PHENOLS RECOVERY AFTER STEAM EXPLOSION OF OLIVE MILL SOLID WASTE AND ITS INFLUENCE ON A SUBSEQUENT BIOMETHANIZATION PROCESS

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Abstract

A promising source of high added value compounds is the Olive Mill Solid Waste (OMSW). The aim of this research was to evaluate the viability of a biorefinery approach to valorize OMSW through the combination of steam explosion, phenols extraction, and anaerobic digestion. Steam explosion treatment increased the total phenol content in the steam exploited OMSW, which was twice than that the total phenol content in raw OMSW, although some undesirable compounds were also formed. Phenol extraction allowed the recovery of 2098 mg hydroxytyrosol per kg of OMSW. Anaerobic digestion allowed the partial stabilization of the different substrates, although it was not improved by the steam explosion treatment. The economic suitability of the proposed biorefinery approach is favorable up to a phenol extract price 90.7% lower than the referenced actual price of 520€/kg.

Keywords:

Phenols recovery; Methane production rate; Improved anaerobic digestion; Olive Mill Solid Waste; Economic assessment; Steam explosion

1. Introduction

Processing industries, especially in developing countries, face the constraints of the high competitive market, space and, in most cases, rigorous government regulations on organic waste disposal (Banerjee et al., 2017). Biorefinery concept has emerged as a potential environmental-friendly waste management model where biomass is used as raw material for the production of bioenergy and biomaterials (Venkata Mohan et al., 2016). The biorefinery sector is growing circa 20% per year (Banerjee et al., 2017; EFIB, 2017). Biorefinery market sales increased to around €228 billion in 2015 and will increase to around €515 billion in 2020 (Banerjee et al., 2017; EFIB, 2017). On a sector level, the largest market potential lies in the production of biopolymers and active pharmaceutical ingredients.

A suitable source of high added value compounds is the Olive Mill Solid Waste (OMSW), which contains phenolic compounds such as hydroxytyrosol or tyrosol, which presents a high economical interest (Rubio-Senent et al., 2013b; Serrano et al., 2017a, 2017b). The economic interest of hydroxytyrosol is due to its excellent properties as pharmacological and antioxidant agent (Serrano et al., 2017a). The OMSW is generated during the olive oil manufacture through the two-phase process.

Approximately, for each ton of olive oil produced, 4 tons of OMSW are generated (Borja et al. 2005). This organic waste is mainly composed of the remains of the olive fruit, including vegetation water, skin, seed, pulp and pieces of stones (Almansa et al.,

2015). This composition entails a high content of fibers, such as lignin, hemicellulose, and cellulose.

Extraction of the added value phenolic compounds from OMSW is technically and economically complex without carrying out a pretreatment process (Rubio-Senent et al., 2013b). Among the available pre-treatments, steam explosion treatment has been widely proposed as pre-treatment method for different fibrous waste such as swine slurry (Ortega-Martinez et al., 2016), reed biomass (Lizasoain et al., 2016), corncob (Zhang et al., 2017), and even OMSW (Donoso-Bravo et al., 2016; Ortega-Martinez et al., 2016; Rincón et al., 2016). Steam explosion treatment involves high-temperature heating combined with a rapid pressure drop that physically disrupts the lignocellulosic structures turning them into soluble compounds (Capári et al., 2016; Zhou et al., 2016). Concretely, steam explosion treatment hydrolyzes hemicellulose and part of cellulose (Capári et al., 2016; Söderström et al., 2003). Other advantages of this method include low environmental impact, unnecessary recycling, and unnecessary addition of chemicals (Avellar & Glasser, 1998; Capolupo & Faraco, 2016). However, steam explosion treatment presents high energy consumption due to the steam generation (Rincón et al., 2016).

Steam explosion treatment of OMSW forms undesirable compounds for further biological processes application (Rincón et al., 2016). Due to these undesirable compounds, the implementation of a biotechnology process for the steam-exploited OMSW can be restricted. The major inhibitors for biological processes are furan derivatives, weak acids, and phenolic compounds, such as furfural, hydroxymethylfurfural, levulinic acid and formic acid (Capári et al., 2016; Ghasimi et al., 2016). Moreover, some phenolic compounds could be linked to other compounds such as sugar or insoluble/soluble fibers during steam explosion treatment forming

complex compounds (Rubio-Senent et al., 2013a). These complex phenolic compounds, including oleuropeinic acid and the glucosides of hydroxytyrosol and tyrosol, exhibit biological activities (Cardinali et al., 2011; Rubio-Senent et al., 2013a).

