1 1 **Olive mill solid waste biorefinery: high-temperature thermal pre-**
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4 2 **treatment for phenol recovery and biomethanization**
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37 13 **Abstract**
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41 14 Circular bioeconomy has become a major issue for sustainable development in recent
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43 15 years. In the agricultural sector, circular economy focuses on the valorization and the
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45 16 pollution footprint reduction of organic waste. Due to the high volume generated and its
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47 17 high polluting potential, it is necessary to develop an economical and environmentally-
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49 18 friendly sustainable treatment of Olive Mill Solid Waste (OMSW). In the present study,
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51 19 a high-temperature thermal pre-treatment carried out at 170 °C for 60 min and a
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53 20 subsequent phenol extraction were proposed for OMSW valorization. A further
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55 21 anaerobic digestion step was proposed for the stabilization and energy recovery of pre-
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57 22 treated OMSW, with the necessity to study the effect of the inhibitory metabolites
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generated during the thermal pre-treatment in order to assess the viability of the process.

Thermal pre-treatment induced organic matter solubilization and phenol generation with respect to untreated OMSW, with increases of 26.3% and 60.4%, respectively. Phenol extraction allowed the recovery of 1600 mg of hydroxytyrosol **per 1** kg of OMSW.

Thermal pre-treatment resulted in an improvement in the liquid fraction of both methane yield and methane production rate compared to untreated OMSW up to 16.9% and 6.9%, respectively. Further extraction of phenols produced a more significant enhancement of both methane yield and methane production rate in the de-phenolized liquid fraction compared to untreated OMSW, reaching improvements of 44.1% and 103%, respectively. The proposed economic assessment showed that the combination of high temperature thermal pre-treatment, phenol recovery and the subsequent biomethanization of the substrates was the most attractive treatment option. The economical suitability of the proposed biorefinery concept is favorable for a phenol extract price higher than 67.0 €/kg, 87% lower than the referenced actual price of 520 €/kg.

Keywords:

Phenol recovery; Methane production rate; Improved anaerobic digestion; Olive Mill Solid Waste; Economic assessment; Thermal Pre-treatment

Nomenclature

AD	anaerobic digestion
BMP	biochemical methane potential
COD	total chemical oxygen demand (g O ₂ /kg)

1	1	DLP	de-phenolized liquid phase
2	2	dOMW	decanted olive mill wastewater
3			
4	3	G	cumulative specific methane production
5			
6			
7	4	G_{max}	ultimate methane production
8			
9	5	HMF	hydroxymethylfurfural
10			
11	6	IRR	internal rate of return
12			
13			
14	7	λ	lag time
15			
16			
17	8	LP	liquid phase
18			
19	9	n.d.	not detected
20			
21			
22	10	NPV	net present value
23			
24	11	OMSW	olive mill solid waste
25			
26	12	R_{max}	maximum methane production rate
27			
28			
29	13	σ_{est}	standard error of estimate
30			
31	14	sCOD	soluble chemical oxygen demand (g O ₂ /kg)
32			
33			
34	15	SP	solid phase
35			
36	16	t	time
37			
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39	17	TS	total solids (g/kg)
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41	18	VS	total volatile solids (g/L; mg/kg; g/kg)
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50	21	1. Introduction	

22 Olive oil production is an agro-industrial sector which generated more than 3 million
 23 tonnes of olive oil worldwide in 2014, which was consumed in over 160 countries
 24 (IOOC, 2016). There are approximately 12,000 olive oil mills in the world, more than 90%
 25 of which use centrifugal systems (Rincón et al., 2016). The two-phase centrifugation system

1 separates olive paste into two phases: olive oil and wet pomace or Olive Mill Solid Waste
2 (OMSW). OMSW is a residual by-product composed of olive husk, olive pulp and olive
3 vegetation water (Dermeche et al., 2013). OMSW must be correctly managed to avoid
4 severe environmental impacts such as negative effects on agricultural soil quality,
5 polluting of aquatic ecosystems and atmospheric contamination (Aharonov-Nadborny et
6 al., 2016).

7 Within the different treatment methods, anaerobic digestion has been widely proposed
8 as a suitable management method for OMSW (Roig et al., 2006). Anaerobic digestion
9 allows the treatment of OMSW through its conversion to a partially stabilized digestate
10 and biogas, which could be employed as a renewable energy source (Wheatley, 1990,
11 Kastner et al., 2012, Bustamante et al., 2014). Moreover, anaerobic digestion is an
12 environmentally friendly management method whose total carbon dioxide emissions are
13 more than 6 times lower than the natural degradation of OMSW (González-González
14 and Cuadros, 2013, Ahamed et al., 2016). However, OMSW is a lignocellulosic
15 substrate with a significant concentration of phenolic compounds which inhibit the
16 biomethanization process (Borja et al., 1997, Chen et al., 2008).

17 Phenolic compounds exhibit a wide range of health benefits and physiological
18 properties. These compounds are usually employed as food additives to avoid the
19 oxidative deterioration of fats and oils (Balasundram et al., 2006). Due to their high
20 economic interest as well as their potentially negative effect on anaerobic digestion,
21 prior recovery of phenols from OMSW could improve the further biomethanization
22 process, and obtain high-added value compounds at the same time. Among the different
23 phenolic compounds present in OMSW, hydroxytyrosol is one of the most important
24 due to its excellent properties as pharmacological and antioxidant agents (Rodríguez-
25 Gutiérrez et al., 2012).

