



# Energy recovery from food waste and garden and park waste: Anaerobic co-digestion versus hydrothermal treatment and anaerobic co-digestion

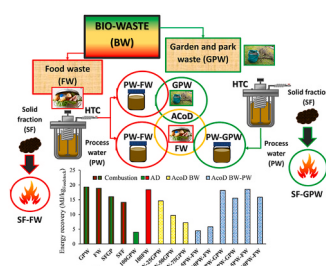
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## HIGHLIGHTS

- Anaerobic digestion allows maximum energy recovery contained in the food waste (FW).
- Hydrothermal treatment, the best option for garden and park waste valorization.
- Anaerobic co-digestion (AcoD) of FW and GPW enhances stability and biodegradability.
- AcoD of FW+5% process water (COD basis) shows similar energy recovery that FW alone.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The feasibilities of the anaerobic co-digestion of two of the most relevant biowastes, food waste and garden and park waste, were evaluated and compared with the hydrothermal treatment of each waste and the anaerobic co-digestion of raw biowastes with the process water generated. The effects on the process stability and energy recovery were also analyzed. Anaerobic digestion was the best option for food waste treatment from an energetic point of view, with 81% recovery of the energy stored in the feedstock, while the highest energy recovery from garden and park waste was obtained for the solid fraction generated from hydrothermal treatment (85.5%). In addition, the anaerobic co-digestion of food waste with 5% of the process water generated from garden and park waste showed a similar energy recovery to that of food waste only (~80%), thus improving the biological stability of the process.

## 1. Introduction

Biowaste (BW) management has become a major global concern and a topic of particular interest for the European Commission in terms of

working toward a circular economy. In 2019, approximately  $14 \times 10^6$  tonnes of BW was generated in the European Union (European Environment Agency, 2020), only a small fraction of which was processed as a useful resource. Instead, most of this BW was landfilled or dumped,

**Abbreviations:** AcoD, anaerobic co-digestion; AD, anaerobic digestion; BW, bio-waste; FW, food waste; GPW, garden and park waste; HHV, higher heating value; HTT, hydrothermal treatment; PW, process water; SF, solid fraction; SFF, solid fraction of food waste; SFGP, solid fraction of garden and park waste; SCOD, soluble COD; SMP, specific methane production; TA, total alkalinity; TCOD, chemical oxygen demand; TKN, total Kjeldahl nitrogen; TS, total solids; TVFA, total volatile fatty acids; VFA, volatile fatty acids; VM, volatile matter; VS, volatile solids; YSF, solid fraction yield; YPW, process water yield.

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leading to multiple environmental problems (Sharma et al., 2019). The need for sustainable BW management strategies in Europe has been reinforced by the revision of the Waste Framework Directive and Landfill Directive to reduce landfill disposal (European Parliament, 2018a, 2018b). Several technologies, mainly classified as biological (composting and anaerobic digestion (AD)) and thermochemical (combustion, pyrolysis, torrefaction, gasification, and hydrothermal) treatments, can be used to accomplish this purpose (Rajaeifar et al., 2017).

Anaerobic digestion is a widely established biological process that converts organic matter into two valuable products: a nutrient-rich digestate, with various applications such as in agriculture, and a methane-enriched biogas that can be used to generate electricity and heat, or be upgraded to natural gas substitutes (Peng et al., 2020). Biogas production plays an important role in the energy systems of some European countries because of the high availability of BW throughout the year, with 11,084 biogas plants in Germany, 1655 in Italy, and 837 in France (Annual Statistical Report of the European Biogas Association, EBA, 2019). Seventy-two percent of these plants are fed with agricultural residues, while the rest are fed with organic waste, thereby improving the sustainability of BW management and alleviating the dependence on fossil fuels.

