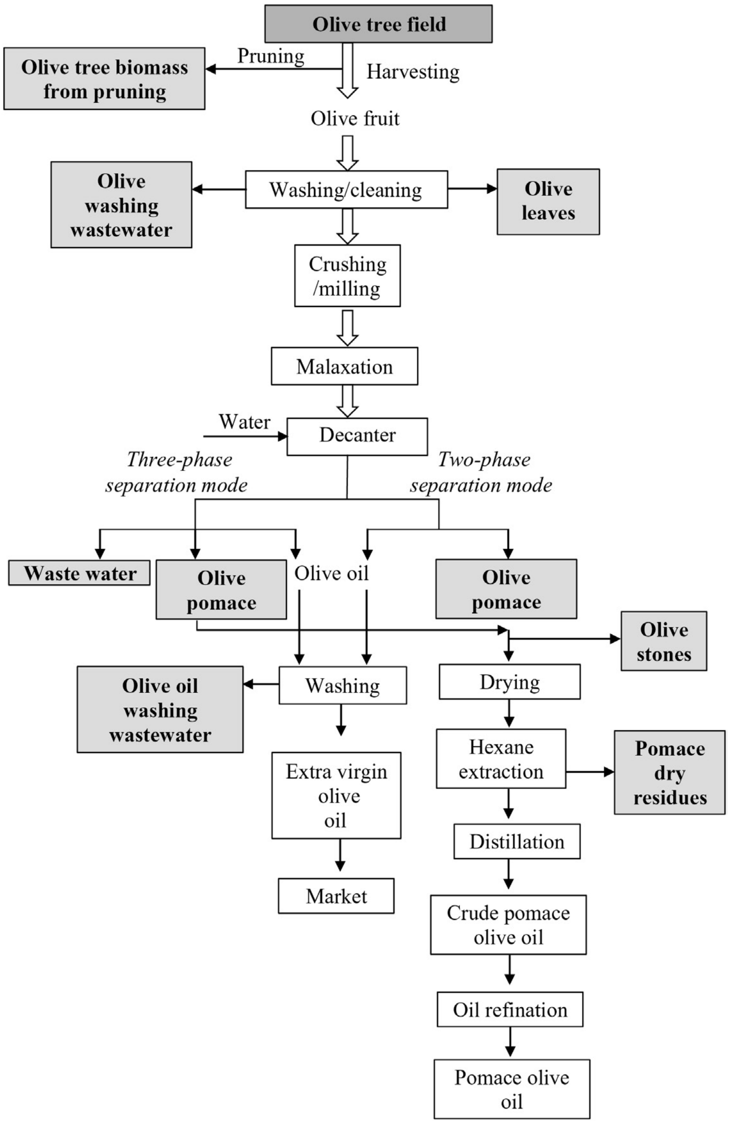

FIGURE 3.1 Simplified Process for Olive Oil Production

Reprinted from Romero-García, J.M., Niño, L., Martínez-Patiño, C., Álvarez, C., Castro, E., Negro, M.J., 2014. Biorefinery based on olive biomass. State of the art and future trends, Bioresour. Technol. 159, 421–432. Copyright (2016), with permission from Elsevier.

some polyphenols. It can be further processed to extract the oil and obtain the so-called "pomace oil" and a final solid residue is generated called " extracted dry pomace residue," which can be integrated in the biorefinery for energy production or other applications. It is characterized by a similar composition in dry weight basis than olive pomace; high extractives content that can overcome 30% (dwb) and carbohydrates accounting from 20% to 30% (dwb) (Table 3.1).

Table 3.1 Reported Chemical Composition Values of Main Lignocellulosic Biomass Residues From Olive Crop and Olive-Oil Industry (When Available, Value Range is Given)

	Main Component (wt.% dry basis)					
Raw Material	Cellulose	Hemicellulose	Lignin	Ash	Extractives	References
Olive tree pruning	26.1–36.6	16.4–25.0	16.6–27.7	3.3	14.1–31.4	Romero-García et al. (2014); Ballesteros et al. (2011)
Olive stones	28.1–40.4	18.5–32.2	25.3–27.2	0.7	19.2	Lama-Muñoz et al. (2014); Cuevas et al. (2015b); Ballesteros et al. (2001)
Olive oil pomace	12.8	7.5	28.4	2.2	47.8	Ballesteros et al. (2001)
Extracted dry pomace	11.1–15.8	9.0–15.6	24.2–40.4	7.7–13.9	20.0–33.7	Unpublished data from the authors
Olive leaves	5.7	3.8	39.6		36.5	García-Maraver et al. (2013)

Olive stones can be recovered from the olive pomace after oil separation. Cellulose, hemicellulose, and lignin content from olive stone are in the range 28.1–40.4%; 18.5–32.2%; and 25.3–27.2% (dwb), respectively. Other components are proteins and phenolic compounds, such as tyrosol, hydroxytyrosol, oleuropein, and others, which make this residue an important by-product source of valuable compounds (Rodríguez et al., 2008).

Regarding olive mill wastewater (OMWW), several water streams are generated at three different points: during the cleaning of the olive fruits; from the horizontal centrifuge (decanter) during the three-phase separation step; and during the washing process from the secondary centrifuge of virgin olive oil. Chemical composition of OMWW is very variable depending of many factors, such as the system used for oil extraction, the variety of olive trees, and the degree of maturity and fruit storage time. In general, apart from water (83–92%), the average content of organic matter (polysaccharides, proteins, organic acids, and polyphenols) is in the range of 4–16% and also contains 0.4–2.5% of salts (Dermeche et al., 2013). The high chemical organic demand (COD) and the high concentrations of polyphenols, up to 12 g/L, (Daâssi et al., 2013) makes the treatment of OMWW difficult and costly.

