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**Anaerobic co-digestion of the process water from waste activated sludge hydrothermally treated with primary sewage sludge. A new approach for sewage sludge management**

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**Abstract**

Hydrothermal carbonization (HTC) is a suitable technology for managing wastes with a high moisture content, providing a carbon-rich and high energy density material called hydrochar and a process water (PW) with significant organic matter content. The aim of this work was to develop a new approach to sewage sludge management involving anaerobic digestion (AD) of the PW of dewatered waste activated sludge (DWAS) with primary sewage sludge (PSS). The process was optimized by performing semi-continuous experiments with different feed mixture compositions (10% PW/90% PSS and 5% PW/95% PSS, on a COD basis), organic loading rates (OLR; 1.5 and 2.5 g COD L<sup>-1</sup> d<sup>-1</sup>), and temperature regimes (mesophilic and thermophilic). The combination of mesophilic conditions, a 10% PW/ 90% PSS feed mixture and OLR of 1.5 g COD L<sup>-1</sup> d<sup>-1</sup> provided concentrations of volatile fatty acids < 400 mg COD L<sup>-1</sup> in addition to a methane yield (172 ± 11 mL CH<sub>4</sub> g<sup>-1</sup> COD<sub>added</sub>), 1.15 times the value for the control test (100% PSS). Therefore, the energy content of hydrochar from HTC of DWAS followed by AD of the process water with primary sewage sludge enhances the valorization of this renewable residue.

*Keywords:* Anaerobic digestion; hydrothermal carbonization; HTC process water; mesophilic and thermophilic operation; semi-continuous operation; sewage sludge valorization.

## **1. INTRODUCTION**

The main purpose of wastewater treatment plants (WWTP) is to reduce harmful emissions toward water bodies. Municipal and industrial wastewater is most often treated with conventional activated sludge processes [1]. Despite its high efficiency in removing organic matter, the process produces large amounts of waste activated sludge (WAS) that must be periodically removed. Moreover, treating excess sludge may account for up to 65% of a plant's operating costs [1,2]. New technologies producing less sewage sludge are thus needed.

Primary sewage and waste activated sludge from WWTP are usually thickened prior to mixing, stabilized by anaerobic or aerobic digestion and dewatered. Ultimately, sludge is disposed of or valorized by either agricultural usage (composting followed by application to soil), landfilling or thermal treatment [1–3]. One of the main hindrances to stabilizing sewage sludge is the low biodegradability of WAS relative to primary sewage sludge (PSS) owing to the rigid structure of the former preventing cell wall disruption and the release of inner cell products, which otherwise facilitate the breakdown of the overall mass. These problems detract from efficiency in stabilizing sewage sludge with biological means [4]. A number of WAS pretreatment technologies including mechanical (grinding, pressurization, lysis–centrifugation, microwave irradiation, sonication), biological (enzymatic), chemical (alkali or acid pretreatment, ozonation, advanced oxidation processes) and electrical methods have been proposed [5]. Also, sewage sludge can be

valorized by using thermal treatments such as conventional heating or steam injection [6,7].

Hydrothermal carbonization (HTC), a relatively new process for biomass valorization, is usually carried out at moderate temperatures (180–250 °C) and autogenous pressure [8,9]. This process is gaining increasing interest by virtue of its advantages over conventional dry thermal treatments (gasification, pyrolysis, torrefaction, etc.). HTC has some benefits in terms of process performance and economic efficiency, mostly as a result of the ability to process wet feedstock such as dewatered waste activated sludge (DWAS) without prior drying process. The streams from HTC comprises a coal-like product called “hydrochar”, a liquid fraction rich in organic compounds and various gases, but mostly CO<sub>2</sub> [10]. Hydrochar (HC) can be used as fuel for combustion and gasification, and also as a source of precursors for developing low-cost competitive materials (adsorbents, catalysts, electrodes) upon thermal treatment (pyrolysis, physical or chemical activation) [8]. The process water (PW) from the HTC of DWAS comprises high organic matter and nitrogen contents [11], and contains heterocyclic organic compounds (pyrroles, pyridines), phenols, ketones, aldehydes and alcohols, consistent with a common carbonization route [11–13].

Anaerobic digestion is one of the most widely used processes for stabilizing sewage sludge [14]. The widespread use of this technique is a result of its potential advantages, which include a reduction by 30–50% of the volume of sludge ultimately requiring disposal, and the production of energy from methane, which is obtained in excess of the amount required to operate the process [15]. Sewage sludge is usually stabilized under mesophilic or thermophilic conditions (viz., with an optimum temperature of 35 or 55 °C,

respectively) [15]. Thermophilic anaerobic digestion has some advantages over mesophilic digestion including faster reaction and a higher load bearing capacity; as a result, the former exhibits higher productivity and methane production than the latter. However, thermophilic conditions also have some drawbacks such as decreased stability and quality in the effluent; accumulation of  $\text{NH}_3$ , and volatile fatty acids (VFA); susceptibility to the environmental conditions; and increased net energy requirements relative to mesophilic conditions. Although mesophilic systems exhibit better process stability and higher microbial richness, they afford lower methane yields and suffer from poor biodegradability [16].

HTC coupled with anaerobic digestion may be an effective and economical choice compared with conventional anaerobic digestion of mixed sludge. The proposed approach letting obtaining a value-added product (hydrochar) with a higher heating value (HHV) around  $19\text{--}24 \text{ MJ kg}^{-1}$ , comparable to sub-bituminous coals [12], in addition to a liquid by-product containing at least 15% of the initial carbon content [17] and 30% of the total COD [18] and being amenable to anaerobic digestion [10,11,13,19,20]. This technology allows recovering energy as biogas ( $\approx 36 \text{ MJ Nm}^{-3}$ ) in combined heat and power systems (cogeneration) and generators, to produce electricity and heat [21,22]. In this way, the aim of this work was to develop a new approach to sewage sludge management involving HTC of DWAS to obtain hydrochar and then treating the mixture of the PW and PSS by anaerobic digestion. For this purpose, a semi-continuous anaerobic digestion process was optimized in terms of feed mixture ratio (PW/PSS), temperature regime and organic loading rate (OLR). As far as we know, no studies integrating HTC of DWAS and the anaerobic co-digestion of the process water and primary sewage sludge have been carried

out. Therefore, a tentative framework for DWAS hydrothermally treated as a sound alternative to conventional sewage sludge management is proposed.

## **2. MATERIAL AND METHODS**

### ***2.1. Inoculum, substrates and hydrochar***

The mesophilic digesters used were seeded with inoculum from a full-scale WWTP mesophilic digester operating in Madrid (Spain). This mesophilic inoculum was adapted at 55 °C according to Riau et al. [23] for thermophilic experiments. Table 1 summarizes the characteristics of the inoculum and the substrates.

PSS was obtained from the primary treatment of the above-mentioned urban WWTP and DWAS (15% wt.) was collected from a full-scale membrane bioreactor in a cosmetic factory also operating in Madrid, Spain. The main characteristics of DWAS are shown in Table 2. Batch-wise HTC runs of DWAS were conducted in a ZipperClave 4 L stainless steel thermostated reactor with a stirring rate of 100 rpm. In each run, the vessel was loaded with approximately 1.5 kg of DWAS. The target temperature (208 °C) was reached by heating at 3 °C min<sup>-1</sup> and carbonization conditions were held for 1 h. The HTC reaction was stopped by a serpentine cooler located insight into the reactor, the slurry (process water and hydrochar) was centrifuged (3500 rpm – 30 min) and passed through a filter of 0.45 µm pore size. The solid fraction was recovered and dried at 55 °C for 24 h. Then, the hydrochar was ground and sieved to a particle size in the range of 0.1 - 0.25 mm.

## 2.2. *Experimental procedure*

Anaerobic tests were performed in thoroughly mixed borosilicate glass digesters each having a total volume of 2.8 L and a working volume of 2 L. The temperature for mesophilic (35 °C) and thermophilic (55 °C) conditions was adjusted by recirculating water through the double wall of the reactors. Heat losses were prevented by using insulating coats which also reduced the amount of daylight reaching the reactors. Continuous stirring in the reactors was provided by direct drive stirrers furnished with holed paddles.