Food waste (FW) and garden and park waste (GPW) are among the most representative BWs. Generally, FW is characterized by a high water content (>75%) consisting mainly of carbohydrates, fats, and proteins, making it readily biodegradable. This high biodegradability coupled with a usually low C/N ratio (15–36) (Zhang et al., 2007) can lead to the accumulation of intermediate products such as volatile fatty acids (VFA) and/or ammonia, thus inhibiting the AD process (Bong et al., 2018). In contrast, GPW (i.e., tree leaves and branches) consists mainly of hemicellulose, cellulose, and lignin, and is characterized by a high C/N ratio (>50). Owing to the low biodegradability of lignin, the AD of GPW only achieves approximately 10% of its theoretically expected methane production. The hydrolysis step in the AD is generally considered to be a speed limiting step (Li et al., 2017). Therefore, in recent years, significant efforts have been made to improve the performance of AD, with the focus on proving the suitability of effective pretreatments (biological, chemical, physical, or thermal) before AD to increase energy recovery (Hoang et al., 2021).

Hydrothermal treatments are widely used to valorize BW and can also be applicable to overcome the recalcitrant nature of raw lignocellulosic biomass and improve biodegradability of some bio-feedstocks, (Ahmad et al., 2018; Li et al., 2014). Among the hydrothermal treatments, liquid hot water (LHW) treatment of biomass offers an effective solution to replace dilute acid in the pretreatment of herbaceous biomass (Zhang et al., 2020), mainly hydrolysing cellulose and hemicellulose along with a small percentage of lignin (Yang et al., 2019). LHW treatment is commonly performed at 150–260 °C and have a lower cost in terms of capital investments, need less energy and chemical inputs, as well as generate minimal inhibitory products and waste (Chen et al., 2022; Wells et al., 2021).

The slurry obtained after the hydrothermal process contains a solid and a liquid fraction (Mosier et al., 2005). The solid fraction (SF), has potential applications in different fields, including energy recovery. The liquid fraction, called process water (PW), is also produced during HTT, being mainly composed of short-chain organic compounds, especially VFA, sugars, xylose and other hemicellulosic carbohydrates (Zhang et al., 2020), making PW a potential substrate for AD. However, it can also contain refractory compounds, such as furfural, phenols, and furans, which can cause methanogenic inhibition (De la Rubia et al., 2018a, 2018b; Moreno et al., 2019).

Several authors have coupled HTT and AD for a wide variety of biomasses, such as animal manure, sewage sludge and microalgae to produce not only SF with a high higher heating value (HHV), but also biogas from PW, thus allowing the recovery of a significant portion of the energy contained in the feedstock (Jia et al., 2017; Song et al., 2021). Most studies focus on improving biodegradability and valorization of SF

or PW by downstream AD to enhance the overall energy recovery (Fernández-Cegri et al., 2012; Phuttaro et al., 2019). There is some knowledge on the anaerobic co-digestion (AcoD) of SF with raw waste (Ren et al., 2020; Xu et al., 2021). However, there is a lack of knowledge on the co-digestion of the PW generated via HTT and untreated BW, which could lead to improve not only the recovery of stored in the feedstock, but the integration of all products in a single AcoD process allowing the reduction of operational costs. Moreover, considering the characteristics of GPW, a possible treatment strategy could be AcoD of the obtained PW obtained after HTT with a more biodegradable waste such as FW, balancing the C/N ratio at ~20–30 (Labatut and Pronto, 2018), thus avoiding VFA accumulation and improving methane yield (Mata-Alvarez et al., 2014; Yang et al., 2015).

The main goal of this work is to study the integrated valorization of the two most abundant BWs, FW and GPW, by i) determining the effect of the FW/GPW ratio on the feasibility of the AcoD process, and ii) performing HTT on each waste in combination with the AcoD of the obtained PW and raw BW. Thus, batch AcoD tests were carried out to determine and compare their biochemical methane potentials and the time evolution of several variables of interest, such as pH, alkalinity, ammoniacal nitrogen, soluble chemical oxygen demand (SCOD), and VFA.

## 2. Materials and methods

### 2.1. Inoculum and biowaste

The inoculum used for AD and AcoD assays was granular anaerobic sludge obtained from an industrial digester that treats brewery wastewater under mesophilic conditions (35 °C). The inoculum characteristics were as follows: pH  $7.4 \pm 0.1$ , total solids (TS)  $50.7 \pm 2$  g TS/L, volatile solids (VS)  $41.9 \pm 2$  g VS/L, and total COD (TCOD)  $61.4 \pm 1.7$  g O<sub>2</sub>/L.

