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1	Is the anaerobic digestion a current feasible alternative for the
2	energetic valorisation of the olive mill solid waste? A critical review
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11	ABSTRACT
12	The use of olive mill solid waste (OMSW) for energy production has been promoted
13	mainly through combustion processes. However, the European Union promotes the
14	substitution of combustion in favour of greener alternatives. Several publications have
15	stated that the energy obtained from anaerobic digestion (AD) is a feasible waste-to-
16	energy technology for OMSW. However, the question of which energetic method, AD or
17	combustion, is better for the energetic valorisation of OMSW has lacked of a reliable
18	energy balance that can answer it. The present research work aims to answer this question
19	by evaluating the energetic potential of the biomethanization of OMSW, in comparison
20	with the current combustion technology, based on the review of the available scientific
21	literature. The present analysis demonstrates that AD of OMSW can generate a net energy
22	production in the same range than the obtained by the OMSW combustion, enabling the
23	AD as a greener alternative to combustion but not clearly offering a surplus of energy

24 production.

Keywords: olive mill solid waste; anaerobic digestion; combustion; drying; energy
 production; pre-treatment

## **3 1. INTRODUCTION**

The olive oil is one of the most important agricultural products in Mediterranean climate 4 areas. Despite inter-annual variations, the global olive oil production has increased 5 around 30% in the last 20 years, reaching annual productions above 3 million tons.<sup>1</sup> This 6 7 increase of the production is very noteworthy taking into account the competition with other low-cost vegetable oils as the palm oil, with a high increasing global demand in the 8 last years.<sup>2</sup> The most extended industrial process to obtain olive oil is the two-phases 9 system, which has gained attention in many countries in decrement of the three-phases 10 system. Although the three-phases system obtains a higher olive oil recovery, implies 11 12 high water consumption and, hence, the generation of vast volumes of wastewater to be treated.<sup>3</sup> In Spain, the highest producer worldwide (30% globally) around 97% of the 13 14 olive oil is obtained through the two-phase system, as well as in other countries with water shortages such as Italy. Greece or Chile.<sup>4,5</sup> 15

As by-product, the two-phase system generates four tons of olive mill solid waste 16 (OMSW) per produced ton of olive oil.<sup>6</sup> The OMSW is a thick organic substrate 17 composed by the husks, fruit pulp and olive vegetation water.<sup>7</sup> Instead of a waste to be 18 treated, the OMSW has been considered a resource for obtaining energy through 19 20 combustion. In the south of Spain, around 47% of the generated OMSW is destined to energy production through combustion in centralized co-generation plants.<sup>8</sup> These plants 21 produced around 20% of the total renewable energy of the region, i.e. 809.0 GWh per 22 23 year, equivalent to the domestic consumption of a population of 513,921 inhabitants, or 188,685 households.<sup>8</sup> Additionally, around 40% of the OMSW is used for heat generation 24 during the extraction of olive pomace from the own OMSW.<sup>8</sup> The use of OMSW for 25

energy production has been promoted by government subsidies for this industry.
 However, the European Union is stablishing a hierarchy on waste-to-energy where the
 combustion belongs to the second last desirable category, i.e. other recovery, being
 necessary to favour the implementation of greener alternatives from higher categories.<sup>9</sup>

One management alternative already implemented is composting, where the OMSW is 5 stabilized in the form of an organic amendment to return nutrients to the soil.<sup>8,10</sup> However, 6 7 composting is considered a waste management method rather than a valorisation method due to the low economic value of the generated product, entailing a cost to the olive oil 8 sector.<sup>11</sup> Furthermore, the implementation of composting as management method for the 9 OMSW would entail a decrease in the production of renewable energy produced by 10 combustion.<sup>12</sup> Due to these drawbacks, composting is a management method applied to 11 only 14.3% of the OMSW,<sup>8</sup> and mainly used by small producers that have no access to 12 the existing centralized management plants. 13

14 Another explored alternative for the management and valorisation of the OMSW is the 15 anaerobic digestion (AD) technology. AD is a robust and well-developed technology that has been applied in wastewater treatment, management of animal manures, energy crops, 16 food waste or agricultural waste.<sup>13-15</sup> The AD processes occur in the absence of oxygen, 17 where the organic matter is degraded by the action of microorganisms to biogas (methane 18 and CO<sub>2</sub>), which can be used as a renewable source of energy.<sup>11</sup> Up to date, the research 19 on AD of OMSW for biogas production has mainly focussed on the optimization of the 20 21 methane production by determining the most favourable operational parameters or by implementing different pre-treatment technologies.<sup>14,16,17</sup> The use of pre-treatments 22 23 technologies aims to improve the methane yield, as well as to reduce the biodegradation time, by the break-down of the lignocellulosic fibres and/or the removal of phenolic 24 compounds contained in OMSW.<sup>18</sup> The break-down of the lignocellulosic fibres aims to 25

facilitate the hydrolysis of the OMSW, which uses to be the rate limiting step for solid
 waste in AD.<sup>19</sup>