The reactors were operated in a semi-continuous mode (one feed per day) at two different PW to PSS mixture ratios (5 and 10 % PW, on a chemical oxygen demand (COD) basis) for 250 d. A control experiment with PSS as bare substrate was also performed in parallel. In what follows, the experiments carried out are referred to as 5PW (5% PW), 10PW (10% PW) and control (100% PSS), respectively. PW to PSS mixture ratios were chosen according to the results of the batch-wise anaerobic digestion of PW and PSS, where inhibition was substantial with PW proportions exceeding 25% in the mixture [24]. Two different OLRs (1.5 and 2.5 g COD L<sup>-1</sup> d<sup>-1</sup>, corresponding to a solid retention time (SRT) of 44 and 26 d, respectively, under mesophilic and thermophilic conditions) were used. Based on the low volatile solid (VS) concentration provided by PW, an OLR on a VS basis of ca. 3 g VS L<sup>-1</sup> d<sup>-1</sup> was used in all tests. Attainment of the steady-state under each set of conditions tested was verified after a period equivalent to 3 times SRT by checking the effluents for constancy in their properties. Reactor effluents (raw samples) were collected during each steady-state period, centrifuged at 8000 rpm for 15 min and vacuum-filtered through glass microfiber filters of 0.45 µm pore size (soluble samples).

### 2.3. Analytical methods

Total solids (TS), volatile solids (VS), soluble COD (SCOD) and total ammonia nitrogen (TAN) were determined by using standard methods [25] (2540b, 2540d, 5220-d and 4500-NH<sub>3</sub>, respectively), while free ammonia nitrogen (FAN) was calculated according to Hansen et al. [26]. pH was measured with a glass electrode (Crison Basic pH meter). Alkalinity was determined by titration with 0.02 N H<sub>2</sub>SO<sub>4</sub> to endpoints of pH 5.75 and 4.30, which allowed total (TA), partial (PA) and intermediate alkalinity (IA) to be calculated [27]. Total COD (TCOD) was determined according to Raposo et al. [28] and total Kjeldahl nitrogen (TKN) according to Villamil et al. [11]. Total organic carbon (TOC) was measured with a Shimadzu TOC-VCPN autoanalyzer and volatile fatty acids (VFAs) were quantified on a Varian 430-GC gas chromatograph [29]. Chemical species were identified on a GC–MS CP-3800/Saturn 2200 instrument equipped with a Varian CP-8200 autosampler injector [29]. Biogas volumes were directly measured with a Ritter MilliGas counter (MGC-1 V3.4 PMMA) from Ritter Apparatebau GmbH and collected in Tedlar<sup>®</sup> gas sampling bags. Gas composition (H<sub>2</sub>, H<sub>2</sub>S, CO<sub>2</sub>, and CH<sub>4</sub>) was determined by gas chromatography separation (Thermo Scientific Trace 1310) with an 8 ft. x 1/8 in SS column packed with HayeSep Q 80/100 mesh and a thermal conductivity detector (TCD). The injection volume was 1 mL. Injector and detector temperatures were maintained at 110 and 150 °C, respectively. Helium was used as carrier gas at a flow rate of 30 mL min<sup>-1</sup>. A calibration gas standard with the following composition (vol %): 7.35% H<sub>2</sub>; 3.01% H<sub>2</sub>S; 59.84% CH<sub>4</sub>, and 29.8% CO<sub>2</sub> (Praxair, S.A.) was used for system calibration.

The elemental composition (C, H, N, and S) of DWAS and hydrochar was determined by a CHNS analyzer (LECO CHNS-932). ASTM methods in the analysis sample of coal and

coke D3173-11, D3174-12, and D3175-17 were used to determine the moisture, ash and volatile matter (VM), respectively [30]. The metal content was determined by inductively coupled plasma atomic emission spectroscopy (ICP-MS) using a model Elan 6000 Sciex Perkin Elmer apparatus.

#### 2.4. Data analysis and energy yield of DWAS hydrothermally treated

The HHV was determined according to the technical specification UNE-EN 15400 for solid recovered fuels [31] using a calorimetric bomb (IKA C2000). The hydrochar yield ( $Y_{HC}$ ), energy densification ( $E_{dens}$ ), energy yield ( $E_{yield}$ ), and carbon recovery ( $C_{recov}$ ) were calculated as follows:

$$Y_{HC}(\%) = \frac{HC \text{ mass}}{DWAS \text{ mass}} \cdot 100 \quad (1)$$

$$E_{dens} = \frac{HHV_{HC}}{HHV_{DWAS}} \quad (2)$$

$$E_{yield}(\%) = Y_{HC} \cdot E_{dens} \quad (3)$$

$$C_{recov}(\%) = \frac{C_{HC} \cdot HC \text{ mass}}{C_{DWAS} \cdot DWAS \text{ mass}} \cdot 100 \quad (4)$$

### 3. RESULTS AND DISCUSSION

#### 3.1. Thermophilic operation

Figure 1 shows the time course of biogas, IA/TA ratio, total ammonia nitrogen and pH along the anaerobic digestions of 10PW run with an OLR of 2.5 g COD L<sup>-1</sup> d<sup>-1</sup> at thermophilic temperature, and Table 3 collects the experimental final values of the main variables affecting anaerobic digestion after 65 d of operation. Under these operational conditions, the pH decreased slightly during the anaerobic treatment (from 8.1 to 7.5), and a high buffer capacity (ca. 4 g CaCO<sub>3</sub> L<sup>-1</sup>) was observed, and allowed the system to

cope with VFA accumulation better. However, the IA/TA ratio increased from 0.3 to 0.6, which suggests overloading of the system through VFA accumulation as the likely result of the pH drop observed despite the high buffering capacity of the medium. Thus, the TVFA concentration amounted to 7.6 g COD L<sup>-1</sup> (21% acetic, 57% propionic, 13% isobutyric + butyric and 9% isovaleric acid). Zhang et al. [32] found high propionate concentrations resulting in increased methanogenic inhibition and leading to anaerobic digestion failure, owing to the complicated biodegradation pathway and the involvement of unusual enzyme systems. This is consistent with the potential overload suggested by the high IA/TA ratio.

The TAN concentration in the effluent was around 1.4 g L<sup>-1</sup>, which is close to the inhibitory values obtained by Chen et al. [33], 1.5–7.0 g N L<sup>-1</sup>. Ammonia nitrogen, presents as ammonium bicarbonate, is an essential nutrient for microorganisms, as well as contributes buffering the system, which explains above-described high total alkalinity. However, thermophilic conditions involved not only an increased temperature, but also an increased pH, which may have displaced the ammonium/ammonia equilibrium to ammonia (acetoclastic methanogens are believed to be most sensitive to FAN [34]). The FAN concentration, 490 mg L<sup>-1</sup>, was fairly lower than the level potentially causing severe inhibition under thermophilic conditions [34], 1 g N L<sup>-1</sup>, although unacclimated inoculum could be sensitive to inhibition. An acceptable initial methane yield (150 mL STP CH<sub>4</sub> g<sup>-1</sup> COD<sub>added</sub>, equivalent to 0.61 L biogas L<sup>-1</sup> d<sup>-1</sup>) was obtained which, however, fell to very low levels with time. The high TKN values for PW, which were mainly due to the presence of nitrogen-containing species (viz., refractory pyrazines such as 2-ethyl-5-methylpyrazine and aromatic amines such as 4,5-dimethyl-*o*-phenylenediamine), together with the thermophilic conditions used, resulted in accumulation of these

recalcitrant compounds (Figure A.1 and Table A.1). On the other hand, 4-methylphenol, 7-methyl-1H-indole and indole, which were detected at low concentrations in the control (100% PSS) experiment, were accumulated in the 10PW run (see Figure A.1). Because indole can be degraded by methanogens and sulfate-reductive microbial populations [35,36], its presence suggests poor digestion leading to terminal process inhibition. By contrast, the presence of phenols, pyrazines and amines can be ascribed to compounds detected in the initial PW [29]. Moreover, as noted earlier, the high concentrations of TVFA, TAN and FAN prevented stable operation under thermophilic conditions.