Garden and park waste was collected from the Migas Calientes composting plant, located in Madrid, Spain. The feedstock was ground and sieved to a particle size of <3 mm, dried at 100 °C for 48 h, and finally stored in closed containers at room temperature until use. The main characteristics of the collected GPW were:  $947 \pm 9$  g TS/kg,  $900 \pm 8$  g VS/kg,  $0.97 \pm 0.02$  g/kg total Kjeldahl nitrogen (TKN) and TCOD  $1241 \pm 51$  g O<sub>2</sub>/kg.

Food waste was obtained from a municipal solid waste treatment plant located in Madrid. The collected FW was crushed until a smooth paste was obtained and stored in airtight buckets at 4 °C until use. The main characteristics were:  $158.6 \pm 3$  g TS/kg,  $145.8 \pm 3$  g VS/kg,  $0.2 \pm 0.02$  g/kg TKN and TCOD  $327 \pm 14$  g O<sub>2</sub>/kg.

### 2.2. Hydrothermal treatment experiments

Both BWs were subjected to HTT at 180 °C for 1 h. In the case of FW, no water was added because of its low solid content, while GPW was mixed with deionized water in a 20:80 (wt.%) ratio. The experiments were performed in a ZipperClave 316 stainless steel pressure reactor with a total volume of 4 L. Each BW was stirred at 150 rpm using a Rushton impeller, and the operating temperature was reached at a heating rate of 3 °C/min and maintained for 1 h. The reaction was stopped by cooling with an internal heat exchanger using tap water. The HTT experiments were performed in duplicate. First, SF and PW were separated by centrifugation (SIGMA 3–16 L) at 3500 rpm for 10 min and subsequently filtered through a 0.45 µm filter. Then, PW was characterized and stored in air-tight buckets at 4 °C until the AcoD tests, while SF was oven-dried to a constant weight, ground, and sieved using a Filtra No. 38373 sieve to reduce particle size (<0.25 mm) for sample characterization. For FW, the obtained SF and PW were labeled as SFF and PWF, while those for GPW were labeled as SFGP and PWGP, respectively.

### 2.3. Anaerobic digestion. Experimental set-up and procedure

Anaerobic co-digestion tests were carried out in 120 mL glass serum vials, which were filled with 60 mL of a suspension of inoculum (15 g VS/L) and substrates in basal medium with macro- and micronutrients, as recommended by Villamil et al. (2018). The suspensions were flushed with N<sub>2</sub> for 3 min before the vials were sealed with rubber stoppers and metallic crimps. The vials were placed in a thermostatic shaking water bath at mesophilic temperature (35 ± 1 °C) and 130 rpm.

Two AcoD assays were performed:

1. *AcoD of FW and GPW*: The inoculum to substrate ratio (ISR) was maintained at 2, on a VS basis. Mixtures of different FW to GPW ratios (on a VS basis) (25%, 50%, and 75% FW), as well as the two individual residues (FW and GPW) were tested. These assays are referred to as 25FW, 50FW, 75FW, 100FW, and 100GPW, respectively.
2. *AcoD of PW and BW*: The ISR was maintained at 2 on a COD basis, as suggested by Villamil et al. (2018). The raw substrates (FW and GPW) were mixed with low percentages of PW (5% and 10% on a COD basis) to avoid inhibition by non-biodegradable compounds. Both raw substrates were mixed with PW obtained from the HTT of FW, and the one generated from GPW was also combined with FW. Considering the low methane production obtained for GPW in the previous assay, no trials based mainly on it were carried out. The AcoD assays are denoted as the main substrate (F or GP), and percentage (5 or 10) and type of PW (GP for the obtained from GPW and F for the obtained from FW), that is, F5GP, F10GP, F5F, F10F, GP5F, and GP10F, respectively.