1 Thermal pre-treatments of OMSW have been proposed to allow the extraction of
2 phenolic compounds by their displacement to the liquid phase generated during the
3 thermal pre-treatment (Rubio-Senent et al., 2013). Low-temperature thermal pre-
4 treatments (50-90 °C) mainly induce the de-flocculation of macromolecules with
5 minimal solubilization of the lignocellulosic matter (Jain et al., 2015). At temperatures
6 above 150-180 °C, parts of the lignocellulosic biomass will start to be solubilized, first
7 the hemicelluloses and shortly after that the lignin (Garrote et al., 1999, Hendriks and
8 Zeeman, 2009). The solubilization of complex compounds, such as fibers, results in the
9 generation and release of phenolic compounds, as well as an enhancement in substrate
10 biodegradability (Zheng et al., 2014). For example, Chandra et al. (2012) reported that
11 the solubilization of wheat straw by a thermal pre-treatment at 200 °C for 10 min
12 resulted in an increase of around 20.0% in methane production. Heat pre-treatment of
13 lignocellulosic biomass entails a risk of formation of different phenolic and heterocyclic
14 compounds, like vanillin, vanillin alcohol, furfural and HMF, which have been
15 considered as inhibitory for the anaerobic digestion processes (Hendriks and Zeeman,
16 2009, Ghasimi et al., 2016). In fact, some authors have reported that increases in the
17 soluble matter through thermal pre-treatment of fiber rich substrates does not always
18 entail an improvement in methane production (Fernández-Cegri et al., 2012, Lizasoain
19 et al., 2016). The extraction of phenolic compounds could be an interesting alternative
20 which allows obtaining economic benefit from these valuable compounds, as well as
21 enhancing the further OMSW anaerobic digestion. The combination of high added-
22 value compound recovery and energy valorization could ensure economic and
23 environmental sustainability in OMSW management, although it is necessary to
24 evaluate energy consumption, operational costs, and installation costs (González-
25 González and Cuadros, 2013).

The aim of this research was first to evaluate the effect of a high-temperature thermal pre-treatment on OMSW; and second, to evaluate a phenol recovery process after the thermal pre-treatment and its effects on the subsequent anaerobic digestion process. In addition, an economic assessment was developed to compare the viability of the different proposed options for OMSW management.

2. Materials and Methods

2.1. Olive Mill Solid Waste and anaerobic inoculum

OMSW was obtained from the centralized management plant “Oleícola El Tejar” located in Marchena (Seville), Spain. Prior to its characterization and use, OMSW was preserved under freezing conditions (-18 °C) to avoid undesirable fermentation processes.

The anaerobic inoculum was obtained from a full-scale anaerobic reactor treating sewage sludge from the “COPERO” wastewater treatment plant (Seville, Spain). The main characteristics of the anaerobic inoculum were: pH = 7.8 ± 0.1 ; alkalinity = 5600 mg CaCO₃/L; VS = $17,535 \pm 375$ mg/kg; ammoniacal nitrogen = 953 ± 10 mg/kg.

2.2. High-temperature thermal pre-treatment and phenol recovery system

High-temperature thermal pre-treatment was carried out in a 100-L reactor which can operate at temperatures between 50 and 180 °C by vapor injection or indirect heating and at a maximum pressure of 1.20 MPa. OMSW was loaded into the reactor and treated for 60 min at a fixed temperature of 170 °C by vapor injection and 0.85 MPa

1 pressure. The injected water ratio was 1.1 L per kg of OMSW (Under patent,
2 P201031236, 09/08/2010). Then, pre-treated material was centrifuged at 4700 g
3 (Comteifa, S.L., Barcelona, Spain). The centrifugation allowed the separation of pre-
4 treated OMSW into a solid phase (SP) and a liquid phase (LP) at a ratio of 23:77, on
5 wet basis, respectively. Samples were stored at 4 °C before characterization.

6 Phenols were recovered using an industrial chromatographic system under patent (WO
7 2013/007850A1; Serrano et al., 2017). The obtaining of a de-phenolized liquid phase
8 (DLP) by extraction of phenols from LP did not produce a significant decrease in the
9 DLP volume compared to the LP volume.

11 *2.3. Anaerobic digestion experimental procedure*

12 The anaerobic digestibility of untreated OMSW and the different pre-treated phases was
13 evaluated by biochemical methane potential (BMP) tests. Additionally, the mixtures
14 SP:LP and SP:DLP, at a ratio of 23:77, on wet basis, were also assayed. This ratio
15 corresponded to the obtained ratio of the phases during the high-temperature thermal
16 pre-treatment. BMP tests were carried out in 250 mL Erlenmeyer flasks at mesophilic
17 temperature (35 °C) using a working volume of 220 mL. Mechanical stirring was
18 provided at 300 rpm to facilitate an adequate mass transfer between inoculum and
19 substrate. In all cases, the BMP reactors were loaded with an inoculum to substrate ratio
20 of 2, based on VS. All these assays were carried out in triplicate. BMP reactors were
21 sealed and the headspace of each flask was flushed with nitrogen at the beginning of the
22 assay. The produced biogas was passed through a 2 N NaOH solution to capture CO₂
23 and the remaining gas was assumed to be methane. The volume of methane was
24 measured by liquid displacement. The BMP tests were carried out in the time interval

required to exhaust gas production and VS removal (22-day period). Methane production was monitored daily throughout the process.