Several publications have stated that the energy obtained from the AD is a feasible 3 energetic alternative to the combustion process for different biomasses.<sup>20,21</sup> However, 4 these studies lack of reliable energy balances that can assess this statement. The present 5 research work aims to evaluate the energetic potential of the biomethanization of OMSW, 6 7 in comparison with the current combustion technology. This evaluation has been based on the review of the experimental data for the AD of OMSW in the literature to be able 8 to develop a complete energy balance for different scenarios. Furthermore, an analysis of 9 10 the different operation alternatives for AD, i.e. implementation of pre-treatments, operation mode, etc., proposed in the literature to maximize energy production has also 11 12 been analysed.

#### 13 2. MATERIALS AND METHODS

#### 14 **2.1 Literature review scope**

15 The review scope was focused on the analysis of the indexed publications at Journal Citation Report (JCR) during the last 17 years (2003-2019) on anaerobic digestion of 16 17 OMSW from the two-stage olive oil extraction process (Table 1). The review offers an overview of the most relevant parameters related to the anaerobic digestion of OMSW, 18 19 including the characteristics of the substrate, operational parameters, methane production or biodegradability. Results derived from co-digestion of the OMSW with other organic 20 21 substrates were not considered in the present research since its practical application is strongly dependent on the seasonal availability of a co-substrate at the specific location. 22 The units of generation of methane, or so-called methane yield, were set to ml CH4 23 produced per g VS (volatile solids) treated. When authors expressed the methane yield in 24

1 terms of mL CH<sub>4</sub>/g COD (chemical oxygen demand) removed or mL CH<sub>4</sub>/g VS removed,

2 the substrate biodegradability was used to re-calculate the methane yield for comparison

3 of the results.

Table 1

4

## 5 2.2 Energetic valorisation comparative

An energy balance was undertaken to compare the net energy production per kilogram of
OMSW that can be obtained via AD with that generated by OMSW combustion (Figure
1).

Figure 1
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9

In both AD and combustion, a cogeneration engine for simultaneous production of 10 11 electricity and heat has been used. Net energy production, defined as the difference 12 between the energy production and the energetic requirement of each system, was used as the main comparison parameter. Net energy production, i.e. the sum of the thermal 13 14 energy and the electricity, is expressed as total equivalent energy production (kJeg/kg OMSW). For this, factors of 1.1 kJeq/kJthermal and 2.6 kJeq/kJelectricity, which are based on 15 average values for energy production efficiencies, were applied to the values of net 16 thermal energy and electricity, respectively.45 AD systems, with and without OMSW pre-17 treatment, were defined based on the information obtained from the review of the 18 19 available literature (Table 1).

#### 20 3. RESULTS AND DISCUSSION

#### **1 3.1 Energetic valorisation parameters**

Based on the literature review, all consideration and assumptions adopted for the
operational parameters of the comparative can be found next:

4 - OMSW composition. The same total solids (TS) and VS composition for OMSW was 5 set in all cases, i.e. 266 g TS/kg OMSW and 250 g VS/kg OMSW. This composition was selected as it is within the range reported in literature for the different OMSWs (Table 1). 6 The revision of the available literature on AD of OMSW showed that TS concentration 7 (wt%) of the OMSW was in a range from 23 to 28% in the most of the cases, although 8 some authors reported values of up to 83.3%<sup>29</sup> and 53.5%.<sup>23</sup> The lowest TS concentrations 9 corresponded to the characterization of OMSW after a thermal (170°C, 60 min)<sup>44</sup> and 10 steam explosion (200°C, 5 min)<sup>46</sup> pre-treatments, i.e. 10.9% and 7.3%, respectively. Thus, 11 12 these low TS concentrations are explained by the addition of the steam applied for heating. Regardless of the TS content, the ratio between VS and TS was very constant 13 throughout the reviewed literature with a mean value of  $0.91 \pm 0.04$  (Table 1). The 14 consensus in the TS content and TS/VS ratio in the reviewed literature facilitate the 15 implementation of the energetic valorisation comparative in the present manuscript. 16

OMSW drying. A drying stage is needed before OMSW combustion (Figure 1). For
this, 2176 kJ/kg OMSW are reported to be necessary to reduce the moisture content to
10%wt in a trammel.<sup>47</sup> An electricity consumption of 18 kJ/kg OMSW for the
transportation of the OMSW during the drying process was also considered in the OMSW
drying process.<sup>48</sup> More details about these calculations are detailed in the supplementary
material (Section S.2 and Calculation tool file).