All the experiments were run for 43 d until no significant gas production was observed (for the last day, the production was <2% of the accumulated methane produced), suggesting that biodegradation was essentially completed (De la Rubia et al., 2011). For each assay, three blank runs were used for subtracting the methane production due to biomass decay and the possible presence of residual substrate in the inoculum. Three positive controls (tests with starch as the only substrate) were used to verify the inoculum activity, yielding approximately 350 mL CH<sub>4</sub>/g COD added at standard temperature (273.14 K) and pressure (1 bar). For each mixture tested, 10 batch reactors were run: 3 were used for biogas analysis (volume and composition), while 7 were sacrificed and removed every 1–2 d initially before increasing to every 7 d to study the temporal evolution of the AD process.

### 2.4. Analytical methods

The inoculum and feedstock were characterized by measuring the TS and VS according to the standard methods 2540 B and 2540E, respectively (APHA, 2005). The TCOD was determined using a thermoreactor (P-Selecta Bloc Digest 12) following the method proposed by Raposo et al. (2008). The TKN was determined by digestion, distillation and titration according to the standard method 4500-Norg B (APHA, 2005). The elemental composition of the feedstock was also analyzed (LECO CHNS-932, model 601-800-500) following the manufacturer's standard procedure. The neutral detergent fiber (NDF), and acid detergent fiber (ADF) and acid detergent lignin (ADL), determined according to ISO 16472:2006 and ISO 13906:2008, respectively, were used to calculate hemicellulose (as difference between NDF and ADF), cellulose (as difference between ADF and ADL) and lignin (ADL) of feedstocks and SF.

The obtained SFs were characterized by elemental composition and proximate analysis (moisture, ash, volatile matter (VM), and fixed carbon (FC)) performed by thermogravimetric analysis (TGA) (ASTM, 2015). The elements were quantified by inductively coupled plasma–atomic emission spectroscopy (ICP–OES) on an Elan 6000 Sciex instrument (PerkinElmer). The HHVs of the feedstock and SF samples were determined using Schuster's equation (Eq. (1)) (Channiwal and Parikh, 2002):

$$HHV \text{ (MJ / kg)} = 0.3491 \%C + 1.1783 \%H + 0.1005 \%S - 0.0151 \%N - 0.103 \%O - 0.0211 \%Ash \quad (1)$$

Supernatants from the AcoD tests were withdrawn, centrifuged, and filtered (0.45 µm) to determine the following parameters: pH (Crison 20 Basic pH meter); partial and total alkalinity by pH titration with 0.02 N H<sub>2</sub>SO<sub>4</sub> to 5.75 and 4.3, respectively, using the standard method 2320B (APHA, 2005); SCOD using the 5220D standard method (APHA, 2005); ammoniacal nitrogen by distillation and titration according to the standard method 4500-NH<sub>3</sub>B-C (APHA, 2005). Individual VFAs (C2–C7, including iso-forms) were identified using gas chromatography (GC, Varian 430-GC instrument) as described by De la Rubia et al. (2018a, 2018b). Species identification in the assays involving PW was performed at the beginning and end of the experiments using gas chromatography/ion trap mass spectrometry (GC–MS (CP-3800/Saturn 2200) (De la Rubia et al., 2018b). Compounds were identified using the NIST 2008 library.

Biogas production was determined using a manometric method (Rozzi and Remigi, 2004) by measuring the pressure increase in each vial using an electronic pressure monitor (IFM, PN 7097). Biogas composition was determined using a Thermo Fisher Trace 1300 GC equipped with a thermal conductivity detector (TCD) (De la Rubia et al., 2018b).

### 2.5. Kinetic analysis

The modified Gompertz model (Eq. (2)) was used to describe the kinetics of methane production during the AcoD experiments.

$$G = G_{max} \exp \left\{ - \exp \left[ \frac{\mu}{G_{max}} (\lambda - t) + 1 \right] \right\} \quad (2)$$

where  $G$  is the cumulative specific methane production (mL CH<sub>4</sub>/g VS<sub>added</sub>),  $G_{max}$  is the ultimate methane production (mL CH<sub>4</sub>/g VS<sub>added</sub>),  $t$  is the digestion time (d),  $\mu$  is the maximum methane production rate (mL CH<sub>4</sub>/g VS<sub>added</sub> · d), and  $\lambda$  is the lag-phase time constant (d).