Anaerobic digestion can be a suitable biological post-treatment for the steam-exploited OMSW (Rincón et al., 2016). Anaerobic digestion allows the partial stabilization of the substrate recovering energy as biogas (Capári et al., 2016). Due to its high calorific power, biogas can be used to supply the energy for the proposed biorefinery approach, i.e. steam explosion, phenol extraction and anaerobic digestion (Serrano et al., 2017a; Wheatley, 1990). The proposed biorefinery presents a novel closed loop approach, wherein OMSW is valorized through high added-value compound recovery and energy production. This approach is in line with the proposed strategies for a sustainable management of organic waste, which involves recovery, recycling and refinery steps (Thi et al., 2016).

The aim of this research was to evaluate the viability of an OMSW biorefinery approach. For this, the effect of a steam explosion treatment on OMSW was evaluated. A phenol recovery process after the steam explosion treatment and its effects on the subsequent anaerobic digestion process of the different steam-exploited phases were evaluated. Finally, an economical assessment was developed for the proposed OMSW biorefinery.

2. Material and Methods

2.1. Olive Mill Solid Waste

Olive Mill Solid Waste (OMSW) was obtained from the centralized management plant “Oleícola El Tejar” located in Marchena (Seville), Spain. Previously to its characterization and use, OMSW was preserved under freeze conditions (-18 °C) to avoid spontaneous fermentation processes.

2.2. Steam explosion treatment

Steam explosion treatment was carried out using a 2-L pilot-scale reactor, with a maximal operating pressure of 42 kg/cm², equipped with a ball valve opening. All experiments were carried out on samples corresponding to around 135 g of dry weight. The samples were steamed for 5 minutes at 200 °C, prior to a rapid decompression (explosion), according to Rincón et al. (2016). After cooling the wet material was centrifuged at 4700 g (Comteifa, S.L., Barcelona, Spain) for solid and liquid separation. The centrifugation allowed the separation of steam-exploited OMSW into a solid phase (SP) and a liquid phase (LP), in a ratio of 69:31, based on VS (total Volatile Solids), respectively. Samples were stored at 4 °C before characterization.

2.3. Phenol recovery system

Phenols were recovered from LP using an industrial chromatographic system under patent (WO 2013/007850A1). The obtaining of a dephenolized liquid phase (DLP) by extraction of phenols from LP did not entail a significant decrease in DLP volume compared to LP volume.

2.4. Analysis of individual phenols

Phenols 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 µL loop). The mobile phase A was Milli-Q water acidified with 0.01 % trichloroacetic acid and acetonitrile utilizing 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).

2.5. Anaerobic digestion experimental procedure

The anaerobic digestibility of untreated OMSW and the different steam-exploited phases was evaluated by biochemical methane potential (BMP) tests. Additionally, the mixtures SP:LP and SP:DLP, in a ratio 69:31, based on VS, were also assayed.

The anaerobic inoculum was obtained from a full-scale anaerobic reactor treating sewage sludge from “COPERO” wastewater treatment plant (Seville, Spain). The main characteristics of the anaerobic inoculum were: pH= 8.2 ± 0.1 ; alkalinity= 8170 ± 50 mg CaCO₃/L; VS= $21,990 \pm 220$ mg/kg; ammoniacal nitrogen= 1495 ± 60 mg/kg.

BMP tests were carried out in 250 mL Erlenmeyer flasks at mesophilic temperature (35 °C), using a working volume of 220 mL and an inoculum to substrate ratio of 2, based on VS. Mechanical stirring was provided at 300 rpm to facilitate mass transfer between inoculum and substrate and to keep the homogeneity of the reactor contents. All these assays were carried out in triplicate. BMP reactors were sealed and the headspace of each flask was flushed with nitrogen at the beginning of the assay. The produced biogas was passed through a 2 N NaOH solution to capture CO₂, the remaining gas was assumed to be methane. The BMP tests were carried out the time interval required to

exhaust gas production and VS removal (c.a. 25-day period). Methane production was monitored daily throughout the process.

2.6. Kinetics of methane production

The kinetics of the anaerobic processes was evaluated by applying the modified-Gompertz equation to the experimental value pairs of methane production/time during BMP tests (eq. 1). The application of the modified-Gompertz equation has been previously reported in batch biomethanization processes of several organic substrates carried out, including OMSW biomethanization (Donoso-Bravo et al., 2010; Serrano et al., 2017a). This model is defined as follows:

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

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).