### 3.2. Mesophilic operation

Figure 2 shows the methane yield for the 5PW, 10PW and control experiments at the two OLR checked (1.5 and 2.5 g COD L<sup>-1</sup> d<sup>-1</sup>). A yield of 172 ± 11 mL STP CH<sub>4</sub> g<sup>-1</sup> COD<sub>added</sub> (15% more than in the control run) was obtained at OLR of 1.5 g COD L<sup>-1</sup> d<sup>-1</sup> for 10PW run, which reveals increased methane production under those specific conditions. With 5PW, however, the methane yield was similar to that for the control test. On the other hand, methane production at 2.5 g COD L<sup>-1</sup> d<sup>-1</sup> was fairly similar with 5PW (164 ± 2 mL STP CH<sub>4</sub> g<sup>-1</sup> COD<sub>added</sub>), but lower for 10PW run at the lowest OLR (151 ± 1 mL STP CH<sub>4</sub> g<sup>-1</sup> COD<sub>added</sub>). Villamil et al. [24] obtained a methane yield of 172 mL STP CH<sub>4</sub> g<sup>-1</sup> COD<sub>added</sub> with a 25% PW/75% PSS mixture under batch-wise conditions. Although methane yield tends to be higher under batch conditions than under semi-continuous conditions [37], in this case resulted similar values pointing out the different PW to PSS ratios.

The average methane production at the highest OLR in the control test was 211 ± 1 mL STP CH<sub>4</sub> g<sup>-1</sup> COD<sub>added</sub>, which is 1.4 times greater than the methane yield obtained with

the lowest OLR. Therefore, the methane yield for the PSS tests increased with decreasing SRT. This was a result of the lowest OLR providing under optimal conditions for anaerobic digestion of PSS. The methane yield for 10PW run at OLR of  $1.5 \text{ g COD L}^{-1} \text{ d}^{-1}$  was slightly lower than the obtained with OLR of  $2.5 \text{ g COD L}^{-1} \text{ d}^{-1}$ , though SRT with the highest OLR is more adequate for full scale operation and close to the usual value for anaerobic digestion of mixed sludge (20–25 d) according to Silvestre et al. [38]. The methane yields obtained at the latter OLR value (SRT of 26 d) for 5PW and 10PW runs ( $151$  and  $164 \text{ mL STP CH}_4 \text{ g}^{-1} \text{ COD}_{\text{added}}$ , respectively) were higher than those reported by de la Rubia et al. [39] and Choi et al. [40] for mixed sewage sludge digested under similar conditions ( $120$  and  $149 \text{ mL CH}_4 \text{ g}^{-1} \text{ COD}_{\text{added}}$ , respectively). Therefore, HTC allows the poor degradability of WAS (especially with long sludge retention times) to be circumvented.

The methane yields obtained under the different conditions assessed were closely related to TVFA concentration (Figure 3). At the lowest OLR for 10PW run, TVFA concentration amounted to  $390 \pm 38 \text{ mg COD L}^{-1}$  and consisted mainly of acetic acid (85%) and propionic acid (15%). This value exceeded that of PSS but falls in the acceptable range for stable reactor operation ( $< 2400 \text{ mg acetic acid L}^{-1}$ ) [41]. The highest OLR ( $2.5 \text{ g COD L}^{-1} \text{ d}^{-1}$ ) led to a 1.09 times greater TVFA concentration —89% was acetic acid— consistent with the decrease in the methane production by 12%. TVFA concentrations for 5PW run were lower than those of 10PW experiment (ca.  $280 \text{ mg COD L}^{-1}$ ), with acetic acid accounting for  $200\text{--}250 \text{ mg L}^{-1}$  and propionic acid for  $80 \text{ mg L}^{-1}$ . These TVFA concentrations were maintained within adequate levels, which means that there was no imbalance in the anaerobic process.

TAN (Figure 4) and TA values (Figure 5) for 10PW run were almost identical at both OLR levels ( $1.2 \text{ g TAN L}^{-1}$  and  $4.8 \text{ g CaCO}_3 \text{ L}^{-1}$ , respectively). Because this TAN concentration is lower than the inhibitory level for the process, the system was not inhibited by ammonia nitrogen [42]. With 5PW, TAN concentration was ca.  $950 \text{ mg L}^{-1}$  and TA value close to  $3.8 \text{ g CaCO}_3 \text{ L}^{-1}$ . Both values are lower than those obtained with 10PW experiment, probably used as buffer to maintain the concentration of VFA, but still higher than the  $3.0 \text{ g CaCO}_3 \text{ L}^{-1}$  determined by Yang et al. [43] for a stable digestion of PSS.

Methane production was clearly related to organic matter removal as COD (Figure 6). Thus, COD was removed by about 59% for 5PW run, but slightly less extensively at the highest OLR ( $59.2 \pm 1.1\%$  vs.  $53.2 \pm 2.3\%$ ) with 10PW. The slightly less efficient removal of COD in the 10PW experiment can be ascribed to the increased amount of PW present in the feed and also to accumulation of pyrazines (2-ethyl-3-methyl-pyrazine, 2,3-diethylpyrazine), phenols [2-methyl-6-(2-propenyl)-phenol] and alcohols (3-methyl-2-heptanol) in the effluent (Figure A.2 and Table A.2). The COD removal values (ca. 56%) are consistent with that obtained by de la Rubia et al. [39], by treating mixed sewage sludge under experimental conditions (OLR and SRT) similar to those used in our tests at the highest OLR, but greater than that reported by Choi et al. [40], 42%, also operating at OLR of  $2.5 \text{ g COD L}^{-1} \text{ d}^{-1}$ . On the other hand, COD removal at both OLR levels in the control treatment was ca. 63% and consistent with the value of Yang et al. [43] for the digestion of PSS as sole substrate. VS concentrations were reduced by at least 54% at both OLR levels and mixture ratios, which is higher than the acceptable value for full scale sewage sludge digestion (40% reduction) under mesophilic conditions [15].

Regarding performance, an increased proportion of PW in the mixture with PSS seemingly hinders anaerobic digestion relative to PSS alone owing to the high concentration of inhibitory compounds formed and accumulated. In fact, more than 10% PW in the mixture made the process inviable, and using exactly 10% PW required operating at low OLR, which increased SRT to an unusually great extent for anaerobic digestion of sewage sludge (44 d). Lower proportions of PW, such as 5%, allow stable operation at OLR and SRT similar to those commonly used in anaerobic digestion process (26 d). Therefore, hydrothermal carbonization not only provides a hydrochar with a substantial HHV (ca. 22 MJ kg<sup>-1</sup>), but also improves the methane yields in comparison with anaerobic digestion of mixed sewage sludge [23,39].

### ***3.3. Energy balance of the proposed approach (HTC + anaerobic digestion)***

Table 2 shows a representative analysis of the hydrochar. The hydrochar yield under the experimental conditions used (208 °C and 1 h) was 40.3% (eq. (1)). The carbonization process reduced the fixed carbon and the volatile matter of DWAS, meanwhile increased the ash content up to 19.7%. Because of this, part of the VM was partially transferred to process water as well as minerals were retained in hydrochar. Parshetti et al. [44] reported low values of VM (41.7%) and high ash content (40.4%) after HTC of DWAS at 250 °C for 15 min. The increase in ash content and the decrease in fixed carbon values are common after HTC of municipal wastewater streams (PSS, DWAS, mixed sludge, and digestate) due the high inert fraction of these feedstocks [18,44–46].