2.4. Data fitting

The kinetics of the anaerobic processes was evaluated by applying the modified-Gompertz equation to the experimental data of methane production during BMP tests (eq. 1). The application of the modified-Gompertz equation was prior reported in batch mode biomethanization processes of several organic substrates carried out by different authors (Donoso-Bravo et al., 2010, Ortega-Martinez et al., 2016), and is defined as:

$$G = G_{max} \cdot \exp \left[-\exp \left(\frac{R_{max} \cdot e}{G_{max}} (\lambda - t) + 1 \right) \right] \quad (1)$$

where G (mL CH₄/g VS_{added}) is the cumulative specific methane production at time t (d), G_{max} (mL CH₄/g VS_{added}) is the ultimate methane production, R_{max} is the maximum methane production rate (mL CH₄/(g VS_{added}·d)), λ is the lag time (d) and e corresponds to $\exp(1)$, equal to 2.7183. Additionally, r^2 , Error (%) and standard error of estimate (σ_{est}) were determined to evaluate the goodness-of-fit of the experimental data to the selected modified Gompertz equation. Error was defined as the difference in percentage between the experimental accumulated final methane production and G_{max} .

The kinetic parameters for each experiment and mathematical adjustment were determined numerically from the experimental data obtained by non-linear regression using the software Sigma-Plot (version 10.0).

2.5. Chemical analyses

The following chemical analyses were used for the characterization of the inoculum and OMSW as well as for the effluents from each BMP test at the end of the process. The concentration of total solids (TS; g/kg), total volatile solids (VS; g/kg), alkalinity (mg CaCO₃/L), and pH were carried out according to the recommendations of the Standard Methods of APHA (2005). Specifically, TS and VS were determined according to the Standard methods 2540B and 2540E, respectively. Alkalinity was determined by pH titration to 4.3. pH was analyzed using a pH-meter model Crison 20 Basic. Chemical Oxygen Demand (COD; g/kg) was determined using the method described by Raposo et al. (2008), while soluble COD (sCOD; g/L, mg/L) was determined by the closed digestion and the colorimetric standard method 5220D (APHA, 2005). Total phenols were quantified by spectrophotometry with a calibration curve of gallic acid through the Folin-Ciocalteu method, after an extraction with a methanol/water solution (80:20) (García et al., 2016). Soluble phenols (mg/L) were quantified by the same procedure after filtration through a Millipore 0.45 µm filter (Albet GF 47mm, Dassel, Germany). Ammoniacal nitrogen (mg/L) was also determined from filtered samples by spectrophotometry at 635 nm. Total carbohydrates (mg/L) were determined according to the colorimetric method described by Bellou and Aggelis (2013) by using UV/Vis spectrophotometer (DU 730, Beckman Coulter, USA) at 632 nm.

2.6. Analysis of individual compounds

Individual phenols and acetic acid were quantified using a Hewlett-Packard 1100 liquid chromatography system with a C-18 column (Mediterranea SEA 18, Teknokroma, 250 mm x 4.6 mm, i.d. 5 µm) and diode array detector (DAD, the wavelengths used for

quantification were 254, 280, and 340 nm) with Rheodyne injection valves (20 μ L loop). The mobile phase was Milli-Q water acidified with 0.01% trichloroacetic acid and acetonitrile (A) using the following gradient over a total run time of 55 min: 95% A initially, 75% A in 30 min, 50% A in 45 min, 0% A in 47 min, 75% A in 95 min, and 95% A in 52 min until completion of the run. Quantification was carried out by integration of the peaks at different wavelengths in function of the compounds, with reference to calibrations made using external standards.

Hydroxymethylfurfural (HMF), furfural and trichloroacetic acid were obtained from Sigma-Aldrich (Deisenhofer, Germany). Hydroxytyrosol was obtained from Extrasynthese (Lyon Nord, Geney, France). Tyrosol was obtained from Fluka (Buchs, Switzerland). HPLC-grade acetonitrile was purchased from Merck (Darmstadt, Germany) and ultrapure water was obtained using a Milli-Q water system (Millipore, Milford, MA, USA).

2.7. Economic assessment

Net present value (NPV), Internal Rate of Return (IRR) and payback period were used to compare the economic profitability of the three alternatives studied in this work: (1) anaerobic digestion, (2) anaerobic digestion plus thermal pre-treatment – (A) with heat recovery and (B) without heat recovery - and (3) anaerobic digestion plus thermal pre-treatment including phenol extraction (see Figure 1). In addition, two financing scenarios were defined: (M) with mortgages and without mortgages. The adopted assumptions were:

- An influent of 50,000 metric tons of OMSW per year. The anaerobic digester was assumed to operate 8000 hours per year with a 20-year life-time.

1 - The energy production was obtained applying a scale-up factor of 0.85 to the G_{max}
2 experimental values obtained for each alternative. The efficiency in the energy obtained
3 through a cogeneration biogas engine was 39% for electricity and 45% for thermal
4 energy production (Eder and Schulz, 2007).

5 - Anaerobic digester and co-generation biogas engine. An investment was assumed of
6 3000 € per installed kWe for the construction of the anaerobic digester and the co-
7 generation biogas engine facilities. Complementary costs ought to be considered
8 regarding feasibility studies and administrative and authorization requirements (30,000
9 €) (Gonzalez-Gonzalez and Cuadros, 2013). Operational and maintenance costs for this
10 sections were estimated as 2% of the construction cost. Electric energy self-supply of
11 the anaerobic digester was assumed as 15% of the electricity generated by the co-
12 generation biogas engine (Angelidaki et al., 2006). The thermal energy required to
13 maintain the anaerobic digester at 38 °C was estimated as 200 kJ/kg OSMW.