2.7. Chemical analyses

The following chemical analyses were carried out 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), Chemical Oxygen Demand (COD; g/kg), soluble COD (sCOD; g/L, mg/L), alkalinity

(mg CaCO₃/L), and pH were carried out according to the recommendations of the Standard Methods of APHA (2005). Total and soluble phenols were quantified by spectrophotometry through the Folin-Ciocalteu method, after an extraction with a methanol/water solution (80:20) (García et al., 2016). Ammoniacal nitrogen (mg/L) was also determined from filtered samples by spectrophotometry at 635 nm. Soluble carbohydrates (mg/L) were determined according to the colorimetric method described by Bellou and Aggelis (2013).

2.8. *Economic assessment*

Net Present Value (NPV), Internal Rate of Return (IRR) and payback period were used to study the economic profitability of the biorefinery approach proposed in this study. Two full-scale cases have been defined for this purpose: case 1, an anaerobic digestion (AD) plant, and case 2, an AD plant including both steam explosion treatment and phenol extraction sections (Figure 1). In addition, two financing scenarios were defined: (+M) with mortgages and without mortgages. The adopted assumptions to evaluate the economic profitability of the biorefinery approach were:

- An influent of 50,000 metric tons of OMSW per year. The anaerobic digester was assumed to operate 8000 h per year with a 20-year lifetime. The biogas production was obtained applying a scale-up factor of 0.85 to the G_{max} experimental values obtained for both alternatives.
- Energy Integration. The efficiency in the energy obtained through a cogeneration biogas engine is considered 33% for electricity and 55% for thermal energy (30% in hot water and 25 % in exhausted gas). The thermal energy contained in the exhausted gas from the biogas engine and an additional stream of natural gas are used to obtain the necessary high-pressure steam supply (Figure 2) (Cano et al., 2014). The electricity required for case 2 was assumed to be twice of case 1 (Serrano et al., 2017a).

- Anaerobic digester and co-generation biogas engine. An investment of 3000 € per installed kWe was assumed for the construction of the anaerobic digester and the co-generation biogas engine facilities (Serrano et al., 2017a). The cost of these sections was assumed the same in both cases and equal to the obtained for the case 1, higher than case 2 because of the higher number of installed kWe in case 1. Complementary costs ought to be considered regarding feasibility studies and administrative and authorization requirements (30,000 €) (González-González & Cuadros, 2013). Operational and maintenance costs for these sections were estimated as 2% of the construction cost. Electric energy self-supply of the anaerobic digester in both cases was assumed as 15% of the electricity generated by the co-generation biogas engine (Angelidaki et al., 2006).

- Steam Explosion. An investment of 4,200,000 € was assumed for the construction of the pre-treatment facility. This cost is based on the highest value found in the range of steam explosion inversion cost in the literature (Cano et al., 2014; Shafiei et al., 2014). A scaling exponent of 0.6 was used to adapt the inversion cost to the plant size (Aden et al., 2002). Operational and maintenance costs for this section were estimated as a 2% of the construction cost. High-pressure steam supply was 0.3 kg/kg OMSW.

- Phenol extraction section. An investment of 21,000,000 € was assumed for the construction of the phenol extraction section (Serrano et al., 2017a). Operational and maintenance costs for the phenol extraction section were estimated as 25,000,000 €/y, mainly due to the use of sorbents. The phenol extract production was obtained applying a scale-up factor of 0.85 to the experimental results, i.e. 14.9 g 10 wt% phenol extract/kg OMSW.

- Prices. 0.12 €/kWh of electricity (EUROSTAT, 2016), 0.86 €/kg of diesel (Fuel-prices-europe, 2017), 520 €/kg of 10% phenol extract (Ciriminna et al., 2016), 0.04 €/kWh of Natural gas (endesaonline.es, 2016). The use 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 (González-González & 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 steam explosion treatment on the substrate characteristics

The proposed steam explosion treatment allowed the separation of OMSW in two phases, i.e. SP and LP. Table 1 shows the physicochemical characterization of untreated OMSW and the different phases obtained after the steam explosion treatment.

According to Table 1, the values of COD and VS of the sum of the LP and the SP presented values quite similar than those obtained for untreated OMSW, i.e. only 0.7% of COD and 6.8% of VS were released during steam explosion treatment. This is in contrast to thermal pre-treatments carried out in open systems, where volatile compounds are released (Serrano et al., 2017b).