The HHV of hydrochar obtained in this work (21.6 MJ kg<sup>-1</sup>) was higher than those reported for PSS (17.5-18.7 MJ kg<sup>-1</sup>) [12], mixed sludge (18.6 MJ kg<sup>-1</sup>) [47], DWAS (18.3-20.2 MJ kg<sup>-1</sup>) [48], and digestate (17.0-17.8 MJ kg<sup>-1</sup>) [18]. The anaerobic digestion,

previously subjected, can explain the low value of hydrochar from digestate. However, it is difficult to compare directly the HHV of hydrochar reported in the literature and those measured in this study, since reaction time, reactor design, initial solids concentration, and temperature, influence the degree of carbonization. In addition, the HHV of hydrochar was higher than those of the brown coal and lignite are ( $< 17.4 \text{ MJ kg}^{-1}$ ). Moreover, significant energy densification (eq. (2)) up to 1.23 occurred because of decarboxylation and dehydration reactions took place, increasing the carbon content 1.12-fold with respect to the feedstock. This was also confirmed by reduction in H/C and O/C atomic ratios of DWAS, reaching H/C and O/C values of 1.61 and 0.46, respectively. The energy yield (eq. (3)), which relates the energy remaining within the hydrochar to that of the original biomass, was 50.1%, fairly lower than the reported by Danso-Boateng et al. [12] (73%) and Aragón-Briceño et al. [18] (70%) for HTC of PSS and digestate, respectively. Meanwhile a carbon recovery of 41.9% for hydrochar was reached (eq. (4)). These results show the verified conversion of DWAS to energy through HTC by potential applications of hydrochar (the main product of the HTC process) as a solid fuel, while the remaining carbon in the liquid fraction can be recovered as biogas by anaerobic digestion.

With the aim of deepening on the performance of HTC of DWAS coupling with anaerobic co-digestion of the PW with PSS, a simplified mass and energy balance of the whole process has been carried out (Fig. 7). The balance was referred to 1 kg of DWAS (d.b.). Firstly, the DWAS was hydrothermally treated ( $208 \text{ }^{\circ}\text{C}$  for 1 h), obtaining a slurry (hydrochar and process water). The energy input ( $7.1 \text{ MJ kg}^{-1}$  DWAS) of the hydrothermal carbonization of DWAS was calculated using equations (5) and (6) [48].

$$m_w \cdot (H_{l,HTC} - H_{l,298K}) + [(m_s \cdot C_p + C_{bulk} + h_{bulk} \cdot A \cdot \tau) \cdot (T_{HTC} - T_{amb})] = m_{steam} \cdot (H_{g,HTC} - H_{l,HTC}) \quad (5)$$

$$E_{HTC,in} = m_{steam} \cdot (H_{g,HTC} - H_{l,298 K}) \quad (6)$$

where  $m_w$  is the amount of water in DWAS;  $H_{l,HTC}$  the enthalpy of water at target temperature (481 K);  $H_{l,298 K}$ , the enthalpy of water at 298 K;  $m_s$  the dry solid content DWAS;  $C_p$ , the specific heat capacity of DWAS;  $C_{bulk}$ , the heat capacity of the reactor (1550 kJ K<sup>-1</sup>);  $h_{bulk}$ , the convective heat transfer coefficient;  $A$ , the surface area of the HTC reactor ( $h_{bulk} \cdot A = 0.032 \text{ kW K}^{-1}$ ) [49]; and  $\tau$ , the reaction time.

After HTC of DWAS, the slurry was dewatered, reaching a solid concentration of 50%, similar value to the reported by Lucian et al. [50] and Hitzl et al. [51]. The energy consumption of mechanical hydrochar dewatering is 0.1 MJ kg<sup>-1</sup> DWAS [48], achieving a complete solid separation. Meanwhile, a drying energy consumption of 1.2 MJ kg<sup>-1</sup> DWAS [52] was necessary to reach a residual moisture content of 8% in the hydrochar.

With the aim to evaluate the energy efficiency of this new treatment, the energy recovery rate was calculated using eq. (7).

$$Energy \text{ recovery rate } (\%) = \frac{E_{HTC} + E_{dew} + E_{dry}}{E_{hd} + E_{met}} \cdot 100 \quad (7)$$

where  $E_{HTC}$ ,  $E_{dew}$ , and  $E_{dry}$  are the energy consumption of HTC reaction, mechanical dewatering and drying, respectively, while  $E_{hd}$  and  $E_{met}$  are the energy recovered from the combustion of hydrochar and methane. All these terms are expressed as MJ kg<sup>-1</sup> DWAS.

Regarding the energy consumption, the HTC of DWAS and hydrochar drying represent 84.5 and 14.3%, respectively, of the overall energy required in the process, while the

energy needed for hydrochar dewatering is negligible (1.2%). The energy recovery (methane and hydrochar) reached a value around 20 MJ kg<sup>-1</sup> DWAS. Thus, the energy recovery rate was 41.5% operating with 10PW at OLR 1.5 g COD L<sup>-1</sup>. Zhao et al. [48] reported energy recovery rate of 50% for HTC of sewage sludge at 200 °C for 30 min, while Mena et al. [53] determined 25-57% for HTC of a mixture of orange peel and the organic fraction of municipal solid waste at pilot scale. Also, it must be taken into account the significant environmental and cost benefits to reduce the landfilling disposal of digestate in our process (PW + PSS) compared to conventional anaerobic digestion (mixed sludge) process, considering that the taxes for landfilling in Spain are around 25 €/t [54].

From our point of view, further studies should be developed to determine the energy efficiency of the HTC technology through modelling approach, energy integration and heat recovery using pinch analysis. Also, investigation into the design and simulation of the hydrothermal carbonization process could produce interesting findings related to investment and operational costs saving for a large-scale HTC plant.

#### **4. CONCLUSIONS**

HTC of dewatered waste activated sludge and anaerobic co-digestion of PW and PSS provides an efficient technology for the production of a solid fuel (hydrochar) and a methane-rich biogas. Under thermophilic conditions, the co-digestion showed a progressive inhibition evidenced by indole accumulation that, in addition with high VFA and NH<sub>3</sub> concentrations resulting in a low methane yield. Operating at low OLR (1.5 g COD L<sup>-1</sup> d<sup>-1</sup>) under mesophilic conditions led to a 1.15 times higher methane yield with 10PW than with the control treatment (100% PSS). COD removal was at least 53%,

irrespective of the operating conditions. Meanwhile, TAN, alkalinity and VFA fell within the ranges for a stable anaerobic digestion. Therefore, applying HTC to dewatered waste activated sludge and co-digesting the process water with primary sewage sludge provides an improved management method for this renewable waste as well as a positive energy balance.