3.3 REVALORIZATION TECHNOLOGIES TO CONVERT OLIVE RESIDUES INTO BY-PRODUCTS AND BIOFUELS

As mentioned earlier, residues produced in olive oil industry can be categorized as either low/medium- or high-moisture materials. The conversion of low/medium biomasses (in general, lignocellulose) can be directed to heat and power production by thermochemical processes, or be upgraded into added-value products by biochemical/chemical routes (Fig. 3.2). Biochemical processes generally involve fractionation and hydrolysis of polymers (carbohydrates and lignin) into oligosaccharides or

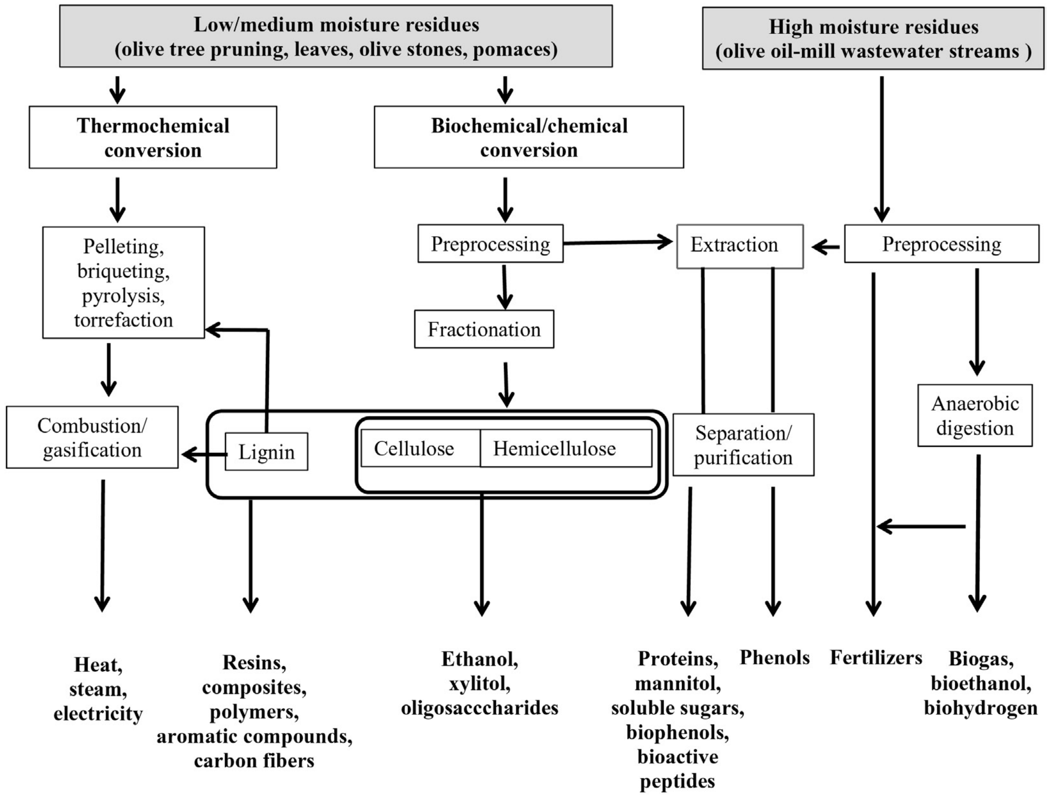

FIGURE 3.2 Valorization Scheme for the Different Residues Generated in the Olive Oil Industry

monomers that can further be converted into a wide variety of products. The conversion of wet biomass (wastewater streams) generally involves biofertilization and/or anaerobic digestion.

3.3.1 PROCESSES FOR LOW/MEDIUM-MOISTURE RESIDUES

3.3.1.1 Direct Conversion to Heat, Steam, and Electricity

The conversion of wastes generated from the olive mill industry into thermal and electrical power is an interesting option in the case of low-moisture residues, as the olive stones or the extracted dry pomace residue produced in the olive pomace oil industry (Galanakis, 2011). Currently, the use of olive stones as a biofuel for thermal applications is quite widespread in olive oil productive regions, especially in agroindustries, livestock farms, greenhouses, and domestic heating systems. Extracted dry pomace residue is used as a fuel in some local industries too, like the ceramic industry. However, this residue is less used than olive stones in domestic heating systems because of the higher generation of pollutant emissions. In the pomace olive oil extraction industry, extracted dry pomace residue is usually used to dry the wet olive pomace whereas olive stones are often employed in the industrial boilers to obtain process steam because it causes less corrosion problems. In recent years, the use of olive stones as a fuel in olive mills boilers instead of extracted dry pomace residue has been progressively increased.

Indeed, the practice of removing most of the olive stone contained in the wet olive mill pomace has been becoming more usual. Consequently, the extracted dry pomace residue composition resulted poorer in olive stones leading to worse combustion properties.

On the other hand, olive stones and extracted dry pomace residue are also currently applied for the generation of electrical energy or cogeneration (simultaneous steam and electricity production) through combustion. OTP can be also used in plants of electric production, in a lesser extent. Concerning medium-moisture wastes, such as the two-phase olive mill pomace, there are also some experiences about its energetic use, but it is more difficult due to its moisture content (Alburquerque et al., 2004).

Besides combustion, other thermochemical technologies have been investigated in recent years for this kind of residues, such as pyrolysis or gasification (Christoforou and Fokaides, 2016). Pyrolysis implies the biomass heating without air. Depending on the temperature and the rate of heating different products can be obtained as solid, liquids, or gaseous biofuels. Concerning gasification, it refers to the biomass conversion into syngas by partial oxidation at temperatures generally in the range 800–900°C. This technology has been emerging as a promising way for the production of energy from olive tree and olive mill residues. For example, Campoy et al. (2014) found that extracted dry pomace residue is a suitable fuel in a pilot fluidized bed gasifier, while Vera et al. (2014) investigated the use of olive stones and OTP in a downdraft gasifier.

Chemical composition is an important factor that affects the performance of the thermochemical processes. The main structural components of the different residues coming from the olive cultivation and the olive mill industry are generally cellulose, hemicellulose, and lignin. The thermal degradation of these components is different. In thermogravimetric analysis (TGA) with olive oil pomace, Ozveren and Ozdogan (2013) reported hemicellulose, cellulose, and lignin degradation temperature ranges of 150–295°C, 300–400°C, and 150–480°C, respectively. Apart from the moisture content and chemical composition, other important parameters involved in the process effectiveness are the reaction temperature, the particle size, and the heating rate (Christoforou and Fokaides, 2016).