SP retained most of the organic matter, around 69.5% and 69.4% of the organic matter expressed as COD or VS, respectively (Table 1). During steam explosion treatment, the organic matter present in the OMSW was partially hydrolyzed. sCOD was increased around 10.7% in the sum of the LP and the SP respect to the untreated OMSW. This increase is mainly a consequence of the solubilization of the hemicelluloses and, to a

lesser extent, the degradation of the lignin (Hendriks & Zeeman, 2009; Singh et al., 2015). Most of the soluble compounds were displaced to the LP, which retained 6 times more sCOD than the SP (Table 1). sCOD/COD ratio indicated that 55.0% of the organic matter in the LP was in soluble form, whereas SP presented a markedly lower sCOD/COD ratio than LP, i.e. 3.8%. pH values of steam-exploited phases and untreated OMSW were similar (Table 1). Acetic acid concentration was not increased during the steam explosion treatment (Table 1).

Total phenols concentration was measured in untreated OMSW and in the different steam-exploited phases. Steam explosion treatment increased the total phenol content in the sum of the LP and the SP, which value was twice the total phenol content in OMSW, concretely 95.7% more (Table 1). This increase has been reported as a consequence of the disruption of hemicellulose and lignin, especially in acidic environments (pH of untreated OMSW was 4.79 ± 0.01) (Hendriks & Zeeman, 2009; Singh et al., 2015). Among the steam-exploited phases, most of the total phenols were displaced to the LP, i.e. total phenols were distributed 80.9% in LP and 19.1% in SP (Table 1).

Individual phenolic compounds were also measured for untreated OMSW and the steam-exploited phases (Table 2). The sum of individual phenols in both LP and SP was four times higher than in untreated OMSW (Table 2). It is interesting to notice that the sum of individual phenols was significantly lower than total phenols for OMSW and the different steam-exploited phases (Table 2). Serrano et al. (2017a) reported that at less severe pre-treatment conditions, i.e. 170°C during 60 min, the sum of individual phenols was equal to total phenols in the LP from the thermal pre-treatment of OMSW. The difference between total phenols and the sum of individual phenols could be a consequence of the formation of complex phenolic compounds, such as soluble lignin

compounds, during the steam explosion treatment, as reported by Rubio-Senent et al. (2013a).

Among the different individual phenols, hydroxytyrosol presented the highest interest due to its higher concentration respect to the other individual phenols and to its antioxidant properties (Ciriminna et al., 2016; Visioli et al., 1998). During steam explosion, the amount of hydroxytyrosol was increased and it was mainly displaced to LP. The amount of hydroxytyrosol in LP was close to four times higher than in the untreated OMSW. Only 12.5% of hydroxytyrosol was retained in the SP.

It is worth to notice that steam explosion treatment also entailed the formation of undesirable phenolic compounds, i.e. furfural, hydroxymethylfurfural, and vanillin (Hendriks & Zeeman, 2009). Hydroxymethylfurfural and vanillin reached concentrations of 77 ± 9 mg/L and 42 ± 3 mg/L, respectively, in LP. Vanillin was mainly retained in the SP, reaching a concentration of up to 260 ± 30 mg/L. The formation of these undesirable compounds was reported to be related to the degradation of hemicellulose (Fang et al., 2011; Hendriks & Zeeman, 2009; Singh et al., 2015).

3.2. Phenols extraction from the liquid phase (LP)

After steam explosion treatment, the subsequent extraction process by an industrial chromatographic system allowed the recovery of phenols from LP and obtaining DLP. The proposed extraction process presented an efficiency of 48.1% and 82.3% for total phenols and for the sum of the measured individual phenols, respectively. The extraction efficiency for the sum of the measured individual phenols was slightly higher than that described by Serrano et al. (2017b) and Serrano et al. (2017a), in low- and high-temperature thermal pretreatments, for which extraction efficiencies of around 70-75% were reported. Extraction of hydroxytyrosol presented an efficiency of 84.5% and allowed the recovery of 2098 mg of hydroxytyrosol per kg of OMSW (Table 2).

Additionally, extraction process allowed decreasing the presence of undesirable compounds, i.e. hydroxymethylfurfural and vanillin, in DLP, with extraction efficiencies higher than 87.0%. Part of the non-soluble organic matter in LP was also retained by the chromatographic system during the extraction process. In fact, DLP presented a non-soluble COD concentration 65.6% lower than that contained in LP (Table 1).