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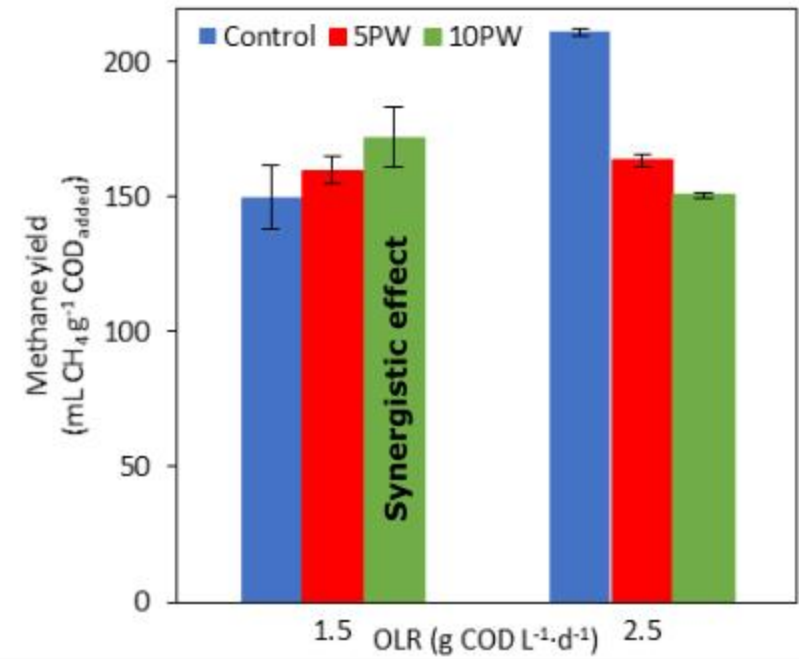
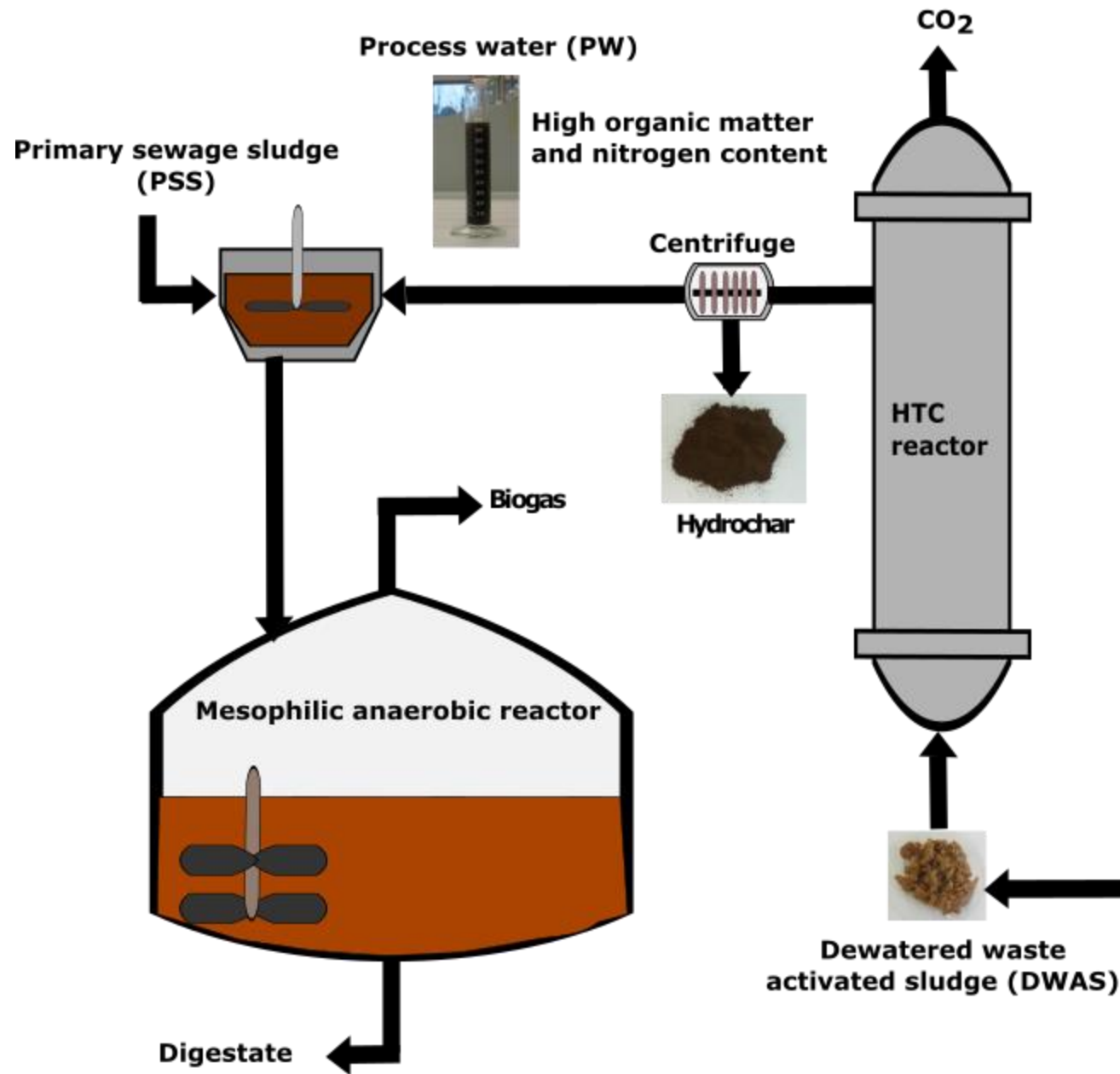


Table 1. Representative analysis of inocula and substrates.

	<b>Inocula</b>		<b>Substrates</b>	
	<b>Mesophilic inoculum</b>	<b>Thermophilic inoculum</b>	<b>PSS</b>	<b>PW</b>
<b>pH</b>	7.5 ± 0.1	8.1 ± 0.1	4.9 ± 0.1	4.8 ± 0.1
<b>Total Solids (g kg<sup>-1</sup>)</b>	31.0 ± 1.1	21.0 ± 0.8	31.8 ± 1.4	51.9 ± 0.5
<b>Volatile Solids (g kg<sup>-1</sup>)</b>	20.5 ± 0.1	12.5 ± 0.1	26.2 ± 1.3	46.2 ± 0.5
<b>Total COD (g O<sub>2</sub> L<sup>-1</sup>)</b>	43.5 ± 1.2	36.6 ± 3.3	61.3 ± 1.8	85.9 ± 1.7
<b>TOC (g L<sup>-1</sup>)</b>	-	-	-	42.6 ± 0.9
<b>TKN (g N L<sup>-1</sup>)</b>	3.9 ± 0.2	4.0 ± 0.3	3.8 ± 0.3	8.7 ± 0.1

Table 2. Representative analysis of the DWAS and hydrochar (composition in wt%, dry basis).

	DWAS	Hydrochar
<b>C<sup>a</sup></b>	48.1 ± 0.1	53.7 ± 0.2
<b>H<sup>a</sup></b>	7.0 ± 0.1	7.2 ± 0.1
<b>N<sup>a</sup></b>	7.9 ± 0.1	5.7 ± 0.1
<b>S<sup>a</sup></b>	0.8 ± 0.1	0.2 ± 0.1
<b>O<sup>a,b</sup></b>	36.3 ± 0.1	33.0 ± 0.1
<b>Ash content (wt%)</b>	13.7 ± 0.1	19.7 ± 0.1
<b>Volatile matter (wt%)</b>	73.6 ± 0.1	65.4 ± 0.3
<b>Fixed carbon<sup>c</sup> (wt%)</b>	12.7 ± 0.1	14.9 ± 0.1
<b>HHV (MJ kg<sup>-1</sup>)</b>	17.6 ± 0.1	21.6 ± 0.1

<sup>a</sup> Dry ash free

<sup>b</sup> Calculated by difference 100–(C+H+N+S)

<sup>c</sup> Calculated by difference 100–(ash+volatile matter)

Table 3. Experimental final values of the main variables influencing the anaerobic digestion of 10PW experiment at OLR 2.5 g COD L<sup>-1</sup> d<sup>-1</sup> under thermophilic conditions.

<b>pH</b>	7.7 ± 0.1
<b>Alkalinity (mg CaCO<sub>3</sub> L<sup>-1</sup>)</b>	4351 ± 45
<b>IA/TA</b>	0.63 ± 0.01
<b>TVFA (mg COD L<sup>-1</sup>)</b>	7611 ± 31
<b>TAN (mg N L<sup>-1</sup>)</b>	1335 ± 8
<b>FAN (mg N L<sup>-1</sup>)</b>	490 ± 3
<b>Biogas (mL L<sup>-1</sup> d<sup>-1</sup>)</b>	120 ± 10

Table A.1. Chemical species detected in control and thermophilic digesters operated at OLR 2.5 g COD L<sup>-1</sup> for 10PW experiment.

<b>Compound</b>	<b>Retention time (min)</b>	<b>Peak number</b>
2-Ethyl-5-methylpyrazine	5.0	1
4-Methylphenol	6.3	2
4,5-Dimethyl-o-phenylenediamine	6.5	3
Indole	10.5	4
7-Methyl-1H-indole	12.5	5

Table A.2. Chemical species detected in control and mesophilic digesters operated at OLR 1.5 g COD L<sup>-1</sup> for 10PW experiment.