14 - Thermal pre-treatment. An investment was assumed of 165,000 € for the construction
15 of the pre-treatment facility (Rodriguez-Gutierrez, et al., 2005 and 2007). This
16 investment was duplicated in the case of including heat recovery reaching 330,000 €.
17 Operational and maintenance costs for this sections were estimated as a 2% of the
18 construction cost. The thermal energy requirement was assumed to be 3436 kJ/kg
19 OMSW (Rodriguez-Gutierrez, et al., 2005 and 2007). As this energy requirement is
20 higher than the thermal energy generated in the anaerobic digester, a diesel boiler with a
21 thermal efficiency of 80% was considered for the supply of the rest of the necessary
22 thermal energy. In the case of including the heat recovery system, the amount of
23 required thermal energy was reduced by 80% (Franchetti, M., 2013).

24 - Phenol extraction section. An investment was assumed of 21,000,000 € for the
25 construction of the phenol extraction section (Rodriguez-Gutierrez, et al., 2005 and

2007). Operational and maintenance costs for the phenol extraction section were estimated as 25,000,000 €/y, mainly due to the use of sorbents. The energy requirement for the phenol extraction section was 0.5% of the electricity generated by the co-generation biogas engine (Rodriguez-Gutierrez, et al., 2005 and 2007). Based on experimental results, a production of 10.28 g 10 wt% phenol extract/kg OMSW was considered.

- Prices. 0.12 €/kWh of electricity (EUROSTAT, 2016), 0.86 €/kg of diesel (fuel-prices-europe, 2016), 520 €/kg of 10% phenol extract (Ciriminna et al., 2016). The employment of digestate as an organic amendment was considered without economic interest (Serrano et al. 2014). The price assigned to the remaining thermal energy was the price of the equivalent diesel whose use could be avoided in other heating operations (Gonzalez-Gonzalez and Cuadros, 2013).

- **Economic outlook.** The value of the discount rate was assumed to be equal to the Spanish ten-year bond yield. The industrial profit taxes were fixed at 25%. The annual re-payment mortgage was calculated at a projected interest rate of 6% paid over 15 years. In addition, a sensibility study was performed in order to study the effect of the price of the phenol extract in the profitability of the project.

3. Results and discussion

3.1. Effect of the high-temperature thermal pre-treatment on the substrate characteristics

Thermal pre-treatment by vapor injection, carried out at 170 °C for 60 min, allowed the separation of OMSW into two phases, i.e. SP and LP. The obtaining of the LP allowed the subsequent extraction of phenols by an industrial chromatographic system, resulting

1 in the DLP. Table 1 shows the physicochemical characteristics of OMSW before
2 carrying out the thermal pre-treatment and the different pre-treated phases obtained after
3 pre-treatment. VS and COD did not decrease during the thermal pre-treatment. The use
4 of a closed system avoided the release of organic compounds. 89.8% of the organic
5 matter from OMSW, measured as VS or COD, was retained in the SP (Table 1). In
6 addition to **facilitating** the separation of SP and LP, thermal pre-treatment by vapor
7 injection partially solubilized the OMSW. The organic soluble compounds, as sCOD,
8 after the thermal pre-treatment, i.e. the sum of the LP and SP, were 26.3% higher than
9 in the untreated OMSW. These soluble compounds were mainly displaced to the LP,
10 which retained around 75% of sCOD of the sum of LP and SP (Table 1). The increase
11 **in** sCOD could be a consequence of the hydrolysis of the fibrous matter from OMSW
12 (Pérez et al., 2007). During thermal pre-treatment, water can penetrate into the biomass
13 cell structure, hydrating cellulose, solubilizing hemicellulose, and slightly removing
14 lignin (Pérez et al., 2007, Zheng et al., 2014). The hydrolysis of polysaccharides, such
15 as hemicellulose, results in soluble oligosaccharides, then into monomeric sugars
16 (Zheng et al., 2014). The displacement of soluble compounds to the LP facilitates the
17 subsequent extraction, which was effected in this research by an industrial
18 chromatographic system. No significant variations in pH values or increases in the
19 acetic acid concentration were observed after the thermal pre-treatment (Table 1). A
20 decrease in the pH of the substrate or an increase in acetic acid concentration could have
21 led to the risk of acidification of the subsequent biomethanization process (Motte et al.,
22 2015).

23 Total phenols were measured in untreated OMSW and in the different pre-treated
24 phases. The thermal pre-treatment by vapor injection increased the total phenol content
25 in the sum of the LP and the SP up to 60.4% with respect to the untreated OMSW

(Table 1). This increase has been reported as a consequence of the thermal hydrolysis of lignocellulosic biomass, which generates by-products, such as furan and/or phenolic compounds (Kumar et al., 2009, Zhao et al., 2009, Ghasimi et al., 2016). As was described for sCOD, total phenols were partially displaced to the LP, reaching a concentration of 64 ± 2 g gallic acid per 1 kg VS, i.e. more than twice than in the SP. According to the total phenol concentration in DLP, the extraction of phenols by the industrial chromatographic system resulted in the retention of 71.2% and 33.9% of the total phenols of the LP and of the sum of LP and SP, respectively.