Logistic challenges should be overcome for the energetic valorization of the solid olive derived residues, especially in the case of the wastes generated from the olive tree cultivation (OTP) because of this low density, dispersion, and the short period of production. Preparation methods as pelleting, briquetting, and pyrolysis could be applied to increase the energy density (Hanandeh, 2015). Concerning medium-moisture wastes, such as the two-phase olive mill pomace, some treatments as the torrefaction combined with briquetting have been investigated to assess the viability of the energy production from these residues (Benavente and Fullana, 2015). Besides that, in order to explore the feasibility of the potential use of the different residues derived from the olive oil industry as solid biofuels, economic, and sustainability studies should be performed (Lanfranchi et al., 2016). In this way, thermochemical biorefineries based on multiproduction (fuels, chemical, and services) could be a promising alternative in order to diminish the risk of investment (Haro et al., 2014).

3.3.1.2 Biochemical/Chemical Conversion Routes

Apart from the revalorization of low/medium biomasses by thermochemical processes, a variety of valuable products can be obtained by biochemical and chemical conversion technologies based on lignocellulosic nature of these residues, as explained later.

3.3.1.2.1 Preprocessing Strategies

Lignocellulosic-type residues from olive crop and oil mill, apart from the structural carbohydrates (hemicellulose and cellulose) and lignin, contains other nonstructural minority compounds that could be extracted before the process conversion of structural components, contributing to the economic viability of a possible biorefinery based on these materials. This is the case of phenolic compounds with antioxidant properties that have a great interest for the food industry as substitutes of synthetic antioxidants. Therefore, a preprocessing strategy, such as an extraction step, could be applied to the residues in order to recover these bioactive components, while improving the yields of the biochemical conversion route of structural components. For example, with OTP, it has been proved that a water extraction step in autoclave at 120°C during 60 min improves the yields of structural sugars that can be obtained in further steps (Ballesteros et al., 2011; Negro et al., 2014). The liquid obtained from this aqueous extraction contains soluble sugars, mannitol, and phenolic compounds with antioxidant capacity, whose removal has also the positive effect of increasing the fermentability of hemicelulosic hydrolysates obtained in subsequent steps (Martínez-Patino et al., 2015). This strategy has also been applied to olive stones (Lama-Muñoz et al., 2014), aimed at the optimization of antioxidant recovery by water extraction at 130°C during 90 min, followed by a dilute acid hydrolysis step for the recovery of fermentable sugars from structural carbohydrates. Protein extraction through a continuous water flow using a high-pressure system (Kazan et al., 2015) has also been proposed as a previous step of a biochemical process to obtain sugars from olive pomace. Another thermal preprocessing method has been applied to improve the recovery of bioactive compounds from olive pomace (Lama-Muñoz et al., 2011). To recover different products from olive cake, such as antioxidant compounds (Rubio-Senent et al., 2012), short-chain oligosaccharides, phenolic glycosides, secoiridoids (Fernández-Bolaños et al., 2014), and pectins (Rubio-Senent et al., 2015), steam-explosion treatment at mild temperatures (150–170°C) has been applied. Bioactive peptides extraction from olive seeds by enzymatic hydrolysis with different proteases followed by ultrafiltration fractionation has also been recently investigated (Esteve et al., 2015).

Olive leaves have been widely studied for the production of different bioactive components with therapeutic and functional applications, including phenolic compounds, secoiridoids, and flavonoids. Besides conventional extraction methods as maceration and Soxhlet extraction, other promising extraction techniques have being developed recently, such as pressurized liquid extraction, subcritical or supercritical extraction, microwave, ultrasound, etc. Different solvents can be used for this purpose apart from water, as short-chain alcohols, ethyl acetate, hexane, and acidic steam (Rahmanian et al., 2015).

3.3.1.2.2 Carbohydrate Conversion

A key issue for the biorefineries is the cost-effective conversion of cellulose and hemicellulose contained in lignocellulose biomass into fermentable sugars, as a first step in the production of high-added value molecules. Particularly for fuel ethanol production from lignocellulose biomass, process technology generally includes a pretreatment step followed by enzymatic hydrolysis and the subsequent fermentation to ethanol of the sugars released, by fermenting microorganisms. Pretreatment is an important first step for efficient carbohydrates (cellulose and hemicellulose) conversion processes, and it is required to alter the structure of lignocellulose biomass making polysaccharides more accessible to the enzymes that hydrolyse them into fermentable sugars. Moreover, an ideal pretreatment should result in a complete fractionation of the biomass into its key constituents, cellulose, hemicelluloses, and lignin, which will facilitate a subsequent conversion of main components into fuels and high value products at high yield. Many pretreatment methods have been evaluated for ethanol production (Alvira et al., 2010). Specifically for OTP biomass, pretreatments tested include mechanical, chemical methods, and various combinations thereof (Romero-García et al., 2014). After pretreatment, lignocellulose biomass is submitted to enzymatic hydrolysis (EH) process, in which the polysaccharides contained in the pretreated lignocellulose biomass are depolymerized. Due to the complex structure of lignocellulose biomass, enzymatic hydrolysis requires the combined action of different hydrolytic enzymes (cellulases, hemicellulases, esterases, arabinofurosidases, etc.) that must be used in an appropriate proportion to achieve a complete hydrolysis.

Steam explosion is one the most suitable method for pretreatment of herbaceous and hardwood biomass in terms of low reaction time, high solid loading, and minimum use of chemicals. It is a physicochemical pretreatment that combines mechanical forces with the chemical effects of acetyl groups easily released from hemicellulose (autohydrolysis). In this pretreatment, biomass is rapidly heated by high pressure steam for a period of time and then the pressure is suddenly reduced, which makes the material undergo an explosive decompression (Talebnia et al., 2010). Temperatures in the range of 190–240°C for 5 min have been tested in olive tree wood (Cara et al., 2006) and OTP (Cara et al., 2008a). However, relatively low enzymatic hydrolysis yields (about 40% and 60% for wood and OTP, respectively) after steam explosion pretreatment were found. It has been reported that an alkaline peroxide delignification step after steam explosion pretreatment of olive tree wood can improve enzymatic hydrolysis yields up to about 61%. (Cara et al., 2006). Also, the addition of sulfuric acid during steam explosion pretreatment of OTP was found to improve the rate and extension of hemicellulose solubilization and the enzymatic hydrolysis yield, reaching a maximum value of about 70% of theoretical. On the other hand, extractive removal previous to steam explosion has been shown to result in 20% more total sugars recovery in comparison to OTP biomass without water extraction stage (Ballesteros et al., 2011).