<b>Compound</b>	<b>Retention time (min)</b>	<b>Peak number</b>
2-Ethyl-3-methyl-pyrazine	6.0	1
2,3-Diethylpyrazine	7.5	2
3-Methyl-2-heptanol	8	3
2-Methyl-6-(2-propenyl)-phenol	10.5	4
7-Methyl-1H-indole	13.7	5

## Figure captions

Figure 1. Time course of biogas, IA/TA ratio, total ammonia nitrogen and pH along the anaerobic digestion of 10PW experiment at OLR  $2.5 \text{ g COD L}^{-1} \text{ d}^{-1}$  under thermophilic conditions.

Figure 2. Average methane yield vs. organic loading rate for 5PW, 10PW and control experiments.

Figure 3. Average total volatile fatty acids (expressed as COD) vs. organic loading rate for 5PW, 10PW and control experiments.

Figure 4. Total ammonia nitrogen (expressed as  $\text{mg N L}^{-1}$ ), vs. organic loading rate for 5PW, 10PW and control experiments.

Figure 5. Total alkalinity vs. organic loading rate for 5PW, 10PW and control experiments.

Figure 6. COD removal (%) vs. organic loading rate for 5PW, 10PW and control experiments.

Figure 7. Mass and energy balance of the HTC of DWAS coupling with anaerobic co-digestion of the PW with PSS.

Figure 1 revised

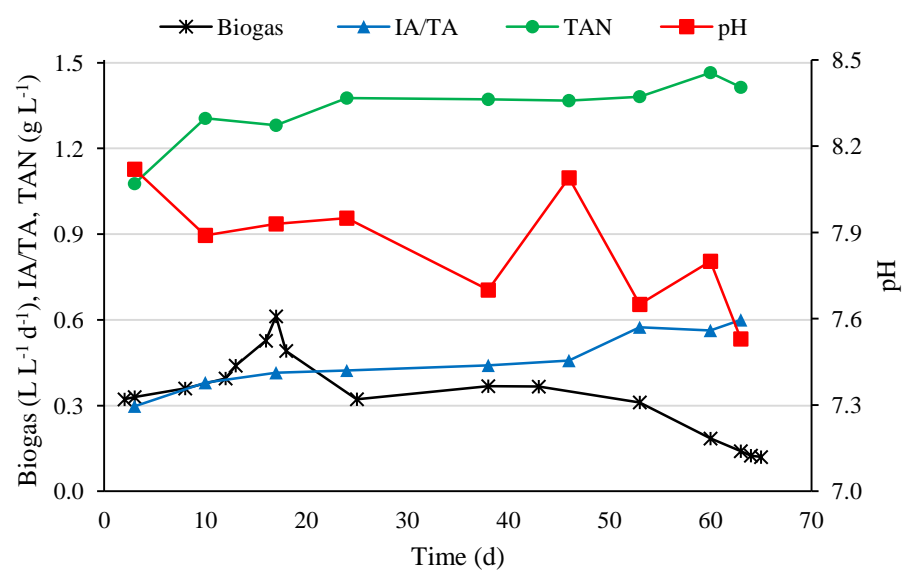


Figure 1. Time course of biogas, IA/TA ratio, total ammonia nitrogen, and pH along the anaerobic digestion of 10PW experiment at OLR 2.5 g COD L<sup>-1</sup> d<sup>-1</sup> under thermophilic conditions.

Figure 2 revised

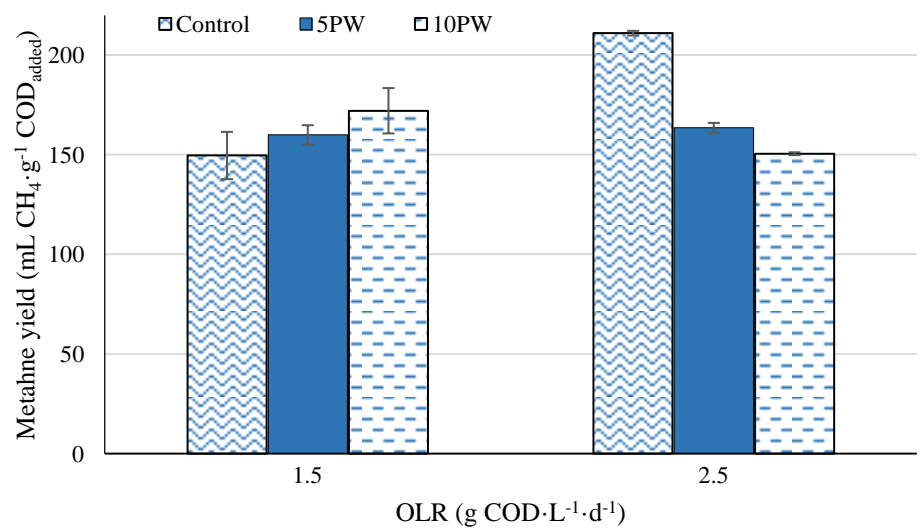


Figure 2. Average methane yield vs. organic loading rate for 5PW, 10PW and control experiments.

Figure 3 revised

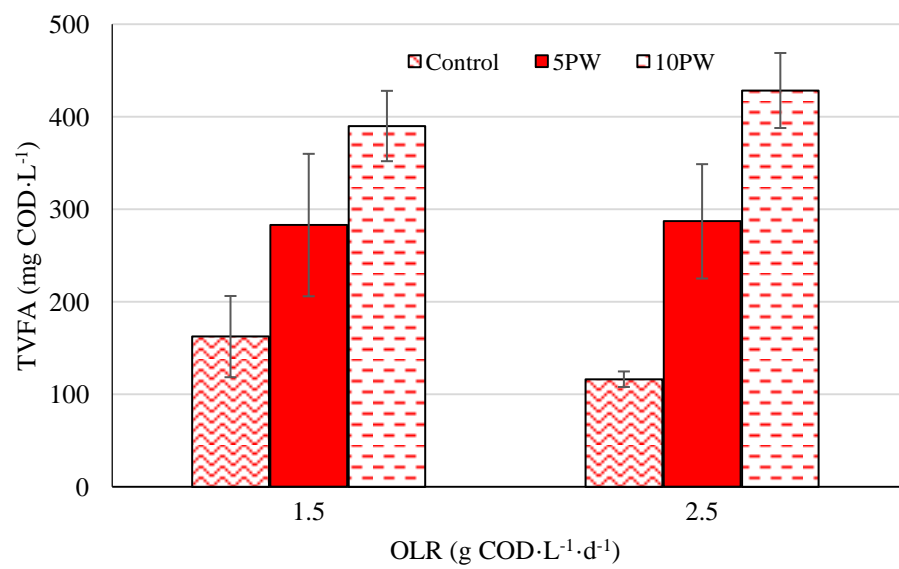


Figure 3. Average total volatile fatty acids (expressed as COD) vs. organic loading rate for 5PW, 10PW and control experiments.

Figure 4 revised

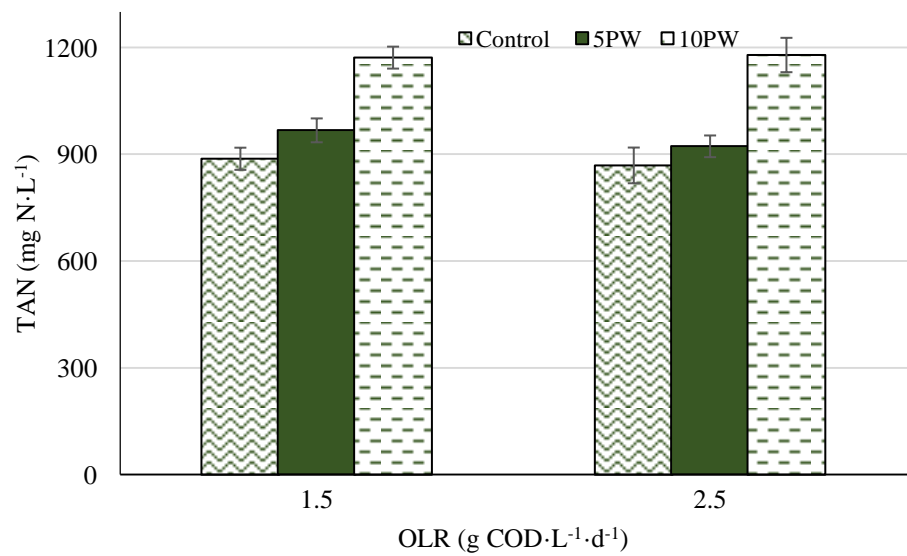


Figure 4. Total ammonia nitrogen (expressed as mg N L<sup>-1</sup>), vs. organic loading rate for 5PW, 10PW and control experiments.