3.2. Effect of thermal pre-treatment and extraction procedure on the individual phenols

Table 2 shows the concentration of the measured individual phenolic compounds in the untreated OMSW, LP and DLP. Thermal pre-treatment by vapor injection increased the sum of the measured individual phenol concentration from 1127 mg gallic acid per 1 L in untreated OMSW to 2772 mg gallic acid per 1 L in the LP, i.e. around 2.5 times higher (Table 2). In the LP, the sum of measured individual phenols was very similar to the total phenol concentration determined by the Folin-Ciocalteu method, indicating that most of the phenols were in soluble form in this phase. Hydroxytyrosol, which increased more than twice by the thermal pre-treatment, was the main individual phenol in the LP. Due to its high concentration and its characteristics as antioxidant, hydroxytyrosol can be considered the main active ingredient of OMSW to be valorized (Visioli et al., 1998, Ciriminna et al., 2016). In addition, thermal treatment under the acidic conditions of the substrate, i.e. OMSW pH: 4.79 ± 0.01 , favors the transformation of some sugars to aldehyde-like compounds such as hydroxymethylfurfural or vanillin, which are well-known inhibitors of the anaerobic digestion process (Zheng et al., 2014,

Ghasimi et al., 2016). These compounds were indeed generated during the proposed thermal pre-treatment by vapor injection, up to concentrations in LP of 612 ± 17 mg/L and 113 ± 10 mg/L of hydroxymethylfurfural and vanillin, respectively (Table 2). The subsequent extraction by an industrial chromatographic system presented an extraction efficiency of 76.4% for the sum of the measured individual phenols in DLP compared to LP. The extraction of hydroxytyrosol allowed the recovery of 1600 mg/kg of OMSW (Table 2). Furthermore, the potential inhibitors of the anaerobic digestion, i.e. hydroxymethylfurfural and vanillin, were also partially removed in DLP, with extraction efficiencies compared to LP of 68.1% and 84.1%, respectively. The concentrations of both compounds in DLP were reduced to values markedly lower than the inhibition concentrations for anaerobic processes, which were reported to be around 800 mg/L for hydroxymethylfurfural and 2000 mg/L for vanillin (Ghasimi et al., 2016).

3.3 Stability of the anaerobic process, biodegradability and inhibitory compounds

BMP tests were carried out to evaluate the energy valorization of the different substrates under anaerobic conditions. The stability of the processes was evaluated through the pH, alkalinity and the final acetic acid concentration. pH values remained within the recommended range for an adequate methanogenic activity, which varies in a range from 7.3 to 7.8 (Wheatley, 1990) (Table 3). pH values, together with high alkalinity values and low acetic acid concentration at the end of the BMP tests, assured that an acidification process did not occur (Table 3). The concentrations of ammonia nitrogen were markedly lower than the inhibitory limits described in the literature at the working pH, which widely varies from 1.5 to 14 g/L (Chen et al., 2008, Rajagopal et al., 2013) (Table 3). Table 3 also shows the biodegradability calculated as the removal of VS for

the different substrates and mixtures. Untreated OMSW and SP presented the lowest biodegradability values, whereas both LP and DLP increased the biodegradability up to 33.7% in comparison with untreated OMSW. The enhancement of the biodegradability for the mixtures SP:LP and SP:DLP in comparison to untreated OMSW (Table 3) could be mainly explained by the solubilization of hemicellulose and, to a lesser extent, the alteration of the lignin structure (Hendriks and Zeeman, 2009, Zheng et al., 2014). The obtained biodegradability values showed a reduction in the pollution potential of the substrate, which became partially stabilized. The proposed manage method allowed for pollution footprint reduction, which is one of the objectives of circular bioeconomy.

Table 4 shows the soluble phenol concentration and the individual phenolic compound concentrations at the end of the BMP tests. As can be seen, the phenol removal efficiency was similar for the different substrates and mixtures, with a mean value of $62.4 \pm 4.2\%$. The final concentration of the measured individual phenolic compounds indicated that they were widely metabolized during the biomethanization process in all cases (Table 4).

3.4 Methane yields and kinetic study

Figures 2A and 2B show the accumulated methane yield coefficient throughout the experimental time. The high deviations obtained in the methane production of the SP BMP tests were a consequence of the high heterogeneity and complexity of this fraction, which resulted in significant variations during the exponential phase, but not in the final methane yield coefficient value (Figure 2A).

Table 5 summarizes the parameters obtained from the application of the modified Gompertz equation to the experimental data shown in Figures 2A and 2B, as well as the values of r^2 , Error (%) and standard error of estimate (σ_{est}) to evaluate the goodness-of-fit. The high r^2 values obtained, which were higher than 0.98 in all cases, as well as the low values of Error and standard error of estimate indicated that the experimental data correctly fit to the proposed model (Table 5).