Liquid hot water pretreatment has also been investigated on OTP for sugar production (Cara et al., 2007; Requejo et al., 2012). In liquid hot water the biomass is pretreated with pressurized water at high temperature. Temperature and time revealed the most significant effect in the hemicellulosic-sugars recovery and the yield of subsequent enzymatic hydrolysis of pretreated OTP biomass. This pretreatment produces high hemicellulose solubilization releasing oligosaccharides, which remain soluble in the liquid fraction. However, the allowable solid load is much less than in other hydrothermal pretreatments, that is, steam explosion, which is frequently greater than 40%.

Inorganic acids, such as sulfuric and phosphoric acid have been explored for pretreatment of OTP (Cara et al., 2008b; Díaz-Villanueva et al., 2012; Martínez-Patino et al., 2015). Diluted acid pretreatment results in almost 84% of the hemicellulosic-sugars recovery, and a yield of glucose after enzymatic hydrolysis up to 66% at optimal conditions (180°C, 1% H_2SO_4).

Other chemical agents, such as inorganic salts ($FeCl_3$) have been tested to pretreat olive tree biomass (López-Linares et al., 2013). Results show improved results in comparison to untreated material, reaching a maximum glucose yield of 39 g glucose/100 g glucose in untreated olive tree biomass, at 160°C and 0.275M $FeCl_3$ for 30 min. This value corresponded to an efficiency value of 88.7% of theoretical.

All these pretreatments mentioned earlier have in common the production of a pretreated material in which soluble fraction is mainly composed of the hemicellulose sugars, while cellulose and lignin remain in insoluble solid fraction, while technologies described below aim, in general, at solubilizing lignin fraction from the material, the cellulose, and hemicellulose components remaining in the pretreated solid.

Organosolv pretreatment, which uses organic or aqueous solvents (ethanol, methanol, ethylene glycol, acetone, glycerol, etc.) to extract lignin, has been tested on OTP by Díaz et al. (2011). They found pretreatment severity (in terms of ethanol content and temperature) was positively correlated with delignification (up to 64% at 210°C for 60 min and 66% w/w aqueous ethanol). On the contrary, xylan hydrolysis was promoted by low severity conditions in term of ethanol content, reaching a maximum of 92%. Organosolvent pretreatment of OTP was also addressed by Toledano et al. (2011), who concluded that reaction temperature and ethanol concentration were the most important variables, while reaction time was less significant. In a further step in the research work on organosolv pretreatment of OTP, the authors (Toledano et al., 2013) have proven that it results in a highly digestible cellulose substrate (87.2% EH yield), and that lignin can be successfully recovered after pretreatment.

Apart from hydrothermal and chemical pretreatment technologies, thermo-mechanical processes, such as extrusion have been applied to OTP and other olive derived residues. Extrusion is a process of simultaneous heating, mixing, and shearing that results in physical and chemical changes along the extruder barrel (Duque et al., 2013). Recently, fractionation of OTP by one-step alkaline extrusion has been investigated by Negro et al. (2015). The pretreatment resulted in a cellulose and hemicellulose enriched-solid, which contained 92–100% and 94% of the glucan and xylan, respectively, of untreated OTP. A high value of hemicellulose-sugars recovery in the pretreated solid as that obtained in alkaline extrusion of OTP, is interesting to increase the total fermentable sugars production by enzymatic hydrolysis.

The generation of fermentable sugars from olive stones has also been investigated by using different pretreatments: steam explosion (Felizón et al., 2000; Ballesteros et al., 2001); diluted acid (Saleh et al., 2014; Lama-Muñoz et al., 2014), liquid hot water (Cuevas et al., 2009), and organosolv (Cuevas et al., 2015a). Diluted acid and liquid hot water pretreatments were reported to be suitable technologies for hemicellulose solubilization from olive stones at high temperatures. Oligosaccharides were the main carbohydrates obtained in liquid hot water prehydrolysates (16.9 kg per 100 kg of dry olives stones at 210°C), while diluted acid pretreatment provides the maximum xylose recovery (21 kg per 100 kg of dry olive stones) at 200°C. The ethanol-based organosolv pretreatment with addition of sulphuric acid achieved high delignification (>88%) and provided a solid with cellulose content around 83.3% (dwb) (Cuevas et al., 2015a).

The next step in the conversion of lignocellulose biomass to ethanol is the fermentation of sugars, either from enzymatic hydrolysis of cellulose (C6 sugars) or hemicellulose (C6 and C5 sugars), which is commonly carried out by using yeasts. For C6 fermentation, strains of *Saccharomyces* are generally used, while for C5 sugars microorganisms that are able to ferment them, such as *Pachysolen tannophilus, Candida shehatae, and Pichia stipitis* are utilized.

Regarding the process configuration used to convert OTP sugars from cellulose and hemicellulose fractions into ethanol by enzymatic hydrolysis and fermentation, there are several options (Fig. 3.3); a separated enzymatic hydrolysis and fermentation (SHF) process, a simultaneous saccharification and fermentation (SSF) process and a variation of the last one called liquefaction or presaccharification plus SSF (PSSF). In SHF, in which both step are carried out in different reactors, hydrolysis of the pretreated substrate is carried out at optima enzyme temperature and pH (namely 50°C and pH around 5) and once completed; the resulting sugars are fermented at optima pH and temperature for the fermenting yeast (30–37°C). In SSF, a compromise between the optimal temperature for the hydrolytic enzymes and the yeast is needed (37°C) and the process is carried out in a single step. The SSF scheme minimizes the inhibition by end-product on the enzyme activity, resulting in improved yields, shorter residence time, and allows a reduction in the enzymes doses, contributing to decrease the final process cost. In PSSF, the substrate is incubated with the enzymes at 50°C during a relatively short period of time (8–24 h) and next the media is inoculated with the microorganism to proceed with the SSF.