### 2.6. Energy recovery

The product mass yields were calculated using Eq. (3). The SF yield ( $Y_{SF}$ ) was defined as the ratio of recovered SF ( $W_{SF}$ ) to feedstock ( $W_{GPW}$  or  $W_{FW}$ ) on a dry weight basis.

$$Y_{SF} (\%) = \frac{W_{SF}}{W_{GPW, FW}} \cdot 100 \quad (3)$$

The specific methane production (SMP) obtained from the batch anaerobic tests was converted into HHVs for the different trials using Eq. (4).

$$HHV \text{ (MJ / kg)} = 39.8 \cdot SMP \cdot \left( \frac{VS}{TS} \right) \quad (4)$$

where the coefficient 39.8 is the lower heating value for pure methane in MJ/Nm<sup>3</sup>.

The energy recovery associated with the HTT products was calculated using Eq. (5).

$$\text{Energy recovery (MJ / kg}_{feedstock}) = HHV_{SF} \cdot Y_{SF} \quad (5)$$

## 3. Results and discussion

### 3.1. Feedstock, solid fraction, and process water characterization

Table 1 shows the main characteristics of the raw materials and produced SFs. The elemental analysis results were very similar for both raw materials. The nitrogen content was higher in FW because of the presence of vegetal and animal proteins. A high C/N ratio (52.1 ± 0.1)

**Table 1**

Proximate, elemental and fiber analyses of feedstocks and solid fractions\*.

	Y <sub>SF</sub> (%)	FC (%)	VM (%)	Ash (%)	C (%)	H (%)	N (%)	S (%)	O (%)	Hemicellulose (%)	Cellulose (%)	Lignin (%)	HHV (MJ/kg)
FW	–	13.3	67.6	11.8	44.5	6.2	1.9	0.2	35.4	2.3	10.5	11.1	18.9
GPW	–	18.4	76.5	0.2	46.9	6.1	0.9	0.4	40.6	8.5	45.7	21.1	19.3
SFF	76.5	14.4	79.5	6.1	48	5.8	2.0	0.2	37.9	6.0	23.2	44.9	19.6
SFGP	87.6	29.6	67.1	3.3	49.8	5.3	1.3	0.2	40.1	7.6	43.5	28.9	19.4

\* Each data point shows a standard deviation of  $\leq 0.1$ .

was determined for GPW, whereas a value of  $23.4 \pm 0.1$  was obtained for FW, which is somewhat higher than that observed by other authors ( $<20$ ) (Zhang et al., 2014).