3.3 Stability of the anaerobic process, biodegradability, and inhibitory compounds

Anaerobic digestion allows the recovery of energy and the stabilization of the OMSW after the extraction process. Anaerobic digestion of the untreated OMSW has been compared to the anaerobic digestion of the different steam-exploited phases and mixtures. The stability of the biomethanization of the untreated OMSW and the different steam-exploited phases and mixtures was evaluated in accordance with the pH, alkalinity and acetic acid concentration at the end of the BMP tests (Table 3). In all cases, pH values were in the optimal range for methanogenic activity, i.e. from 6.5 to 7.5, at the end of the BMP tests (Liu et al., 2008). Alkalinity showed a mean value of 7652 ± 204 mg CaCO₃/L for the different BMP tests, whereas acetic acid was not detected in any of the cases (Table 3). The described pH values, the high alkalinity concentration and the absence of acetic acid indicated that acidification processes did not occur during the anaerobic processes. At the end of the biomethanization of untreated OMSW, the steam-exploited phases and mixtures, ammoniacal nitrogen remained at lower concentrations than the wide inhibition range described in the literature, i.e. 1.7-15 g/L (Table 3) (Chen et al., 2008).

Values of biodegradability, calculated as VS removal during the BMP tests, are shown in Table 3. SP showed the lowest biodegradability, i.e. 53.9 ± 5.2 %. The highest

biodegradability values described for LP and DLP were in line with the higher sCOD/COD ratios of both phases respect OMSW and SP (Table 1).

Due to the described solubilization of organic matter during the steam explosion treatment (Table 1), an enhancement in the biodegradability was expected for SP:LP and SP:DLP, in comparison to untreated OMSW. However, SP:LP and SP:DLP showed biodegradability values similar than that obtained for the untreated OMSW (Table 3).

The production of recalcitrant or inhibitory products during the steam explosion treatment could explain the biodegradability values of the mixtures SP:LP and SP:DLP in relation to the untreated OMSW (Carrere et al., 2016; Hendriks & Zeeman, 2009).

sCOD and soluble carbohydrates were also measured at the end of the BMP tests (Table 3). Their low values in both cases indicated that the BMP tests were run up to exhaust the degradation of the biodegradable fraction of each substrate and mixture. The decrease of the biodegradable fraction during the anaerobic process allowed reducing the polluting potential of the OMSW and the steam-exploited phases (Table 3).

Table 4 shows the soluble phenol concentration and the individual phenolic compound concentrations at the end of the BMP tests for each substrate and mixture tested. As can be seen, LP presented a soluble phenol concentration markedly higher than that obtained for the other substrates and mixtures (Table 4). The final concentration of the measured individual phenolic compounds indicated that most of them were completely degraded during the anaerobic digestion, although some compounds were still detected in LP, i.e. 3,4-dihydroxyphenylglycol and hydroxytyrosol (Table 4). Despite the presence of these compounds, the biodegradability of LP was one of the highest (Table 3).

3.4 Methane yields and kinetic study

Figure 3A and 3B shows the methane yield coefficient in the BMP tests throughout the experimental time for the different substrates and mixtures tested. As can be seen, most of the substrates and mixtures exhausted the biogas production after a 10-day period. Only LP required a significantly longer time to finalize the degradation of the substrate, i.e. around 23-day period (Figure 3).

Table 5 summarizes the parameters obtained from the application of the modified Gompertz equation to the experimental data shown in Figure 3A and B, i.e. G_{max} , R_{max} , and λ . Additionally, r^2 , Error (%) and standard error of estimate (σ_{est}) were determined to evaluate the goodness-of-fit. The high values of r^2 and low values of Error and σ_{est} validated the application of the modified Gompertz equation to the obtained experimental data.