Figure 5 revised

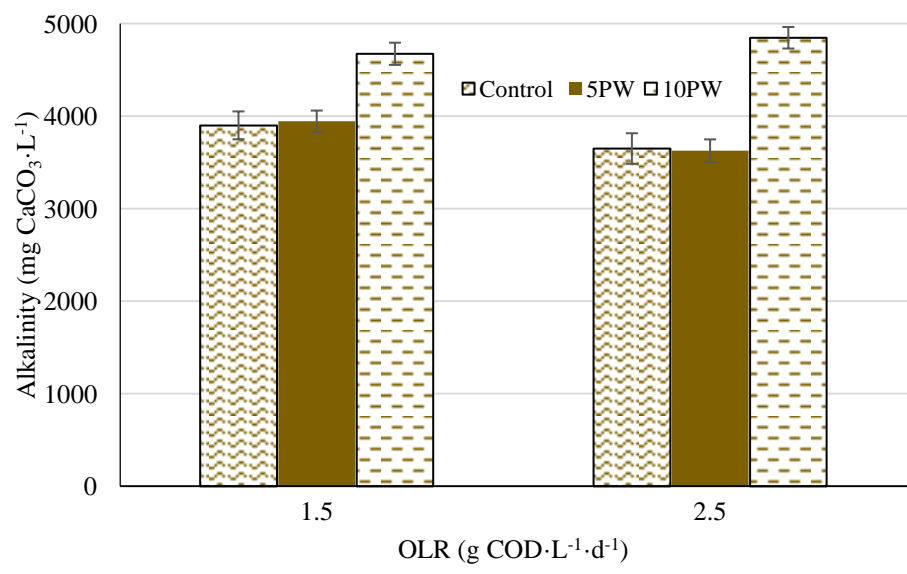


Figure 5. Total alkalinity vs. organic loading rate for 5PW, 10PW and control experiments.

Figure 6 revised

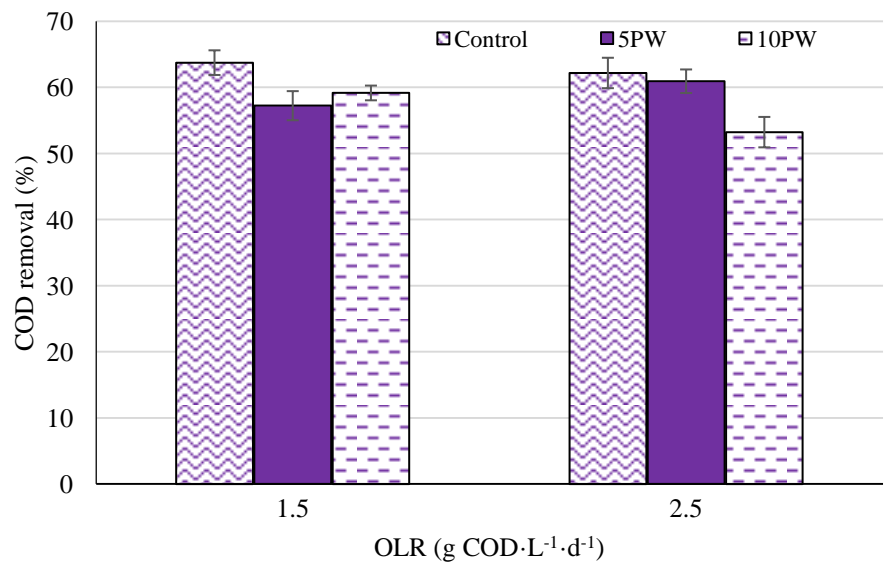


Figure 6. COD removal (%) vs. organic loading rate for 5PW, 10PW and control experiments.

Figure 7

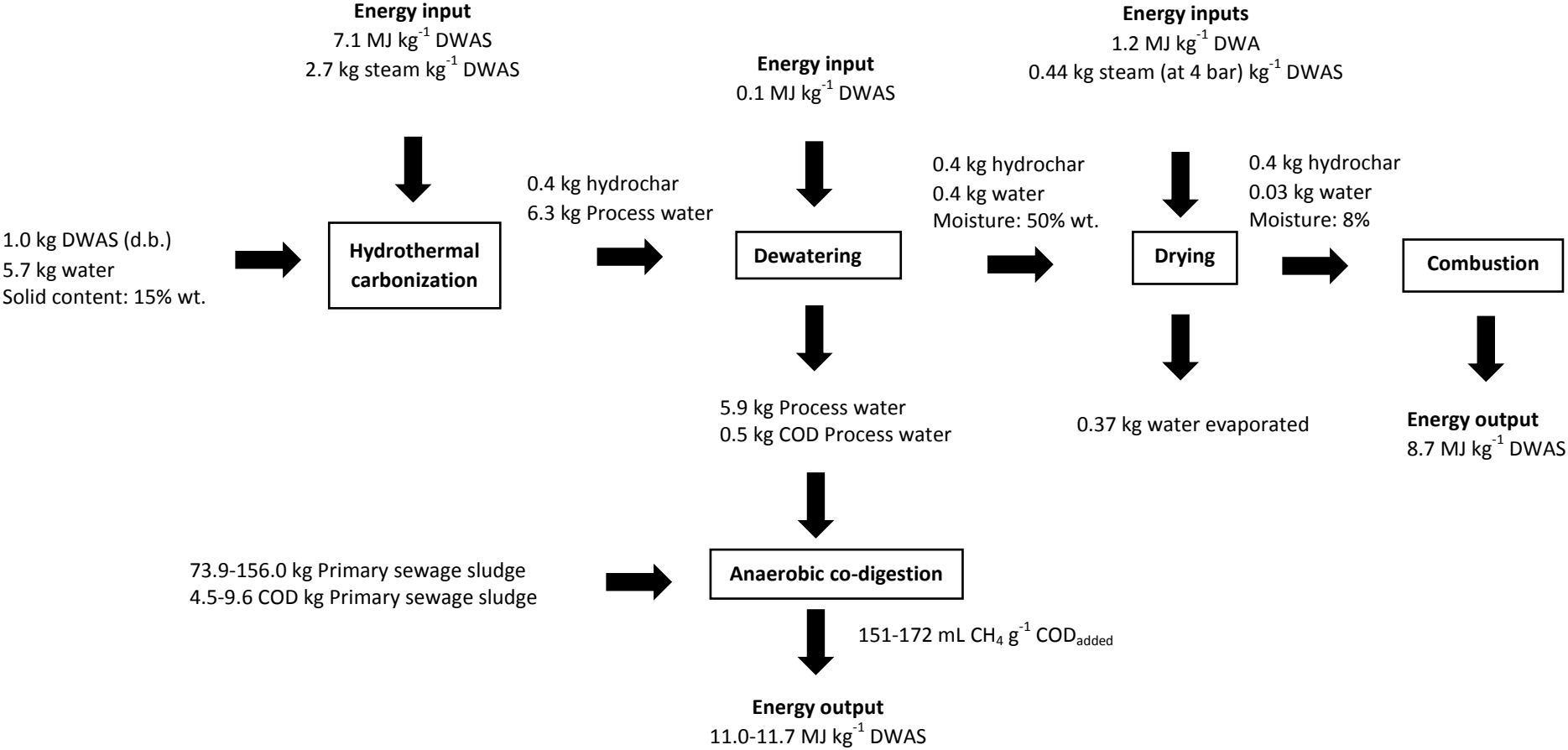
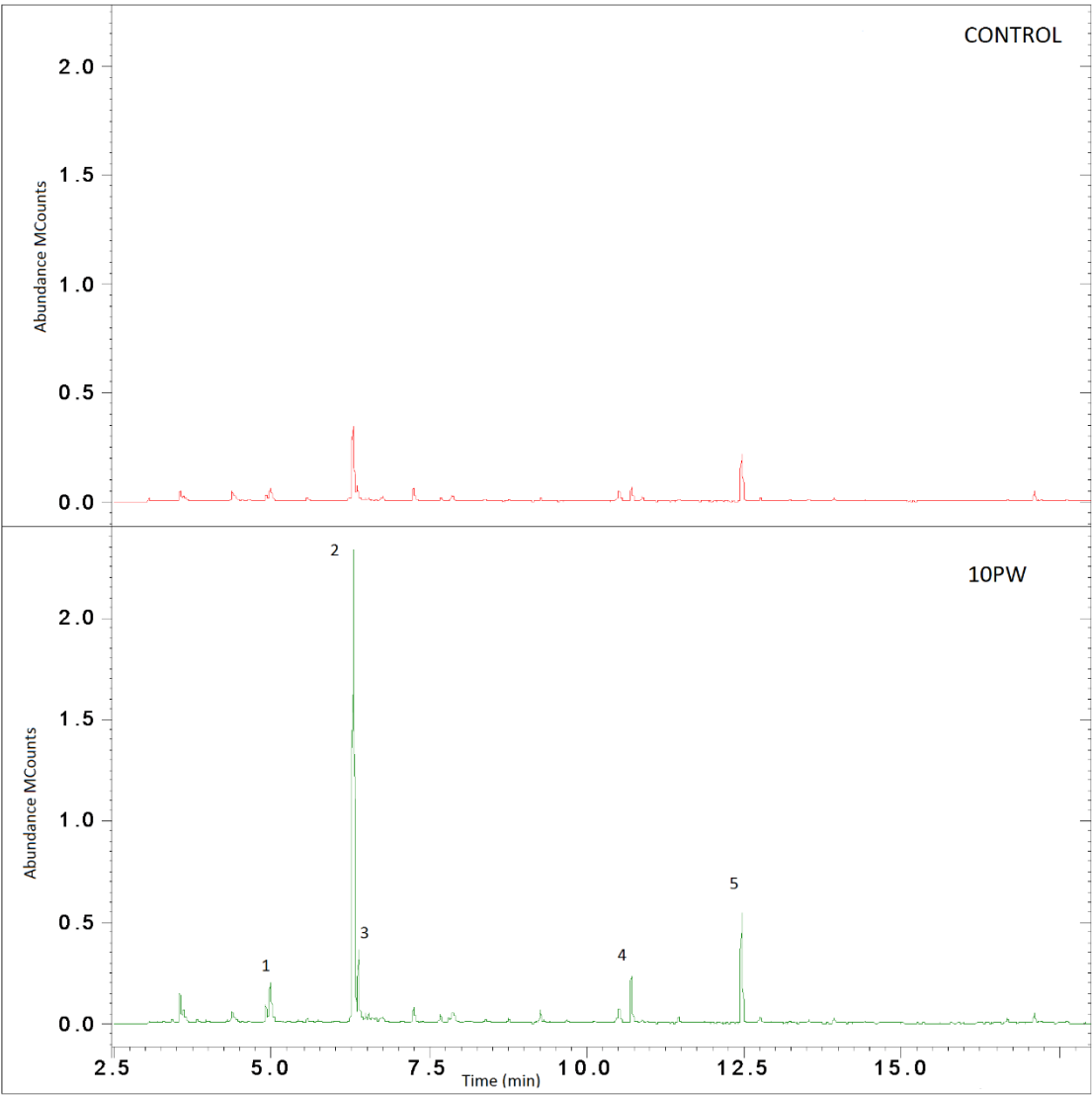