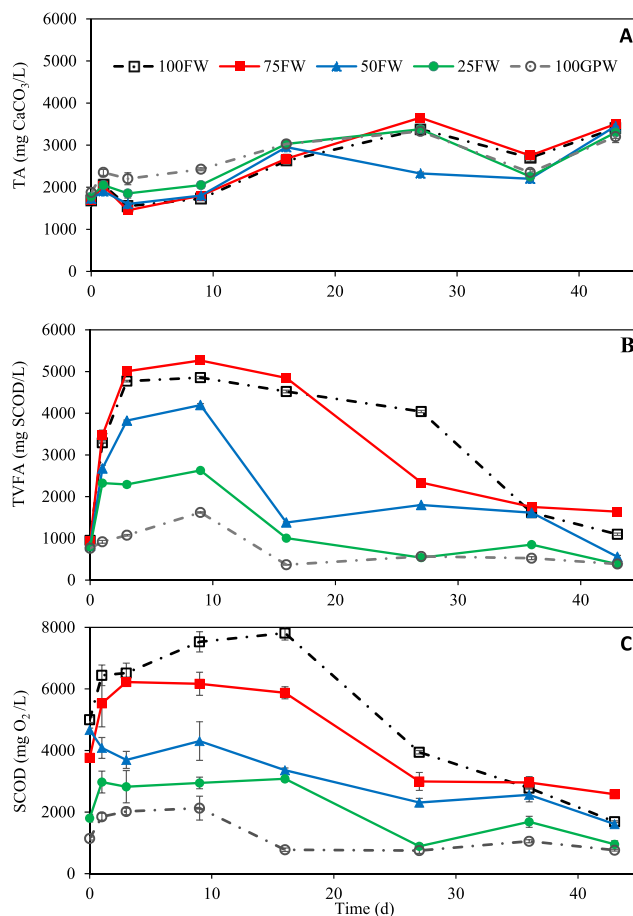
Although the SF yields differed considerably (76.5% for FW to 87.6% for GPW), the HHVs were similar for both SFs. Comparing the feedstocks with the produced SFs (Table 1), the HTT process increased the HHVs in both cases as Eisenbies et al. (2019) observed using wood pellets. For FW, the VM content increased to  $>75\%$  and the ash content reduced, whereas the ash content increased and the VM content decreased for GPW, thus meeting the quality standards for thermally treated biomass (HHV of  $>18$  MJ/kg; VM content of  $<75\%$ ; sulfur content of  $<0.3\%$ ; nitrogen content of  $<2.5\%$ ) (ISO/TS 17225–8). Table 1 also includes the results of fiber analysis. Hemicellulose was partially hydrolyzed after HTT treatment taking into account the fiber content of the feedstocks, while a concentration of cellulose and lignin was obtained, as observed in previous works (Fernández-Cegri et al., 2012).

The PWs from the HTT of the BWs had acidic pH values of  $\sim 5.5$ . The PW of FW showed higher contents of organic matter and nitrogen ( $45 \pm 1$  g VS/L,  $75.8 \pm 1$  g COD/L, and  $1.6 \pm 0.1$  g TKN/L) compared with the PW of GPW ( $31 \pm 3$  g VS/L,  $47.4 \pm 1$  g COD/L, and  $0.6 \pm 0.01$  g TKN/L).

### 3.2. Anaerobic co-digestion of food waste and garden/park waste

A notable difference was observed in the process related to the origin of the feedstock. The trials with higher percentages of GPW (25FW and 100GPW) showed a stable pH of approximately 7–7.5 and a TA of  $\geq 1900$  mg  $\text{CaCO}_3/\text{L}$ , whereas the trials with a higher proportion of FW (100FW, 75FW, and 50FW) exhibited significant decreases in pH (to 5.5–6) and TA (to  $\sim 1500$  mg  $\text{CaCO}_3/\text{L}$ ) (Fig. 1A). These results are related to the buffer demand caused by the high biodegradability of FW and the accumulation of VFA, which were far away from the optimum values for methanogens (pH of 6.8–7.6 and TA of  $>2500$  mg  $\text{CaCO}_3/\text{L}$ , respectively). Once the total VFA (TVFA) content began to decrease, the TA remained above 3000 mg  $\text{CaCO}_3/\text{L}$  and the pH stabilized at  $\sim 7.5$ –8. The TVFA content in the treatments with a higher proportion of GPW (25FW or 100GPW) (up to 2600 mg SCOD/L) was lower than that obtained in the treatments with FW (4200–5300 mg SCOD/L) because of the low hydrolysis and acidification of GPW. A significant decrease in the SCOD was observed in tests containing a higher proportion of FW because of its higher biodegradability compared with GPW (Fig. 1C). In all cases, the release of ammoniacal nitrogen remained below 720 mg/L  $\text{NH}_3\text{-N}$  (data not shown), which was below the critical content (1700 mg/L) and could have led to process inhibition (Ipiates et al., 2021).