The G_{max} value indicates the maximum methane yield coefficient obtained at the end of the experimental time, once the methane production has been exhausted. Untreated OMSW reached a G_{max} value of 261 ± 2 mL CH_4/g VS (Table 5). This value was similar to the one reported by Serrano et al. (2017), who obtained a G_{max} value of 264 ± 1 mL CH_4/g VS in the biomethanization of OMSW under mesophilic conditions. SP gave a G_{max} value similar to the one obtained for untreated OMSW, whereas LP reached an improvement of 17% with respect to the untreated OMSW. Co-digestion of SP and LP did not produce a synergy effect on G_{max} with respect to the biomethanization of untreated OMSW (Table 5). Therefore, the increase in the soluble compounds by the thermal pre-treatment described prior did not mean a significant enhancement of the methane production in these cases. Other authors have also reported that increases in the soluble matter through thermal pre-treatment did not always produce an improvement in methane production (Fernández-Cegri et al., 2012). In the present study, the non significant improvement of methane production after carrying out the thermal pre-treatment can be attributed to the possible generation of non-degradable or toxic compounds during thermal pre-treatments (Hendriks and Zeeman, 2009, Teghammar et al., 2010, Fernández-Cegri et al., 2012). A high increase in G_{max} was obtained for DLP, i.e. around 44% and 23% higher than those obtained for untreated OMSW and LP, respectively (Table 5), probably due to the prior phenol extraction. Co-digestion of

SP:DLP did not result in a synergy effect in the G_{max} value with respect to the individual biomethanization of SP and DLP, however, it did produce an enhancement of up to 34% compared to the untreated OMSW G_{max} value (Table 5). This enhancement could be a consequence of the partial removal of phenolic compounds, especially hydroxymethylfurfural (Fernández-Cegrí et al., 2012, Ghasimi et al., 2016).

R_{max} values presented a similar behavior and trend to that described for G_{max} for the different phases and mixtures. DLP enhanced R_{max} more significantly than LP compared to the untreated OMSW, whereas the proposed co-digestions did not result in any synergy effects (Table 5). Hydroxymethylfurfural, which presented an initial concentration in LP close to the inhibition limit, was degraded at the end of the experimental time in LP and SP:LP BMP tests (Table 2 and Table 4). However, the appearance of 4-ethylphenol in LP and SP:LP BMP tests indicated an incomplete phenolic degradation. The incomplete phenol degradation might be a consequence of the presence of inhibitory compounds, probably with the hydroxymethylfurfural (Table 2) (Carrere et al., 2016). SP presented the lowest R_{max} value, which was around 29% lower than that obtained for untreated OMSW. Furthermore, this fraction showed a lag phase in the methane production of 2.7 ± 0.1 d (Table 5). This could be a consequence of the displacement of the soluble and readily degradable compounds to the LP. The high organic matter content present in the SP should be firstly hydrolyzed, which could be a limiting-rate step in the anaerobic digestion of solid waste (Ortega et al., 2008).

3.5. Economic assessment

The results obtained for each proposed management strategy for OMSW are shown in Table 6. The IRR of 27.5 was found in the literature (Gonzalez-Gonzalez and Cuadros,

2013) for an Anaerobic Digestion case study with decanted olive mill wastewater (dOMW). This value is also very high but lower than the one obtained in Case 1 mostly because of the lower methane production yield obtained with dOMW. Only cases 2A and 2A+M were not fully feasible projects under an economic standpoint. The rest of the cases showed positive NPVs and very high IRR at the end of the life of the projects. Also the payback periods were very short, always less than five years. Although cases 2B and 2B+M were feasible projects, results showed that these were not good alternatives because of their higher initial inversion and lower NPV compared to the cases 1 and 1+M respectively. From an economic standpoint, cases 3B and 3B+M represented the most preferred scenario with a payback period of 1 year (Table 6). However, these cases also involved a very high initial investment, around 26.8 M€. In all cases, the mortgage reduced the NPV but increased the IRR. Figure 3A shows the influence of the price of the phenol extract on the NPV of the cases with phenol extraction. The phenol extract price influenced the NPV linearly. The limit values for which NPV are zero have also been included in Table 6. For a phenol extract price higher than 48.6 €/kg, all alternatives had a positive NPV. For comparison purposes, Figure 3B shows the NPV for cases 1 and 3 for a low range price for phenol extraction. For a price lower than 50.0 €/kg, conventional AD would be the best option in terms of NPV. For a price higher than 52.5 €/kg, case 3A is the best option. A second option would be AD without a mortgage (case 1) up to a price of 59 €/kg, after which the second best option would be case 3A. When mortgage would be necessary, AD would be the best option up to a phenol price of 60.2 €/kg. For a price higher than 60.2 €/kg, case 3B would be the best option and case 1 the second best option up to a price of 67.0 after which case 3A would be the second best option. In light of these results,

phenol extraction would always be the best option for a price higher than 67.0 €/kg, 87% lower than the referenced actual price of 520 €/kg.

3.6. Future perspectives

The proposed management system for OMSW presented in this research could be a suitable and promising treatment, and mainly, a valorization method. This valorization method plays a crucial role within the circular bioeconomy framework. Anaerobic digestion at continuous operation mode should be evaluated to ensure the sustainability of the process. Moreover, studies at pilot and demo scale are highly recommended to study in depth the technical challenges of the proposed management system. Energy consumption for the high temperature pre-treatment step could also be optimized by a continuous reactor, which **would** avoid the pre-heating energy consumption needed in the present study.