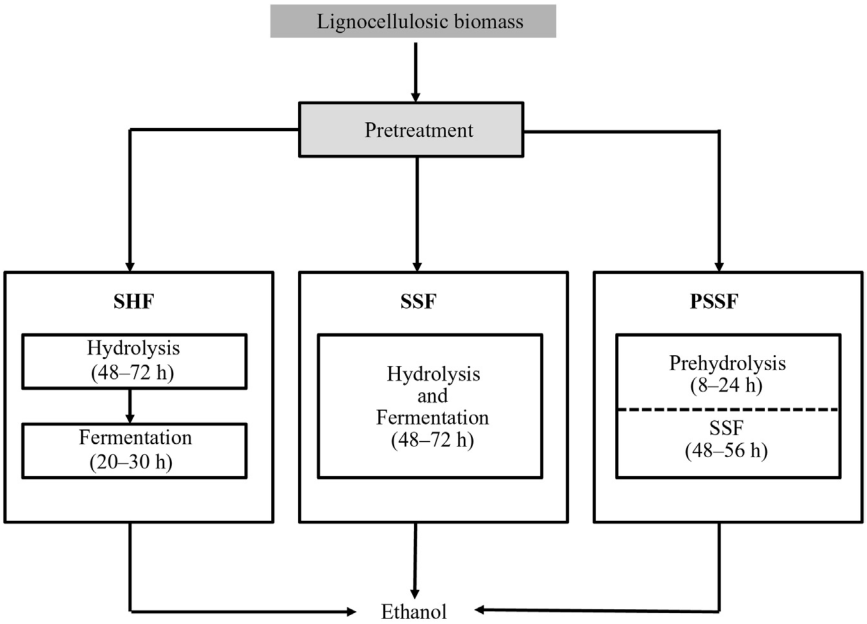

FIGURE 3.3 Different Process Configurations for Lignocellulosic Biomass Conversion to Ethanol

SHF, separated hydrolysis and fermentation; *SSF*, simultaneous saccharification and fermentation, and *PSSF*, prehydrolysis and simultaneous saccharification and fermentation. In *brackets* standard time for each process step.

Manzanares et al. (2011) have reported on the effect of pretreated (liquid hot water and diluted-acid) OTP at different substrate loads on ethanol production in above-mentioned process configurations; SHF, SSF, and PSSF. When comparing both pretreatments, better results were found with liquid hot water-pretreated OTP, reaching 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 the SSF process strategy. In both cases, increasing substrate loading led to a raise in ethanol concentration, which peaked in at about 3.7% (v/v) in experiments performed in liquid hot water-pretreated olive pruning at 23% (w/w) substrate loading by SHF or PSSF. Toledano et al. (2013) performed SHF trials in organosolv pretreated OTP and found similar ethanol concentrations around 36 g/L.

In general, prior to the fermentation step a detoxification treatment of the hydrolysates is required to reduce the inhibitory effect of compounds released from acid pretreated-OTP (Díaz et al., 2009; Negro et al., 2014). Díaz-Villanueva et al. (2012) have studied the ethanolic fermentation of liquid fraction from pretreated olive tree biomass after detoxification (overliming) utilizing *P. stipitis and P. tannophilus,* and compared the performance of both yeasts. The best results were obtained with *P. tannophilus* with values as high as 0.44 g ethanol/g sugar, and conditioning by overliming was proven to improve fermentability of hydrolysates. The fermentation with *P. tannophilus* of sulfuric acid hydrolysed-OTP has also been successfully carried out by Romero et al. (2007), too, who reported maximum ethanol yield of 0.38 g/g glucose. Ethanol production yield from OTP has been assessed in hydrolysates from steam explosion impregnated with phosphoric acid pretreatment and enzymatic hydrolysis, using *S. cerevisiae* and *S. stipitis* (Negro et al., 2014). Again, a detoxification treatment was required before fermentation to alleviate the inhibitory effect of compounds present in the hydrolysate. High ethanol yields about 80% of theoretical were attained in SSF experiments at 15% (w/w) solid loading. Recently, Martínez-Patino et al. (2015) have used an acetate-tolerant ethanologenic strain of *E. coli* (MS04) generated by metabolic engineering (Fernández-Sandoval et al., 2012), to ferment all sugars present in the prehydrolysates from water-extracted OTP pretreated at 170°C and 0.5% phosphoric acid concentration. A total ethanol yield of 13.2 g of ethanol/100 g of original OTP was obtained (16.3 g of ethanol/100 g of extracted OTP), both from liquid and solid fraction after enzymatic hydrolysis.

Despite the fact that most of the research work on ethanol production has been focused on OTP residue, other olive mill-wastes have been studied, too. For instance, olive cake (the solid residue from the traditional oil extraction system) has been explored as substrate for ethanol production by a recombinant *E. coli* strain. Soluble sugars obtained after diluted acid pretreatment (18.1 g/L) and detoxification steps were fermented by *E.coli* FRB5 strain to produce ethanol at a concentration of 8.1 g/L (El Asli and Qatibi, 2009). Besides, the pomace and fragmented olive stones have been tested for ethanol production by the SSF process using a fed-batch strategy. Experiments with fed-batch pretreated olive stones provided SSF yields significantly lower than those obtained at standard SSF procedure (Ballesteros et al., 2001). Recently, Cuevas et al. (2015a) have reported an overall ethanol yield up to 13.1 kg ethanol per 100 kg of olive stones (ethanol concentration 47 g/L) using a thermotolerant yeast (*S. cerevisiae* IR2-9a), after ethanol-based organosolv pretreatment of stones with addition of sulfuric acid.

In addition to ethanol, other compounds can be obtained from sugars contained in olive-mill residues following alternative conversion routes. Particularly from xylose, which is the main pentose in hemicelluloses, xylitol can be produced. Xylitol is a value-added product by its sweetening properties, similar to that of sucrose but with 40% less calories, universally used as sweetener for diabetics. Currently, it is produced in a complex, labor- and energy-intensive process based on the catalytic hydrogenation of xylose that is obtained from hydrolysis of woody hemicellulose or from extracted corn cobs, which are the remains of corn ears after the kernels have been extracted (IEA, 2015). But xylitol may be also produced by biological conversion of xylose fermentation present in hemicellulosic hydrolysates with yeast species, such as *Candida, Pichia, and Pachysolen.*

An example of this application is the study of xylitol production from the liquid fraction obtained after diluted sulfuric acid pretreatment of olive stones carried out by Saleh et al. (2014). The fermentation of the prehydrolysates obtained after optimal pretreatment conditions (195°C, 5 min, and 0.025 M sulfuric acid) and after a detoxification step, 9.2 g of xylitol per 100 g of olive stones, was attained using *Pachysolen tannophiplus*. Xylitol yields (0.44 g xylitol/g xylose) were similar to those obtained by García et al. (2011) in the fermentation with *Candida tropicalis* of acid hydrolysates from olive-pruning biomass, when the overall xylitol reported was 53 g xylitol per kg of dry olive debris.