Regarding the biochemical methane potential, the experimental and simulated cumulative methane production of the tested mixtures are shown in Fig. 2. An increase in the proportion of GPW in the mixtures led to a lower methane production, which was attributed to the gradual increase in non-biodegradable lignin (Sawatdeenarunat et al., 2015). The 75FW run achieved the highest methane production ( $345 \pm 4$  mL  $\text{CH}_4$  STP/g  $\text{VS}_{\text{added}}$ ), being 1.5- and 2-times higher than those obtained for the 50FW and 25FW treatments, respectively. These results were similar to those obtained by Panigrahi et al. (2020) (335 mL  $\text{CH}_4$  STP/g  $\text{VS}_{\text{added}}$ ) using a similar mixture (75FW–25GPW). Although the 25FW and 50FW trials produced higher methane than those obtained with GPW as a bare substrate (95 mL  $\text{CH}_4$  STP/g  $\text{VS}_{\text{added}}$ ), methane production was still low (41%–55%) compared to the methane achieved with



**Fig. 1.** Total alkalinity (A), total volatile fatty acid concentration (B), and soluble chemical oxygen demand (C) versus time for the anaerobic co-digestion of FW and GPW.

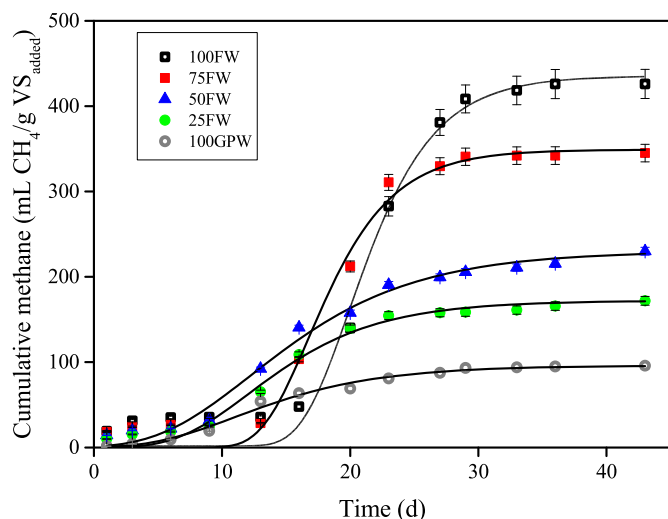
#### 100FW.

The experimental methane production results were fitted to the modified Gompertz model (Eq. (2)) using OriginPro 8 software (OriginLab, USA). Table S1 lists the experimental and estimated methane productions as well as the values of the kinetic parameters. A significant difference in methane production associated with the feedstock was observed. Regression analysis confirmed that FW had the highest ultimate methane production ( $G_{\text{max}}$ ) and methane production rate ( $\mu$ ). Treatments with the highest FW content exhibited a significant lag phase. However, these trials achieved a higher methane production, which is consistent with the findings of Salehiyoun et al. (2019) during the AD of several types of fruit waste.

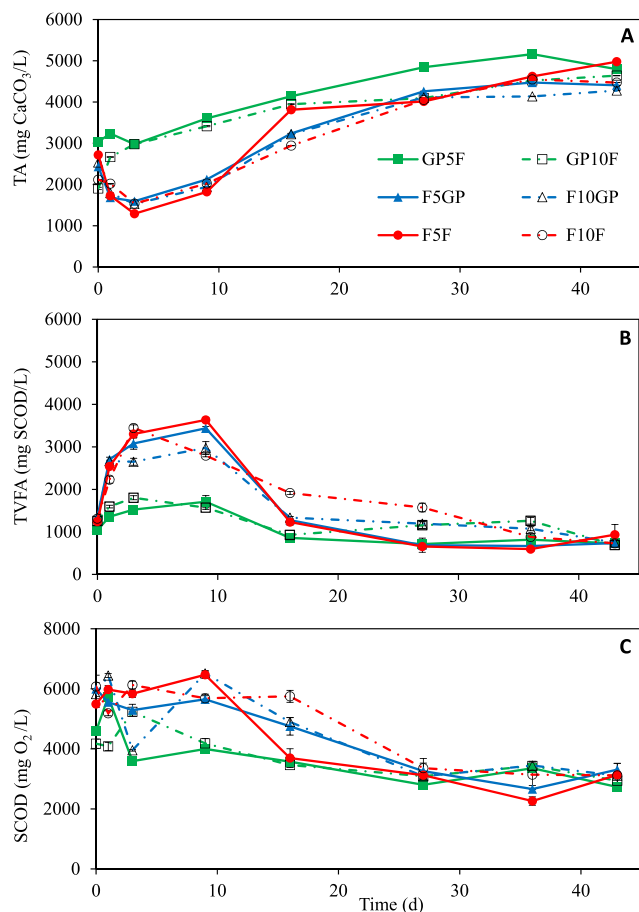
### 3.3. Anaerobic co-digestion of raw biowastes and the process water from HTT