G_{max} values are shown in Table 5. LP showed a G_{max} value of 346 ± 7 mL/g VS, i.e. 23.6% higher than the obtained for the untreated OMSW. This G_{max} value was higher than the reported for LP of OMSW after a thermal pre-treatment at 170° during 60 min by Serrano et al. (2017a), which described a value of 305 ± 3 mL/g VS. The high G_{max} value in LP in the present study could be a consequence of a lower hydroxymethylfurfural concentration in LP respect the concentration described by Serrano et al. (2017a) in the same fraction, i.e. 4.5 mg/kg TS and 12.7 mg/kg TS, respectively. DLP showed the highest G_{max} value, around 26.8% higher than that obtained for the untreated OMSW. A similar value of G_{max} of DLP in the present study was reported for DLP of OMSW after a thermal pre-treatment at 170° during 60 min (Serrano et al., 2017a). In both DLP fractions, hydroxymethylfurfural concentration was below 4.5 mg/kg TS. SP showed the lowest G_{max} values, around 26.5% lower than that obtained for DLP. G_{max} values for the mixtures SP:LP and SP:DLP (Table 5) were compared to the theoretical values calculated from the G_{max} values of the individual

biomethanization of the steam-exploited phases and the mixture ratio, indicating that synergy or antagonism effects were not detected.

R_{max} values described a similar behavior that the obtained for G_{max} , except for LP and SP:LP. LP presented the lowest value of R_{max} , around 26.4% and 41.8% lower than those obtained for the untreated OMSW and DLP, respectively. The differences between LP and DLP indicated that inhibitory compounds were effectively reduced in DLP by the phenol extraction process. Among the soluble phenol in LP, hydroxymethylfurfural can be considered as the most probable compound affecting R_{max} due to its inhibitory potential (Carrere et al., 2016; Ghasimi et al., 2016), even though G_{max} was not affected as previously indicated. Probably due to the same inhibitory compounds, SP:LP presented a R_{max} value around 17% lower than those obtained for OMSW and SP:DLP, whose R_{max} values were very similar (Table 5). R_{max} values for the mixtures SP:LP and SP:DLP (Table 5) were compared to the theoretical values calculated from the R_{max} values of the individual biomethanization of the steam-exploited phases and the mixture ratio, indicating that synergy or antagonism effects were not detected. According to the obtained results, steam explosion treatment did not entail a significant enhancement of the subsequent anaerobic digestion step.

3.5. Economic assessment

The main results of the economic assessment are shown in Table 6. Both cases 1, i.e. anaerobic digestion, and case 2, i.e. steam explosion treatment, extraction process and anaerobic digestion (Figure 1), showed positive NPVs and very high IRR at the end of the life of the projects (Table 6). Results of the same order of magnitude were found in the literature for anaerobic digestion of agroindustrial waste, including olive mill solid waste (González-González & Cuadros, 2013). The payback periods were very short, no more than 2 years in both cases. Although the case 2 represented the most preferred

scenario from an economic standpoint, this case also involved a very high initial investment, 28.3 M€. The high profitability of phenol extraction and high initial inversion were also showed in previous works with OMSW using thermal pretreatment instead of steam explosion (Serrano et al., 2017a). For all cases, in those the mortgage (+M) were necessary, the NPV would be reduced but the IRR would be increased (Table 6). Even though the future trend of food waste valorization by anaerobic digestion is very promising (Thi et al., 2016), combination with extraction of high added values compounds results in an even more economically attractive management option.

Figure 4A shows the influence of the price of the phenol extract on the NPV of cases 2 and 2+M. The phenol extract price influenced the NPV linearly. Cases 2 and 2+M have a positive NPV for a phenol extract price higher than 41.90 €/kg and 43.67€/kg, respectively. Figure 4B shows the NPV for cases 1 and 2 with and without mortgage for a low range price for phenol extract. For a price lower than 43.80 €/kg, case 1 would be the best option in terms of NPV. For a higher value of the extract, case 2 would be always the best option. Second best option would be case 1+M for a price lower than 42.55 €/kg, case 2 for a price between 42.55 €/kg and 43.80 €/kg, case 1 for a price between 43.80 and 48.40 €/kg, and case 2+M for a price higher than 48.40 €/kg. According to these results, steam explosion with phenol extraction and anaerobic digestion would always be the best option for a phenol extract price higher than 48.40 €/kg, 90.7% lower than the referenced actual price of 520 €/kg (Ciriminna et al., 2016). The proposed novel biorefinery approach is a promising management method for OMSW which combines the stabilization of this waste together with a high profitability through the added-value compound recovery and energy production.