The form in which hemicellulose-derived sugars are found in prehydrolysates from lignocellulose biomass pretreatment is highly dependent on the severity of the pretreatment and the nature of feedstock. Mild pretreatment conditions in terms of pH and temperature may lead to incomplete hydrolysis of hemicellulosic polymers and carbohydrates in form of oligosaccharides, which can be found in prehydrolysates instead of, or together with, monosaccharides. These molecules could be used as prebiotic compounds, of great interest for the food, cosmetic, and pharmaceutical industries. According to Mussatto and Mancilha (2007), oligosaccharides are defined as polymers of monosaccharides with variable degree of polymerization (DP) between 2 and 10. These compounds are considered prebiotics since they are not digestible in the stomach and thus can reach the large intestine without any change and promote the growth and/or activity bacterial associated with health (Gibson et al., 2004).

Oligosaccharides from xylan hydrolysis (xylooligosaccharides) have been found by Reis et al. (2003) in prehydrolysate from partial acid hydrolysis of olive pulp and olive seed hull. Structural characterization of these acidic xylooligosaccharides showed differences between the residues; while those from olive pulp were residues mainly substituted with 4-*O*-methyl glucuronic acid, olive seed hull contained glucuronic acid residues. Recently, Cuevas et al. (2015b) have reported on oligosaccharides production from olive stones pretreated by autohydrolysis at 190°C and 5 min, with production yield of 147 g oligosaccharides/kg olive stones. Lama-Muñoz et al. (2012) further identified some bioactive phenol glucosides and poly- and oligosaccharides from thermally treated olive oil by-products.

Oligosccharides production from OTP has been explored by Cara et al. (2012). They found oligosaccharides in prehydrolysate after autohydrolysis pretreatment at 180°C for 10 min, mainly consisting of gluco-oligosaccharides and xylooligosaccharides, in a total concentration of 37.5 g/L. Further treatment of the hydrolysate by preparative gel filtration chromatography and purification allowed separating a range of oligosaccharides fractions with an average degree of polymerization (DP) from 3 to 25, with gluco-oligosaccharides and xylooligosaccharides as the predominant oligosaccharides. Mateo et al. (2013) also studying oligosaccharides production from OTP biomass by liquid hot water pretreatment, proved a great effect of process conditions in oligosaccharides yield. The most suitable pretreatment conditions for the maximum concentration of oligosaccharides as well as monosaccharides corresponded to experiments carried out at 200°C and 0 min, either with H_2SO_4 at 0.025 M or with ultrapure water.

The production of valuable coproducts, such as xylitol or oligosaccharides coupled with the ethanol production process from olive mill-residues would greatly contribute to improve second generation ethanol economically feasibility, while fulfilling the characteristic features of the biorefinery concept.

3.3.1.2.3 Lignin Conversion

In most current applications of biochemical and/or chemical based technologies to lignocellulosic materials, lignin component is contained in the final residue after biomass fractionation and carbohydrate hydrolysis, as a complex and disperse compound (Vishtal and Kraslawski, 2011). A major part of this lignin-rich residue is incinerated to produce process steam and energy, and only a minor part is derived to the production of other valuable products. However, lignin offers a significant opportunity for enhancing the operation of a lignocellulosic biorefinery by the production of more valuable chemicals, such as resins, composites and polymers, aromatic compounds, or carbon fibers. This is viewed as a medium to a long term opportunity depending on the quality and functionality of the lignin that can be obtained (IEA, 2012). The challenge to use lignin as feedstock material is its complex chemical structure, which is highly influenced by its origin and the method of fractionation/extraction and further processing of the lignocellulose biomass. Thus, it is important to know the particular physicochemical characteristics of the lignin-rich residue to direct process decision making in relation to lignin upgrading. Regarding biomass residues from olive crop and olive-oil industry, residual solid materials from the conversion of OTP biomass to bioethanol at laboratory scale have been characterized for their lignin and carbohydrate content, heating value, ash and inorganic elements in our laboratories. Regardless of whether the pretreated biomass is processed by SSF or SHF, process residues are mainly composed of lignin (68–74%), unrecovered sugars (6.8–9%), unrecovered enzymes, and ash (6%). The high proportion of lignin in the residue is in the basis of the high heating value of 22.4 MJ/kg HHV (dwb) found, which makes the residue a suitable green energy source. However, other options must be explored to revalorize this lignin-rich residue by conversion into valuable products. Following this pathway, Santos et al. (2015) have characterized the residue from SSF process on OTP by FTIR and 2D-NMR, as a prior step in the development of added-value products. Results show lignin has a strong predominance of S over G units, as well as high content of β-*O*-4′aryl ether linkages, followed by resinols and phenylcoumarans. According to the authors, the high content of native aryl ether linkages would result in a high molecular mass lignin, which could be interesting for dispersants and composites production.

Another way to address lignin revalorization in lignocellulose biomass feedstocks is to extract or isolate lignin before the material is submitted to the conversion process. Several methodologies have been successfully applied to lignocellulosic materials rendering different types of lignin, depending on the separation process (alkali, organosolv, ionic liquids, microwave, etc.) (Vishtal and Kraslawski, 2011; Manara et al., 2014). Particularly for olive derived residues, organosolvent pretreatment using a mixture of ethanol and water has been applied to OTP 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 (200ºC, 70% ethanol and 90 min.) allowed for the production of higher quality lignin, high acid insoluble lignin content (71.9%) and low contamination (sugars 2.94% and ash 0.39%). Interestingly, lignin seemed to be highly reactive due to its high functionality, which is a promising feature for further applications in the formulation of inks, varnishes and paints (Vishtal and Kraslawski, 2011). Manara et al. (2014) have addressed the study of lignin extraction from olive kernels by different procedures in order to evaluate the effect of extraction conditions and determine lignin chemical structure. A chemical (organosolv-formic/acetic acid) and a physicochemical (water/ethanol with sulphuric acid at 150°C in microwave reactor) pretreatment process were applied and the isolated lignins characterized by FT-IR and TGA. FT-IR spectra profiles were rather similar in both pretreated substrates, indicating a comparable chemical structure of extracted lignins. Results show higher delignification yield after microwave pretreatment, while both procedures rendered high-purity lignins close to 100% purity. On the other hand, the thermal degradation behavior of the derived lignins from TGA analysis gives useful information to explore the potential of conversion to valuable compounds, such as liquid fuels or hydrogen by advanced thermochemical technologies as pyrolysis or gasification, considered of great interest in the context of a biorefinery.