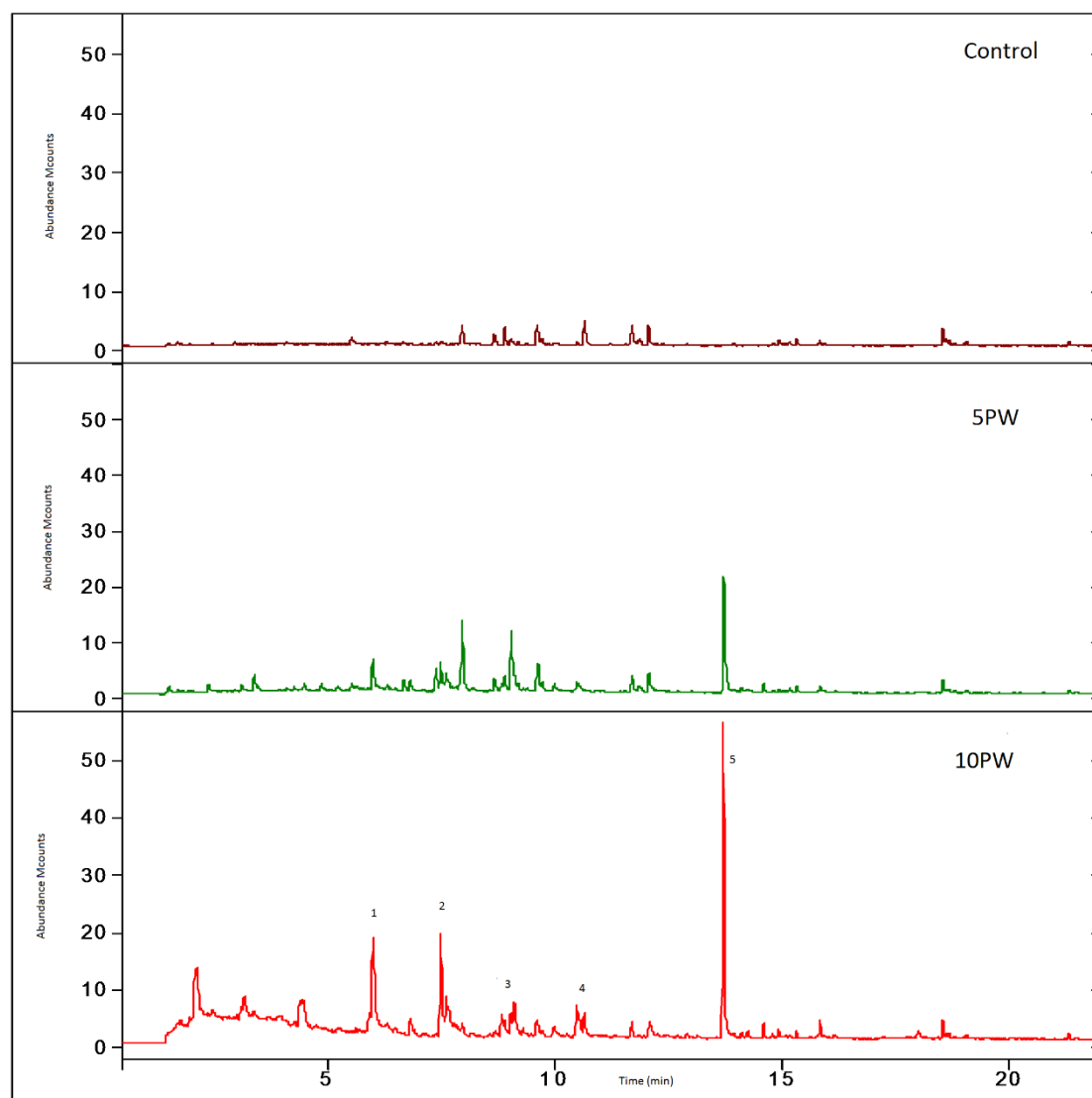
Figure 7. Mass and energy balance of the HTC of DWAS coupling with anaerobic co-digestion of the PW with PSS.

Figure A.1 revised



**Figure A.1.** GC/MS chromatograms of the control and 10PW samples under thermophilic temperature and OLR 2.5 g COD L<sup>-1</sup>

**Figure A.2 revised**



**Figure A.2.** GC/MS chromatograms of the control, 5PW and 10PW samples under mesophilic temperature and OLR 1.5 g COD L<sup>-1</sup>