- AD process of OMSW. The TS concentration in the reactor during the AD process was
 set at 10%wt.<sup>49</sup> Both organic loading rate (OLR) and VS biodegradability values were

6

obtained from the reviewed research works when possible. Default values were set if not 1 given information for OLR and VS biodegradability as 1 g VS/(Lreactor d) and 70%, 2 respectively.<sup>44,46</sup> The electricity consumption was 1800 kJ/m<sup>3</sup> fed to the reactor for 3 pumping and 300 kJ/( $m_{reactor}^3$ ·d) for stirring.<sup>50</sup> The thermal energy requirement was 4 estimated as the necessary energy to heat the fed stream to AD temperature assuming a 5 heat capacity of 4.18 kJ/kg.50 An extra 10% of thermal energy was considered to 6 compensate thermal losses through the AD reactor walls.<sup>51</sup> An average environmental 7 temperature of 20 °C was assumed. The methane production was set on the values 8 reported in literature for each alternative (Table 1). More details about these calculations 9 10 are detailed in the supplementary material (Section S.3 and Calculation tool file).

Cogeneration-combined heat and power engine (CHP). The efficiency in the energy
 obtained through a cogeneration biogas engine is 39% for electricity and 45% for thermal
 energy production.<sup>52</sup> In the case of the cogeneration engine coupled to the OMSW
 combustion boiler, the used efficiencies are 22% and 45% for electricity and heat
 respectively.<sup>8</sup>

- Composting. The obtained digestate from AD was assumed to be stabilized through 16 composting. Direct application of digestate to the soil was not considered since it is a 17 practice that is increasingly limited in the legislation, forcing the implementation of 18 stabilization processes, such as composting, before the reuse of the anaerobic digestate.<sup>53</sup> 19 The digestate is centrifuged in order to separate all remaining solids for composting. The 20 electricity requirement of this process, centrifugation and composting, was set on 3.5 21 kWh per m<sup>3</sup> of digestate.<sup>54</sup> A fraction of the obtained liquid phase is recirculated to the 22 23 AD reactor for dilution. The electricity required for the liquid pumping was included in the fed pumping requirement for AD. 24

Pre-treatment of OMSW for AD. Only those identified pre-treatments that showed an
improvement in methane yield for AD with respect to the reference case without pretreatment were considered in the energetic comparison (Table 1). Impulsion and stirring
electricity consumptions are estimated as described for AD.

5 - Thermal pre-treatment. When no data reported for thermal pre-treatments, addedsteam:OMSW mass ratio has been considered equal to  $0.3^{55,56}$  and  $1.0^{57}$  for steam 6 explosion and high-temperature conventional thermal pre-treatments (higher than 100 7 °C), respectively. A heat recovery was included in these pretreatments according to 8 Franchetti,<sup>58</sup> reducing an 80% the required thermal energy. The thermal energy demand 9 10 of these systems was calculated as the product of the amount of injected steam by its enthalpy (referred to water at 20 °C). Thermal energy requirement for low-temperature 11 pre-treatments (less than 100 °C) was calculated as the necessary energy to raise the 12 temperature of the OMSW to the pre-treatment temperature assuming the thermal 13 capacity of the OMSW equal to 4.18 kJ/kg, as done for heating in AD. Dephenolization 14 15 after thermal treatments involves the centrifugation of the thermally pretreated OMSW stream.<sup>18</sup> The centrifugation electricity requirement was fixed at 2 kWh per ton fed to the 16 centrifuge.59 17

- Energy integration. For the case of OMSW combustion, thermal energy and electricity 18 requirements due to OMSW drying were deducted from the energy produced by the CHP. 19 Same was done for the energy requirements of AD of OMSW, including pre-treatment 20 21 when used, and composting. When thermal energy requirement exceeded thermal energy 22 production, an external energy source was included. The external thermal energy demand 23 was expressed as a negative value in the balance. As thermal energy, a factor of 1.1 kJ<sub>eq</sub>/kJ<sub>thermal</sub> was applied for the calculation of the net energy production.<sup>45</sup> When thermal 24 pre-treatments are applied, energy recovery was considered setting the leaving 25

temperature of the pretreated OMSW stream at the AD temperature value. In these cases,
thermal energy requirement from AD just accounts for heat losses compensation. When
phenols extraction is applied after the thermal pre-treatment, the energy requirement for
heating the dephenolised liquid to raise the AD temperature was included. More details
about these calculations are detailed in the supplementary material (Sections S.1, S.2, S.3
and Calculation tool file).