5. Conclusions

Anaerobic digestion after thermal pre-treatment by vapor injection could be a sustainable management method for lignocellulosic substrates such as OMSW, but the generation of inhibitory metabolites compromises the viability of the process. Extraction of phenols **prior** to the anaerobic digestion has been effective to improve methane production, as well as to allow the recovery of these high-value compounds. The thermal pre-treatment induced organic matter solubilization, which improved **both methane yield and methane production rate in LP compared to untreated OMSW**. Further extraction of phenols resulted in a significant enhancement of both methane yield and methane production rate in DLP compared to LP. The economical suitability

of the proposed biorefinery concept is favorable for a phenol extract price higher than 67.0 €/kg, 87% lower than the referenced actual price of 520 €/kg. Therefore, a combination of phenol extraction and anaerobic digestion could be included in the circular bioeconomy, given the consideration of OMSW as a by-product with high economic interest, and not as a waste.

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1 **Figure captions**

2
3 **Figure 1.** Process Block Flow Diagram of the proposed management strategies for
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5
6 OMSW treatment.
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9 **Figure 2(A) and 2(B).** Variation of the accumulated methane production with time for
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12 untreated olive mill solid waste and pre-treated phases and mixtures.
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15 **Figure 3. (A)** Influence of the price of the phenol extract on the profitability of the
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17 phenol extraction alternative. **(B)** Influence of the price of the phenol extract on the best
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19 alternative selection. (1) anaerobic digestion; (2) anaerobic digestion plus thermal pre-
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21 treatment; (3) anaerobic digestion plus thermal pre-treatment including phenol
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23 extraction; (A) with heat recovery; (B) without heat recovery; and (M) with mortgages.
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Highlights

- Phenols recovery and biomethanization are proposed to Olive Solid Waste management
- Thermal pretreatment at 170°C and 60 min is proposed to allow phenols extraction
- Phenols extraction allows to recover 1600 mg hydroxytyrosol **per 1** kg of substrate
- Phenols extraction improved methane production yield and rate up to 44.1% and 103%

Figure 1

Figure 1.

- AD:** Anaerobic digester and biogas engine
TP: Thermal pre-treatment system
ES: Centrifugation and industrial chromatographic system for phenols recovery
- 1) Untreated OMSW
 - 2) Stabilized digestate
 - 3) Electricity
 - 4) AD electricity supply
 - 5) Heat
 - 6) AD heat supply
 - 7) Pre-treated OMSW
 - 8) TP electricity supply
 - 9) TP heat supply
 - 10) TP heat supply from a diesel engine
 - 11) Pre-treated and dephenolized OMSW
 - 12) ES electricity supply
 - 13) Extracted phenols

Figure 2

Figure 2.

A)

B)

Figure 3

Figure 3

A)

B)

Table 1

Table 1. Physicochemical characterization of untreated OMSW and different pre-treated fractions, where n.d., non detected; Traces, <0.01 mg/L

		Untreated OMSW	Solid phase (SP)	Liquid phase (LP)	Dephenolized liquid phase (DLP)
TS	g/L	266 ± 4	394 ± 3	48 ± 2	31 ± 1
VS	g/L	250 ± 4	381 ± 3	43 ± 2	25 ± 1
COD	g/L	322 ± 11	495 ± 29	53 ± 1	33 ± 2
sCOD	g/L	57 ± 11	38 ± 2	34 ± 1	27 ± 1
Total Phenols	g gallic acid/kg VS (g/L)	24 ± 2 (5.90 ± 0.38)	28 ± 1 (10.5 ± 0.2)	64 ± 2 (2.79 ± 0.06)	32 ± 2 (0.80 ± 0.04)
pH		4.79 ± 0.01	5.65 ± 0.05	4.64 ± 0.01	5.14 ± 0.01
Alkalinity	mg CaCO ₃ /L	6559 ± 5	6027 ± 5	1372 ± 5	664 ± 5
Acetic Acid	mg/L	n.d.	-	Traces	Traces

Table 2

Table 2. Individual phenolic compounds concentration of untreated OMSW and different pre-treated fractions, where n.d., non detected; Traces, <0.01 mg/L

		Untreated	Liquid phase (LP)	Dephenolized	Extraction
		OMSW		liquid phase (DLP)	efficiency (%)
Total phenols (Folin-Ciocalteu method)	mg gallic acid per 1 L	5902 ± 379	2792 ± 66	803 ± 41	71.2
Sum of individual phenols	mg gallic acid per 1 L	1127	2772	655	76.4
3,4-Dihydroxyphenylglycol	mg/L	157 ± 5	29 ± 3	7 ± 1	75.9
Hydroxytyrosol 4-β-D-Glucoside	mg/L	88 ± 5	75 ± 2	27 ± 2	64.0
Hydroxytyrosol	mg/L	540 ± 13	1278 ± 18	284 ± 8	77.8
Tyrosol	mg/L	122 ± 9	215 ± 7	15 ± 1	93.0
Homovanillic acid	mg/L	n.d.	2.7 ± 1	Traces	100
Vanillic acid	mg/L	15 ± 2	16 ± 1	1.2 ± 0.1	92.5
Hydroxymethylfurfural	mg/L	n.d.	612 ± 17	195 ± 17	68.1
Vanillin	mg/L	76 ± 4	113 ± 10	18 ± 2	84.1
p-Coumaric acid	mg/L	32 ± 2	3.6 ± 0.7	Traces	100
4-Ethylphenol	mg/L	n.d.	n.d.	n.d.	-

Table 3

Table 3. Biodegradability (%), CODsoluble (mg O₂/L), ammonia nitrogen (mg/L), acetic acid (mg/L), and total carbohydrates (mg/L) in the BMP tests at the end of the experimental time, where n.d., non detected; Traces, <0.01 mg/L