4. Conclusions

Steam explosion treatment increased the total phenol content in the sum of the LP and the SP twice the total phenol content in OMSW, although some undesirable compounds were also formed. Phenol extraction process allowed the recovery of 2098 mg hydroxytyrosol/kg OMSW. Additionally, the extraction process decreased undesirable compounds around 87.0% in DLP. Anaerobic digestion allowed the partial stabilization of the different substrates, although it was not improved by the steam explosion treatment. The economic suitability of the proposed biorefinery approach is favorable for phenol extract prices higher than 48.40 €/kg, 90.7% lower than the referenced actual price of 520€/kg.

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Figure Captions

Figure 1. Process block flow diagram of the proposed management strategies for OMSW treatment.

Figure 2. Energy and matter block flow diagram for the combination of steam explosion, phenols recovery and anaerobic digestion processes.

Figure 3(A) and 3(B). Variation of the accumulated methane production with time for olive mill solid waste and steam-exploited phases and mixtures.

Figure 4(A) Influence of the price of the phenol extract on the profitability of the phenols extraction alternative. **4(B)** Influence of the price of the phenol extract on the best alternative selection. (1) anaerobic digestion; (2) anaerobic digestion plus steam explosion treatment, including phenols extraction; and (M) with mortgages.

Figure 1.

Case 1

Case 2

AD: Anaerobic digester and biogas engine

SEP: Steam Explosion system

ES: Centrifugation and industrial chromatographic system for phenols recovery

- 1) Untreated OMSW
- 2) Stabilized digestate
- 3) Electricity
- 4) Thermal energy
- 5) High pressure steam
- 6) Pre-treated OMSW
- 7) Dephenolized OMSW
- 8) Extracted phenols

Figure 2.

Figure 3.

A)

B)

Figure 4.

A)

B)

Table 1. Physicochemical characterization of untreated OMSW and different steam-exploited fractions.

		Untreated OMSW	Solid phase (SP)	Liquid phase (LP)	Dephenolized liquid phase (DLP)
Mass	kg/kg of treated OMSW	1.00	0.47	4.86	4.86
TS	g/L	266 ± 4	356 ± 2	17 ± 1	12 ± 1
FS	g/L	16 ± 1	10 ± 1	3 ± 1	2 ± 1
VS	g/L	250 ± 4	346 ± 3	14 ± 1	10 ± 1
COD	g/L	322 ± 11	474 ± 20	20 ± 1	14 ± 2
sCOD	g/L	57 ± 11	18 ± 1	11 ± 1	10 ± 1
sCOD/COD ratio	%	17.7	3.8	55.0	71.4
Total Phenols	g Gallic Acid/kg VS (g/L)	24 ± 2 (5.90 ± 0.38)	14 ± 1 (4.71 ± 0.16)	131 ± 9 (1.92 ± 0.13)	99 ± 6 (1.00 ± 0.06)
pH		4.79 ± 0.01	4.95 ± 0.03	4.80 ± 0.01	5.30 ± 0.01
Acetic Acid	mg/L	n.d.	n.d.	n.d.	n.d.

n.d., non detected; Traces, <0.01 mg/L

Table 2. Individual phenolic compounds concentration of untreated OMSW and different steam-exploited phases.

		Untreated OMSW	Solid phase (SP)	Liquid phase (LP)	Dephenolized liquid phase (DLP)
Total phenols (Folin-Ciocalteu method)	mg Gallic Acid/L	5902 ± 379	4711 ± 169	1924 ± 135	998 ± 57
Sum of individual phenols	mg Gallic Acid/L	1127	1330	825	146
3,4-Dihydroxyphenylglycol	mg/L	157 ± 5	35 ± 4	39 ± 1	5 ± 1
Hydroxytyrosol 4-β-D-Glucoside	mg/L	88 ± 5	40 ± 5	30 ± 4	17 ± 2
Hydroxytyrosol	mg/L	540 ± 13	640 ± 28	432 ± 21	67 ± 8
Tyrosol	mg/L	122 ± 9	163 ± 12	91 ± 6	11 ± 1
Homovanillic acid	mg/L	n.d.	1 ± 0	1 ± 1	1 ± 1
Vanillic acid	mg/L	15 ± 2	14 ± 1	6 ± 1	Traces
Hydroxymethylfurfural	mg/L	n.d.	Traces	77 ± 9	10 ± 1
Vanillin	mg/L	76 ± 4	260 ± 30	42 ± 3	18 ± 2
p-Coumaric acid	mg/L	32 ± 2	n.d.	5 ± 1	n.d.
4-Ethylphenol	mg/L	n.d.	32 ± 6	n.d.	n.d.

n.d., non detected; Traces, <0.01 mg/L

Table 3. pH, alkalinity (mg CaCO₃/L), acetic acid (mg/L), ammonia nitrogen (mg/L), biodegradability (% based on VS), sCOD (mg O₂/L), and soluble carbohydrates (mg/L) in the BMP tests at the end of the experimental time.