3.3.2 PROCESSES FOR HIGH-MOISTURE RESIDUES

As above mentioned, the process of obtaining olive oil generates highly polluting olive mill wastewater streams (OMWW), comprising vegetation water, soft tissues of the olives and the water used in the different stages of oil production. Due to its low biodegradability and high phytotoxiticy, OMWW is one of the most environmentally concerning food processing effluents in the Mediterranean countries.

Natural evaporation in open-air lagoons, favored by the Mediterranean weather, is the most conventional method for OMWW treatment (Cegarra et al., 1996; Jarboui et al., 2008). Physicochemical treatments (flocculation, advanced oxidative methods, and electrochemical processes, such as the electrocoagulation) are also used to reduce the organic load of OMWW (Azbar et al., 2004). Biological treatments, such as activated sludge, anaerobic treatments, and membrane bioreactors, have also been used for the reduction of its organic load (Ramos-Cormenzana et al., 1996). Other alternative tested is the direct agronomic application, but its high content in phytotoxic phenolic compounds increases soil hydrophobicity and decreases water retention (Kavvadias et al., 2010).

In an integrated biorefinery approach, aimed at producing high added-value products from OMWW, a preprocessing step to extract the remaining high value antioxidants may represent an economically interesting strategy that provides the triple opportunity to obtain high-added value biomolecules, to increase biodegradability and to reduce phytotoxicity of the effluent.

3.3.2.1 Preprocessing

Most of the phenolic compounds in olives and olive oil (hydroxytyrosol, tyrosol, caffeic acid, rutin, luteolin, and flavonoids) are insoluble in oil and, thereby, remain in wastewater. The water-soluble phenolic compound fractions represent 50–72% of the total phenolic compounds in olives (Alu'datt et al., 2013). The selective recovery of these phenolic compounds in a preprocessing step can achieve both the reduction of the intrinsic wastewater environmental toxicity and the production of high added value molecules.

The main separation strategies (Galanakis, 2012) involves the use of liquid–liquid extraction (LLE) (Zafra et al., 2006; Galanakis et al., 2010b), ultrasound-assisted extraction (Japón-Luján et al., 2006; Roselló-Soto et al., 2015b; Zinoviadou et al., 2015), solvent extraction (Obied et al., 2005; Heng et al., 2015), superheated liquid extraction (Japón-Luján et al., 2006), supercritical fluid extraction (Le Floch et al., 1998), and more recently emerging technologies, such as high voltage electrical discharges and pulsed electric field (Galanakis, 2013; Rahmanian et al., 2014; Galanakis and Schieber, 2014; Roselló-Soto et al., 2015a). Although LLE provides efficient results, the necessity of using large volume of organic solvents is increasing the interest to replace LLE by solid-phase extraction (Scoma et al., 2011).

Membrane processes have also been proposed for the selective fractionation and total recovery of polyphenols, water, and organic substances from OMW (Paraskeva et al., 2007a,b; Coskun et al., 2010; De Leonardis et al., 2008; Galanakis et al., 2010a; Galanakis, 2015). Russo (2007), using a preliminary membrane filtration followed by two ultrafiltration steps (6 and 1 kDa membranes, respectively) and a final reverse osmosis treatment, obtained an enriched and purified low molecular weight polyphenols extract to be used for food, pharmaceutical or cosmetic purposes. The remaining liquid can be used as fertilizers or in the production of biogas in anaerobic reactors as detailed later.

3.3.2.2 Agricultural Uses of Extracted OMWW

The reduction of phytotoxicity of OMWW by polyphenols extraction would allow its use as a valuable fertilizer. Its agronomic application to soils is very convenient in Mediterranean countries since water is a scarce and soils usually suffer from low organic matter content. The land utilization of polyphenols-extracted OMMW represents a cheap source of irrigation water and provides soils with nutrients, mainly K and organic matter. Main inconveniences for the application of OMWW to soil are the high salinity and low pH.

Disadvantages of the application of OMWW to soil can be reduced or eliminated by composting or cocomposting with agricultural residues (e.g., olive pomace or olive tree pruning residues). The agronomic use of composting OMWW does not cause negative effects on crop productivity and produces significant increases of organic matter and organic N in soils (Martín-Olmedo et al., 1995). Cabrera et al. (2005) showed that soils treated with olive mill wastewater sludge compost, increased organic matter, and nitrogen in comparison to untreated or mineral fertilized soils. The nitrogen increase in treated soils was even higher than expected by the N added together with compost, and attributed to nonsymbiotic N fixation. Therefore, the organic composting or cocomposting represents one of the most interesting ways of transforming extracted OMWW into fertilizers.

3.3.2.3 Production of Bioenergy and Biofuels

OMWW, especially after increasing its biodegradability by the extraction of phenolic compounds, could be a good substrate for fermentative transformations. Although some studies have been performed for bioethanol (Massadeh and Modallal, 2008) and biohydrogen (Eroglu et al., 2004, 2009) production, studies have been focused on biomethane production by anaerobic digestion (AD). Among bioprocesses to transform OMWW into biofuels, anaerobic digestion is the best choice since all the macromolecules (lipids, proteins, and carbohydrates) are transformed into biogas. Biogas is a versatile energy carrier that can be used for electricity production, heating purposes, vehicle and jet fuel and replacement of natural gas. In addition, biomethane may be considered as starting compounds for biotechnological production of chemicals.

Anaerobic digestion of complex organic substrates, such as OMWW, proceeds through a series of parallel and sequential steps with several groups of microorganism involved. Anaerobic digestion starts with the hydrolysis of high molecular materials and granular organic substrates (lipids, proteins, and carbohydrates) by fermentative bacteria into small molecular materials and soluble organic substrates (fatty acids, amino acids, and glucose), aided by extracellular enzymes (hydrolases), which are excreted by fermentative bacteria. Next, products formed during the hydrolysis are further degraded into volatile fatty acids (e.g., acetate, propionate and butyrate) along with the generation of by-products (e.g., NH_3, CO_2, and H_2S) in a process known as acidogenesis. Finally, the organic substrates produced in the second step are further digested into acetate, H_2, and CO_2 and used by methanogenic archaea for methane production.