		OMSW	SP	LP	DLP	SP:LP	SP:DLP
pH		7.3 ± 0.1	7.3 ± 0.1	7.5 ± 0.1	7.4 ± 0.1	7.4 ± 0.1	7.4 ± 0.1
Alkalinity	mg CaCO ₃ /L	7362 ± 25	5973 ± 339	7845 ± 106	8001 ± 175	7850 ± 71	7831 ± 33
Acetic acid	mg/L	n.d.	n.d.	n.d.	n.d.	Traces	Traces
Ammonia nitrogen	mg/L	957 ± 38	953 ± 26	986 ± 27	988 ± 16	1002 ± 35	1010 ± 30
Biodegradability	%, in VS	57.3 ± 3.2	54.8 ± 0.2	70.9 ± 5.0	76.6 ± 2.3	63.4 ± 1.3	75.3 ± 3.1
sCOD	mg O ₂ /L	116 ± 10	94 ± 6	246 ± 16	271 ± 19	267 ± 17	193 ± 17
Total carbohydrates	mg/L	25 ± 7	38 ± 8	50 ± 7	26 ± 4	27 ± 4	22 ± 4

Table 4

Table 4. Soluble phenols and individual phenolic compounds concentration at the end of the BMP tests, where n.d., non detected; Traces, <0.01 mg/L

		OMSW	SP	LP	DLP	SP:LP	SP:DLP
Soluble phenols (Folin-Ciocalteu method)	mg gallic acid per 1 L	47 ± 6	48 ± 6	135 ± 28	69 ± 4	95 ± 60	60 ± 2
Removal of soluble phenols	%	64.5	69.1	62.5	61.7	60.3	56.4
Sum of individual phenols	mg gallic acid per 1 L	-	-	58.1	19.2	26.0	2.1
3,4-Dihydroxyphenylglycol	mg/L	Traces	Traces	5.6 ± 2.5	4.6 ± 2.0	5.5 ± 0.2	2.2 ± 1.3
Hydroxytyrosol 4-β-D-Glucoside	mg/L	n.d.	Traces	12.4 ± 0.3	13.5 ± 2.8	Traces	Traces
Hydroxytyrosol	mg/L	n.d.	Traces	3.7 ± 0.1	Traces	Traces	Traces
Tyrosol	mg/L	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Homovanillic acid	mg/L	n.d.	n.d.	n.d.	Traces	Traces	Traces
Vanillic acid	mg/L	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Hydroxymethylfurfural	mg/L	n.d.	n.d.	Traces	Traces	Traces	Traces
Vanillin	mg/L	n.d.	Traces	n.d.	Traces	Traces	Traces
p-Coumaric acid	mg/L	n.d.	Traces	n.d.	n.d.	n.d.	n.d.
4-Ethylphenol	mg/L	n.d.	n.d.	25.0 ± 34.0	n.d.	15.0 ± 21.0	n.d.

Table 5. Kinetics parameters obtained from the modified-Gompertz equation applied to the different BMP tests, where σ_{est} , standard error of estimate

		OMSW	SP	LP	DLP	SP:LP	SP:DLP
<i>G</i>_{max}	mL CH ₄ /g VS	261 ± 2	283 ± 3	305 ± 3	376 ± 3	290 ± 4	350 ± 4
<i>R</i>_{max}	mL CH ₄ /(g VS·d)	58 ± 3	41 ± 2	62 ± 4	118 ± 8	64 ± 4	98 ± 7
<i>λ</i>	d	0	2.75 ± 0.12	0	0	0	0
<i>r</i>²		0.9913	0.9967	0.9865	0.9865	0.9815	0.9847
Error	%	-3.0	1.4	-5.8	-2.4	-5.9	-3.7
<i>σ</i>_{est}		8.3	6.8	12.1	13.6	13.1	13.8

Table 6

Table 6. Economic assessment, where (1) anaerobic digestion; (2) anaerobic digestion plus thermal pre-treatment; (3) anaerobic digestion plus thermal pre-treatment including phenols extraction; (A) with heat recovery; (B) without heat recovery; and (M) with mortgages.

Case	Methane production (m ³ /y)	Diesel requirement (GJ/y)	Initial investment cost (€)	Incoming (€/y)	Annual costs (€/y)	NPV (M€)	IRR (%)	Payback period (y)	Limit phenol price (€/kg)
1	3,262,500	0	4,773,971	2,353,765	94,879	44	58	2	-
1+M	3,262,500	0	4,773,971	2,353,765	586,421	16	10 ⁹	1	-
2A	3,452,076	170,266	5,214,632	1,365,340	3,508,017	< 0	< 0	>20	-
2A+M	3,452,076	170,266	5,214,632	1,365,340	4,044,930	< 0	< 0	>20	-
2B	3,452,076	0	5,379,632	1,396,309	106,993	22	29	4	-
2B+M	3,452,076	0	5,379,632	1,396,309	660,894	7	10 ⁸	1	-
3A	3,740,704	164,455	26,634,323	268,877,079	28,400,223	5,324	1,127	1	55.2
3A+M	3,740,704	164,455	26,634,323	268,877,079	31,142,566	2,120	10 ¹¹	1	57.3
3B	3,740,704	0	26,799,323	269,024,236	25,115,386	5,400	1,136	1	48.6
3B+M	3,740,704	0	26,799,323	269,024,236	27,874,719	2,151	10 ¹¹	1	50.6