#### 7 3.2 Review of the anaerobic digestion of OMSW

Biomethane potential test (BMP) procedure of OMSW accounts above half of the 8 reviewed literature (Table 1). BMP procedure provides baseline data for the performance 9 of AD.<sup>60</sup> Semicontinuous operation experiments have to be set for further studying 10 stability and performance for long-term operation. Around 40% of the reviewed literature 11 12 included the long-term operation of reactors in semi-continuous mode, indicating a high interest in the development of the AD of OMSW (Table 1). The scaling-up of the AD of 13 14 OMSW to pilot or demonstration scale has not been reported, showing that the 15 transference of the acquired knowledge to the industrial sector is still not enough to attract its interest. Regardless of the used experimental set-up, all the reviewed studies reported 16 a mesophilic temperature range, i.e. around 35-37°C for operating the AD process (Table 17 1). 18

19 Methane yield values reported in the literature for BMP of OMSW without any pre-20 treatment varied in a wide range from 154 mL CH<sub>4</sub>/g VS<sup>26</sup> to 415 mL CH<sub>4</sub>/g VS,<sup>61</sup> 21 although most of the reported values are closed to the average methane yield value of 287 22  $\pm$  75 mL CH<sub>4</sub>/g VS (Table 1). The average methane yield value for BMP of thermally 23 pre-treated OMSW is 307  $\pm$  40 mL CH<sub>4</sub>/g VS, which means just a slight enhancement 24 respect the AD of OMSW without pre-treatments, i.e. 6.8% higher (Table 1). Other authors also proposed the addition of chemical reagents during the thermal treatments to
 increase the effect over the OMSW.<sup>23,24</sup>

Most of the authors reporting semi-continuous long-term operation, i.e. at least 3 3 4 hydraulic retention times per condition, reported that the stability of the AD of OMSW was maintained at OLR around 1 g VS/(Lreactor d) (Table 1). On these studies, higher 5 OLRs usually implied the inhibition of the process by the accumulation of volatile fatty 6 acids and phenolic compounds.<sup>35,42,44</sup> Other authors reported operations at much higher 7 OLRs than 1 g VS/(L<sub>reactor</sub>·d) without compromising reactor performance, although in 8 most of the cases the experimentation time was less than 2 hydraulic retention times per 9 condition,<sup>36-38,41</sup> which may not be enough for triggering the inhibition of the anaerobic 10 digestion process. 11

Rincón, et al.<sup>40</sup> reported a stable operation at a very high OLR, i.e. 15.5 g VS/( $L_{reactor}$ ·d), 12 the marked difference with other authors in the field was the use of a first hydrolysis step 13 14 before the biomethanization, resulting in the feeding of a liquid enriched in biodegradable compounds instead of raw OMSW. Similarly, some authors have proposed the use of 15 two-stage AD for OMSW, where a first acidification stage is carried out to enhance the 16 hydrolysis of the substrate.<sup>39,40,42</sup> The methane production rate obtained through two-17 stage AD widely varied from 200 to 370 mL CH<sub>4</sub>/(g VS·d) (Table 1). Therefore, the 18 implementation of an acidification stage is likely not attractive for OMSW as the achieved 19 methane productions were in the same range than for the single-stage AD. 20

It is worth mentioning that the lowest methane production rate corresponded to the obtained for the anaerobic digestion of OMSW after thermal pre-treatments and dephenolization of thermally treated OMSW.<sup>44,46</sup> This implies that thermal pre-treatments could not be suitable for the energetic valorisation of the OMSW, although still can have interest due to the solubilization and recovery of valuable phenolic compounds.<sup>62</sup>

#### **1 3.3 Energetic valorisation comparative**

Table 2 shows the comparison in terms of net energy production of the AD of OMSW against OMSW combustion as described in section 2.2. According to the calculations, OMSW combustion has a total equivalent energy production of 3004 kJ eq./kg OMSW (more details about the calculations in the supplementary material, section S.2 and Calculation tool file). For the calculation of methane production expressed as L CH4/kg OMSW in both BMP and semicontinuous mode, a scale up factor of 0.90 was applied to adjust the methane yield from BMP to a continuous operation mode at 1 g VS/(L<sub>reactor</sub>·d).