The anaerobic degradation of OMWW faces some difficulties due to the high content of hardly degradable cellulosic materials and toxic substance, such as phenols, long-chain fatty acids, ethanol, tannins, etc. (Gunay and Kadarag, 2015). As mentioned earlier, phenols compounds have a strong toxicity on microorganism, hindering their biological degradation by anaerobic bacteria. Combined physical, chemical, and biological methods have been applied prior to anaerobic digestion to eliminate toxic compounds and enhance methane productivity.

Physical pretreatment, such as ultrasound have been used to increase the methane production from OMWW. Recently, Oz and Uzun (2015) have reported 20% more biogas and methane production in anaerobic batch reactor fed with ultrasound pretreated-diluted OMWW compared to control (untreated). Low frequency ultrasound pretreatment resulted in 33% increase of soluble COD and subsequently in biogas production. Other physicochemical alternatives as advanced oxidation technologies also result in a reduction of toxicity and, therefore, in higher biodegradability (Amor et al., 2015).

Another approach to increase biogas production is the aeration of OMWW previously to the anaerobic treatment performance. The consumption of a considerable amount of energy and the removal of a significant part of the organic matter in OMWW are obstacles for its widespread application (Gunay and Kadarag, 2015). Recently, a biological treatment for OMWW has been proposed (González-González and Cuadros, 2015), resulting in 0.39 m^3 methane/kg total chemical organic demand (TCOD) when OMWW was previously aerated for 5 days.

Carbon, nitrogen and phosphorus are the main nutrients for anaerobic bacteria and an appropriate ratio of these compounds is crucial for biogas production. The required optimum C: N: P ratio for enhanced yield of methane has been reported to be 100:5:1 (Steffen et al., 1998). OMMW generally do not have a sufficient C:N:P ratio and codigestion of OMWW with others waste streams as poultry manure or winery residues have been proposed as an interesting technological approach. Alagöz et al. (2015) obtained 17–31% increase in methane production in codigestion of OMWW and wastewater sludge.

3.3.3 OTHER CONVERSION PROCESSES

In addition to the earlier described technologies to convert olive biomass (including solid or liquid wastes) into bioproducts and biofuels, a number of other interesting applications are nowadays being considered at different development stages, such as animal feed, production of activated carbons to be used as biosorbents, or as ingredients in construction materials.

Considering low-moisture residues, such as olive leaves, one of the direct applications is animal feed. For example, feed supplementation in pig diet by olive leaves (up to 25 g/kg) resulted in beneficial effects on the tocopherol content of meat without excessively compromising the growth performance (Paiva-Martins et al., 2014). Olive leaves antioxidants have also been assayed to determine their capacity for preventing oxidation of animal meat (Trebušak et al., 2014).

As far as pomace residues are concerned, the production of biosorbents and the use as construction materials have been identified as potential added-value routes. However, the current valorization method is dominated by the production of olive-pomace oil and the use of the resulting residue as heating biofuel.

Olive stones have been studied as an interesting biosorbent, particularly when used for heavy metal removal. The availability and low cost of olive stones, together with their decontamination potential, are the main advantages for this kind of use (Ronda et al., 2015). Both native and chemically treated olives stones have been studied for the development of new biosorbents (Blázquez et al., 2014).

Producing activated carbon using residual materials has obviously an environmental impact that should also be addressed. The environmental impact of the global process is highly dependent on the different operation steps, such as impregnation, pyrolysis, and drying. Hjaila et al. (2013) recently conducted this kind of study based on the life cycle assessment in Tunisia and determined that impregnation with H_3PO_4 was responsible for the highest environmental impacts for the majority of the indicators (e.g., acidification potential, eutrophication, and fresh water aquatic toxicity and terrestrial toxicity, among others). These authors concluded that those environmental impacts can be reduced by implementing a number of measures in the activated carbon production scheme.

The use of olive oil residues as ingredient in the production of fired clay bricks has been proposed with the double advantage of being a readily available disposal method and, at the same time, reducing the fuel consumption in the clay kiln, because of the effect of the added organic matter present in the olive residue. This application has been studied using olive pomace, OMWW, and the ash obtained from burning olive tree biomass to produce steam, heat, or power. Adding two-phase olive pomace to fired clay brick formulation at different proportions (3–% by weight), resulted in masonry units with several advantages when compared to the conventional products, such as lower densities and higher thermal insulation effectiveness (De la Casa et al., 2012). Partially substitution of process water by two-phase-OMWW produced facing bricks with similar technological properties to conventional bricks. Moreover, heating requirements in the kiln could be reduced in the range 2.4–7.3% depending on the final product, which is an additional advantage to the reduced environmental impact derived from eliminating the OMWW in this application (De la Casa et al., 2009). Three-phase-OMWW was also assessed for partial substitution of fresh water. The resulting bricks showed a significant increase in the volume shrinkage (10%) and the water absorption (12%), while the tensile strength remained constant (Mekki et al., 2008). Olive washing wastewater has also been studied as substitute for fresh water in fired clay ceramic production, resulting in slight improvements in the physical, mechanical, and thermal properties of bricks (Eliche-Quesada et al., 2014). Finally, the ash produced from olive biomass has been assayed as an ingredient for fired clay brick manufacturing and the resulting products fulfill specifications for being used as masonry units (De la Casa and Castro, 2014).

3.4 CONCLUSIONS

The use of different residues derived from olive tree cultivation and olive oil extraction, including waste streams, such as wastewater, olive leaves, or olive stones, in a single installation gives rise to the concept of multifeedstock and multiproduct biorefinery. This modular and intregated biorefinery could transform heterogeneous feedstocks (high- and low-moisture residues) into a number of valuable products (food additives, bioproducts, biomaterials, biofuels, and bioenergy). At the same time, the biorefinery can play an interesting environmental role, since the processes developed at this facility represent an alternative to the classical disposal methods of the residues of the olive oil industry. Depending on the feedstock considered, a wide range of final products have been identified as possible outputs for such an installation. In the case of OTP from the pruning operation, ethanol can be considered the main product to be obtained, although antioxidants, oligosaccharides, xylitol, or electricity can also be produced. High-moisture residues, such as wastewaters produced in several points of the olive oil production scheme, can also be used as raw materials for a number of bioproducts including biogas and phenolics. Despite the strategic relevance of upgrading the residues generated in the olive oil industry, further work is required to address certain issues, such a process optimization, scale up, and process integration before the biorefinery based on olive derived materials can be an industrial reality.

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