		OMSW	SP	LP	DLP	SP:LP	SP:DLP
pH	(%)	7.4 ± 0.1	7.6 ± 0.2	7.4 ± 0.1	7.3 ± 0.1	7.4 ± 0.1	7.3 ± 0.1
Alkalinity	(mg CaCO₃/L)	7676 ± 42	7591 ± 121	8048 ± 142	7572 ± 121	7499 ± 153	7523 ± 155
Acetic acid	(mg/L)	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Ammoniacal nitrogen	(mg/L)	613 ± 9	696 ± 110	640 ± 21	674 ± 46	670 ± 59	738 ± 75
Biodegradability	(%, based on VS)	66.4 ± 0.2	53.9 ± 5.2	83.6 ± 3.8	78.6 ± 3.9	65.0 ± 7.9	60.5 ± 3.1
sCOD	(mg O₂/L)	121 ± 12	79 ± 4	290 ± 17	220 ± 13	133 ± 19	113 ± 17
Soluble carbohydrates	(mg/L)	24 ± 6	25 ± 6	36 ± 2	31 ± 4	31 ± 1	23 ± 2
<i>n.d., non detected</i>							

Table 4. Soluble phenols and individual phenolic compounds concentration at the end of the BMP tests.

		OMSW	SP	LP	DLP	SP:LP	SP:DLP
Soluble phenols (Folin-Ciocalteu method)	mg Gallic Acid/L	42 ± 3	21 ± 2	114 ± 4	63 ± 2	49 ± 3	30 ± 2
Sum of individual phenols	mg Gallic Acid/L	-	-	6.4	0.5	-	-
3,4-Dihydroxyphenylglycol	mg/L	Traces	Traces	2.2 ± 0.1	0.5 ± 0.1	Traces	Traces
Hydroxytyrosol 4-β-D-Glucoside	mg/L	n.d.	n.d.	Traces	n.d.	Traces	Traces
Hydroxytyrosol	mg/L	n.d.	Traces	4.4 ± 0.3	n.d.	n.d.	n.d.
Tyrosol	mg/L	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Homovanillic acid	mg/L	n.d.	Traces	Traces	n.d.	n.d.	n.d.
Vanillic acid	mg/L	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Hydroxymethylfurfural	mg/L	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Vanillin	mg/L	n.d.	n.d.	Traces	n.d.	n.d.	n.d.
p-Coumaric acid	mg/L	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
4-Ethylphenol	mg/L	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d., non detected; *Traces*, <0.01 mg/L

Table 5. Kinetics parameters obtained from the modified-Gompertz equation applied to the different BMP tests.

	OMSW	SP	LP	DLP	SP:LP	SP:DLP
G_{max} (mL/g VS)	280 ± 3	261 ± 1	346 ± 7	355 ± 4	294 ± 2	261 ± 3
R_{max} (mL/(g VS·d))	106 ± 8	90 ± 3	78 ± 9	134 ± 1	91 ± 5	108 ± 9
λ (d)	0	0.17 ± 0.05	0	0	0	0
r^2	0.9771	0.9957	0.9414	0.9697	0.9882	0.9728
Error (%)	-3.9	-2.3	-9.1	-3.8	-4.5	-6.5
σ_{est}	12.2	5.4	26.6	17.3	9.7	12.0

σ_{est} , standard error of estimate.

Table 6. Economical assessment

Case	Methane production (Nm ³ /year)	Natural Gas requirement (kWh/year)	Initial investment cost (€)	Incoming (€/year)	Annual costs (€/year)	NPV (M€)	IRR (%)	Payback period (years)	Limit phenol price (€/kg) ^b
1	3,000,000	0	3,167,480	1,423,679	62,750	26.4	52	2	-
1+M	3,000,000	0	3,167,480	1,423,679	388,882 ^a	9.4	10 ⁸	1	-
2	2,350,000	7,609,779	28,367,480	32,9666,753	25,451,141	6742	1339	1	41.90
2+M	2,350,000	7,609,779	28,367,480	32,9666,753	28,371,935 ^a	2687	10 ⁹	1	43.67

^a Including mortgage repayment quote^b NPV = 0