Table 2

9

The average net energy production obtained without OMSW pre-treatment is  $3250 \pm 1333$ 10 kJeq/kg OMSW. If the extreme values, 34 and 6581 kJeq/kg OMSW, are excluded, the 11 12 average remain almost the same, 3243 kJeq/kg OMSW, but the standard deviation is reduced to 852 kJeq/kg OMSW. As a reference, a minimum methane production of 62.58 13 L CH4/kg OMSW is needed in an AD without pre-treatment to obtain the same amount 14 of net energy production as that obtained via OMSW combustion (calculations detailed 15 in Section S.4 and Calculation tool file). Most of the articles reporting data of AD of 16 17 OMSW without pre-treatments reached enough methane production to match the energy produced through the combustion (Table 2). Some authors reported methane production 18 values that did not reach the OMSW combustion energy production, although the values 19 were in a very close range, i.e. less than 10% of difference.<sup>18,27,30,37</sup> Otherwise, some 20 authors described methane production values markedly lower than the required, resulting 21 in very low net energy production. For instance, Siciliano, et al.<sup>24</sup> reported an unusual 22 methane yield coefficient of 34 mL CH<sub>4</sub>/g VS, which resulted in a production of 44 23

kJ<sub>eq</sub>/kg OMSW of thermal energy and a deficit of electricity, i.e. -6 kJ<sub>eq</sub>/kg OMSW.
Despite of this anomalous result, AD of OMSW without pre-treatment was able to
produce methane to match the net energy production derived from the OMSW
combustion, resulting to be a suitable valorisation alternative.

When the OMSW is pre-treated, the average net energy production is a little bit lower, 5  $3136 \pm 1193 \text{ kJ}_{eq}/\text{kg}$  OMSW than this obtained without OMSW pre-treatment. Excluding 6 the extreme values, 773 and 5397 kJ eq/kg OMSW, as happened with single AD, the 7 average remains almost constant, 3141 kJ eq/kg OMSW and the standard deviation is 8 reduced to 981 kJ eq/kg OMSW. As can be seen in Fig.2, when OMSW is pre-treated 9 10 before AD, the higher the energy consumed in the pre-treatment, the lower is the obtained increment for net energy production respect to single AD. Despite all cases showed in 11 Fig. 2 report a positive increment of the methane production, when the pre-treatment is 12 used, the net energy produced is diminished (blue colour surface) respect single AD, due 13 to the high energy demand of the treatment. According to the results, low temperature 14 thermal pre-treatments<sup>27,30,41</sup> and alkaline<sup>24,27</sup> pre-treatments resulted in the highest 15 improvements of the net energy production. The effect of low-intensive pre-treatments 16 are related to the deflocculating of macromolecules, rather than the degradation of fibrous 17 structures.<sup>30,63</sup> However, the benefit derived from the implementation of these pre-18 treatments is not clear since their net energy productions are in the same range than the 19 20 obtained from the AD of untreated OMSW. Similarly, the implementation of an acidification stage (two-stages operation mode) does not provide a net energy benefit 21 despite the high reported OLR, resulting in an energy production 14% lower than the 22 23 combustion.

Figure 2

2 Regardless of the energy production, the interest of the high-intensity thermal pretreatments, including steam-explosion pre-treatment, would reside in the possibility of 3 4 obtaining a liquid fraction enriched in high valuable phenolic compounds, which can be recovered before the AD.<sup>11,62</sup> However, it is worth to note that the high energy 5 6 consumption of this kind of pre-treatment is rarely compensated by the variation in the 7 biogas production, being the less adequate techniques for pre-treating OMSW for energy valorisation (Table 2). The insufficient effect over the biogas production by high-intensity 8 thermal pre-treatments can be due to the acceptable biodegradability of the untreated 9 10 OMSW or by the formation of inhibitors during the pre-treatments such as the vanillin, the furfural or the hydroxymethylfurfural that might inhibit the AD process.<sup>16</sup> Therefore, 11 the application of high-intensity thermal pre-treatments only advocates in the frame of a 12 biorefinery system, but not in a waste-to-energy scenery. 13

#### 14 4. CONCLUSIONS

15 The review of the available literature showed that the average methane yield for the OMSW without any pre-treatment was 287 ± 75 mL CH<sub>4</sub>/g VS according to BMP 16 experiments, whereas semi-continuous experiments achieved an average methane 17 production rate of  $304 \pm 73$  mL CH<sub>4</sub>/(g VS·d). Accordingly, AD without pre-treatment 18 of OMSW can generate a net energy production in the same range than the obtained by 19 the OMSW combustion, enabling the AD as a feasible alternative but not clearly offering 20 a surplus of energy production. Implementation of greener alternatives for waste 21 treatment favours the use of AD as preferred treatment for OMSW. The positive impact 22 23 over the biogas production by the implementation of pre-treatments rarely compensate the pre-treatment energy requirements. High-intensity thermal pre-treatments, not 24 compensating neither the energy requirements of the pre-treatment with the variation in 25

- 1 the biogas production, offer the possibility of recovering valuable compounds from the
- 2 pre-treated OMSW. Due to the maturity level of the AD of OMSW, future research should
- 3 focus on both, improvement of the energy balances for real cases scenarios and pilot plant
- 4 demonstrations.

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# **1 FIGURE CAPTION**

2

Figure 1. Scheme of A) combustion, and B) anaerobic digestion for olive mill solid
waste valorization.

5

- 6 Figure 2. Relation between the pre-treatment energy consumption (kJeq/kgOMSW) for
- 7 all reviewed studies using pretreated OMSW against the variation in methane
- 8 production (%), and net energy production (%) compared to the untreated OMSW.

# **Table 1.** Indexed publications at Journal Citation Report (JCR) during the last 17 years (2003-2019) on anaerobic digestion of OMSW from the two-stage olive oil extraction process. na: not applied, nr: no reported.

Reference	Experiment al set-up	Operational temperatur e	Substrate characterizatio n		Substrate characterizatio n		Substrate characterizatio n		Substrate characterizatio n		Substrate characterizatio n		ubstrate Pre-treatment racterizatio n		Methane OLR yield		Biodegradability
		(°C)	TS (%)	VS (%)		mL CH4/gVS	(g VS/(L·d))	(mL CH4/(g VS·d))	(VS removal, %)								
Fernández-Rodríguez, et al. <sup>22</sup>	BMP	35	27.2	23.5	na	321	na	na	56.9								
Pellera, et al. <sup>23</sup>	BMP	35	53.5	52.3	Untreated	196.4	na	na	nr								
					1 mmol NaOH/gVS 90°C, 4h	241.9	na	na	nr								
					0.25 mmol NaOH/gVS 25°C, 16h	198.8		na	nr								
Siciliano, et al. <sup>24</sup>	BMP	35	33.8	31.8	Untreated	34	na	na	29								
					0.05 g H <sub>2</sub> O <sub>2</sub> /g COD and 35 g lime/L	390	na	na	78								
Pinto-Ibieta, et al. <sup>25</sup>	BMP	35	26.0	23.6	Untreated	$345 \pm 3$	na	na	80.3								
					Addition of 0.30 mg Co/L	475 ± 6	na	na	83.8								
Rincón, et al. <sup>26</sup>	BMP	35	26.5	22.8	Untreated	154	na	na	nr								
					Steam explosion (200°C, 5 min)	332	na	na	nr								
Donoso-Bravo, et al. <sup>27</sup>	BMP	37	25.7	24.8	Untreated	255.63 ± 2.54	na	na	nr								
					Steam explosion (165°C 15 min)	$\begin{array}{r} 248.38 \pm \\ 3.11 \end{array}$	na	na	nr								
					thermal (148°C, 30 min)	$\begin{array}{r} 434.25\pm\\ 5.48\end{array}$	na	na	nr								

					Enzimatic, 24 h and thermal inactivation (100 °C, 40 min)	351.70 ± 3.04	na	na	nr
Serrano, et al. <sup>28</sup>	BMP	35	26.0	23.6	na	$351\pm4$	na	na	$64.9\pm0.6$
Maamir, et al. <sup>29</sup>	BMP	37	83.3	82.9	Untreated	332	na	na	42
					Fenton (H <sub>2</sub> O <sub>2</sub> /[Fe <sup>2+</sup> ] = 1000, [Fe <sup>2+</sup> ] = 1.5mM, 120 min and pH 3)	168	na	na	nr
					Fenton (H <sub>2</sub> O <sub>2</sub> /[Fe <sup>2+</sup> ] = 1000, [Fe <sup>2+</sup> ] = 1.5mM, 120 min and pH 3) and precipitation with Fe <sup>3+</sup>	224	na	na	nr
Serrano, et al. <sup>18</sup>	BMP	35	26.6	25.0	Untreated	$261 \pm 2$	na	na	57.3 ± 3.2
					Thermal (170°C, 1 h)	290 ± 4	na	na	63.4 ± 1.3
					Thermal (170°C, 1 h) and dephenolization	350 ± 4	na	na	75.3 ± 3.1
Serrano, et al. <sup>30</sup>	BMP	35	26.6	25.0	Untreated	$264\pm1$	na	na	$57.6\pm0.0$
					Thermal (65°C, 1 h)	$353\pm7$	na	na	79.1 ± 7.3
					Thermal (65°C, 1 h) and dephenolization	322 ± 3	na	na	75.5 ± 5.0
Serrano, et al. <sup>31</sup>	BMP	35	26.6	25.0	Untreated	$280\pm3$	na	na	$66.4\pm0.2$
					Steam explosion (200°C, 5 min)	294 ± 2	na	na	65.0 ± 7.9
					Steam explosion (200°C, 5 min) and dephenolization	261 ± 3	na	na	60.5 ± 3.1

Fernández-Rodríguez, et al. <sup>32</sup>	BMP	35	25.6	22.6	na	415	na	na	56.70%
Fernández-Rodríguez, et al. <sup>33</sup>	BMP	35	26.7	23.5	na	375	na	na	58.4
Cabrera, et al. <sup>34</sup>	BMP	35	24.4	22.9	na	572.3	na	na	93.5% COD added
Borja, et al. <sup>35</sup>	Semi- continuous experiments	35	12.4	10.8	na	na	1.25	315 L CH <sub>4</sub> /(d·g COD)	90.9%
Rincon, et al. <sup>36</sup>	Semi- continuous experiments	35	14.6	12.6	na	na	2.33	282.4	97.0–95.6% COD
Rincón, et al. <sup>37</sup>	Semi- continuous experiments	35	14.3	12.6	na	na	7.15	237	97.0%
Rincón, et al. <sup>38</sup>	Semi- continuous experiments	35	14.3	12.6	na	na	7.15	238	77%
Rincón, et al. <sup>39</sup>	Two-stages (semi- continuous) experiments	35	14.3	12.6	Acidification	na	0.67	257	92.8%
Rincón, et al. <sup>40</sup>	Two-stages (semi- continuous) experiments	35	14.3	12.6	Acidification	na	15.5	208	nr
de la Lama, et al. <sup>41</sup>	Semi- continuous experiments	35	26.5	22.8	Thermal (120 °C, 180 min)	na	4.5	382	77.9% COD

Stoyanova, et al. <sup>42</sup>	Semi- continuous	37	23.9/ 33.0	22.9/ 31.7	Untreated	na	0.76	380	nr
	experiments				Pre-acidification	na	1.56	200	nr
					Pre-acidification	na	1	370	nr
Serrano, et al. <sup>43</sup>	Semi- continuous experiments	35	7.3	6.8	Steam explosion (200°C 5 min) and dephenolization	na	2	152 ± 21	nr
Serrano, et al. <sup>44</sup>	Semi- continuous experiments	35	10.9	10.2	Thermal (170°C 1 h) and dephenolization	na	1	$172\pm60$	84.9

Reference	Pretreatment	Pretreatme nt energy consumptio n	Methane production <sup>1</sup>	Net thermal energy production	Net electricity production	Net energy production	Variation in the net energy production respect single AD	More net energy than OMSW combustion? <sup>2</sup>	How much better/worse than OMSW combustion? <sup>2,3</sup>
		(equivalent kJ/kg OMSW)	(L CH4/ kg OMSW)	(kJ/ kg OMSW)	(kJ/ kg OMSW)	(equivalent kJ/kg OMSW)	(%)	(YES/NO)	(%)
Serrano, et al. <sup>28</sup>	no	-	78.98	1193	991	3889	-	YES	29
Maamir, et al. <sup>29</sup>	Untreated	-	74.70	1113	931	3645	-	YES	21
Serrano, et	Untreated	-	58.73	866	708	2795	-	NO	-7
a1.	Thermal (170°C, 1 h)	613	65.25	481	798	2603	-6.85	NO	-13
	Thermal (170°C, 1 h) and dephenolizatio n	658	78.75	565	969	3141	12.41	YES	5
Serrano, et	Untreated	-	59.40	877	718	2831	-	NO	-6
ui.	Thermal (65°C, 1 h)	108	79.43	1169	996	3875	36.88	YES	29
	Thermal (65°C, 1 h) and dephenolizatio n	131	72.45	923	890	3329	17.59	YES	11
<sup>4</sup> Stoyanova, et al. <sup>42</sup>	Untreated	-	95.00	1440	1191	4682	-	YES	56

**Table 2.** Energetic potential of the biomethanization of OMSW of the reviewed studies in comparison with the current combustion technology.

	1			r	-			1	
	Pre- acidification (OLR = 1.56	110	50.00	693	611	2351	-49.79	NO	-22
	gVS/Lday)								
	Pre- acidification (OLR = 1.00	110	92.50	1378	1177	4576	-2.26	YES	52
~	gVS/Lday)		<b>(2</b> 0 0			<b>2</b> 225			
Serrano, et	Untreated	-	63.00	935	768	3026	-	YES	l
al. <sup>31</sup>	Steam explosion (200°C, 5 min)	926	66.15	211	810	2339	-22.70	NO	-22
	Steam explosion (200°C, 5 min) and dephenolizatio	954	58.73	-13	696	1794	-40.71	NO	-40
Pellera et al <sup>23</sup>	Untreated	_	44 19	632	506	2011	-	NO	-33
	1 mmol NaOH/gVS 90°C, 4h	139	54.43	745	644	2494	24.02	NO	-1
Siciliano et	Untreated	-	7.65	44	-6	34	-	NO	-99
	H <sub>2</sub> O <sub>2</sub> +lime, 3 h	5	87.80	1335	1113	4362	12.8E3	YES	45
Pinto-Ibieta, et al. <sup>25</sup>	Untreated	-	77.63	1171	973	3817	-	YES	27
	Addition of 0.30 mg Co/L	0	106.88	1642	1381	5397	41.39	YES	80
Rincón, et al. <sup>26</sup>	Untreated	-	34.65	479	371	1492	-	NO	-50
	Steam explosion (200°C, 5 min)	901	74.70	372	930	2826	89.39	NO	-6

Donoso-	Untreated	-	57.51	836	692	2718	-	NO	-9
Bravo, et al. <sup>27</sup>	Thermal (148°C, 30 min)	608	97.72	1050	1289	4507	65.81	YES	50
	Enzimatic, 24 h and thermal inactivation (100 °C, 40 min)	149	79.13	1196	1053	4055	49.16	YES	35
Rincón, et al. <sup>40</sup>	Acidification	101	52.00	751	675	2581	-	NO	-14
Fernández- Rodríguez, et al. <sup>22</sup>	no	-	72.23	1084	897	3524	-	YES	17
Cabrera, et al. <sup>34</sup>	no	-	128.77	1995	4687	6581	-	YES	119
Rincón, et al. <sup>39</sup>	Acidification	101	64.25	949	733	2950	-	NO	-2
Rincón, et al. <sup>38</sup>	no	-	59.50	879	785	3007	-	SI	0
Rincón, et al. <sup>37</sup>	no	-	59.25	875	781	2994	-	NO	0
Rincon, et al. <sup>36</sup>	no	-	70.60	1058	918	3550	-	YES	18
Borja, et al. <sup>35</sup>	no	-	48.83	707	585	2300	-	NO	-23

de la Lama, et al. <sup>41</sup>	Thermal (120 °C, 180 min)	600	95.50	980	1279	4403	-	YES	47
Fernández- Rodríguez, et al. <sup>33</sup>	no	-	84.38	1280	1066	4180	-	YES	39
Serrano, et al. <sup>44</sup>	Thermal (170 °C, 1 h) and dephenolizatio n	658	43.15	-9	473	1219	-	NO	-59
Serrano, et al. <sup>43</sup>	Steam explosion (200 °C, 5 min) and dephenolizatio n	954	38.00	-347	444	773	-	NO	-74
Fernández- Rodríguez, et al. <sup>32</sup>	no	-	93.38	1425	1192	4666	-	YES	55
OMSW combustion	Drying	2440	-	143	1095	3004	-	-	-

1 A scale up factor of 0.90 was applied to adjust the methane yield from batch experiments to a continuous operation mode, according to the results from previous section

2 <sup>2</sup> In terms of Net Energy Production

3 <sup>3</sup> Negative values were used for reduction in Net Energy Production respect to OMSW combustion

4 <sup>4</sup> Despite the methane yield was not increased, this pretreatment was included due to the achieved reduction of the hydraulic retention time, reducing the energy demand of

5 AD





Figure 2.