Fig. 3 plots the TA, TVFA content, and SCOD versus time during the AcoD of BW and PW. Regarding TA, two different feedstock-related





**Fig. 2.** Experimental and simulated cumulative methane production of anaerobic co-digestion of FW and GPW.



**Fig. 3.** Total alkalinity (A), total volatile fatty acid concentration (B), and soluble chemical oxygen demand (C) versus time for the anaerobic co-digestion of FW and GPW with process water.

behaviors were observed (Fig. 3A). In the GPW-based assays, the TA values exceeded 3000 mg  $\text{CaCO}_3/\text{L}$  throughout the AcoD process, whereas they decreased to 1600 mg  $\text{CaCO}_3/\text{L}$  at the beginning of the FW experiment, indicating buffer consumption. The pH remained at 7–8 for all treatments, agreeing with the results of Villamil et al. (2019) for the

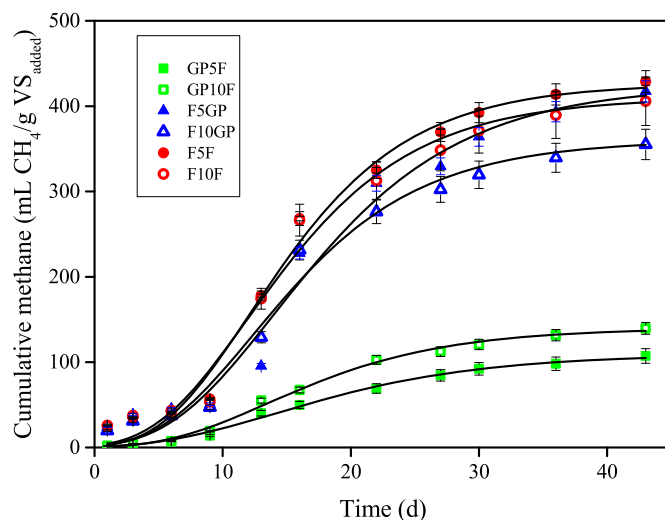
co-digestion of primary sewage sludge and PW from the HTT of secondary sewage sludge. As can be seen in Fig. 3B, the AcoD of FW and PW resulted in a maximum TVFA production ( $\sim 3500$  mg SCOD/L) for the treatments with 5% PW (F5F and F5GP), and 10% PW from the HTT of FW (F10F), whereas the F10GP treatment reached almost 3000 mg SCOD/L, which was significantly lower than the 5000 mg SCOD/L recorded for the AcoD of raw substrates (namely 75FW and 50FW). In the tests performed with GPW (GP10F and GP5F), the TVFA content was approximately 1600–1800 mg SCOD/L, which was similar to that obtained in the 100GPW experiment (Fig. 1B).

Fig. 3C displays the time plot of the SCOD values for the AcoD of BW and PW and shows that SCOD removal ranged from 41% to 49% SCOD, except for the GP10F treatment, which only reached 31%. As for ammoniacal nitrogen, values lower than those considered as inhibitory (1700 mg/L) were observed (Ipiñales et al., 2021).

A similar evolution of the TVFA content was observed for assays F5F and F5GP. However, a faster decrease in the SCOD value was obtained for the F5F treatment between days 9 and 16, which related to the rate of methane production (Fig. 4). The final cumulative methane production was similar for both treatments ( $\sim 425$  mL  $\text{CH}_4$  STP/g  $\text{VS}_{\text{added}}$ ), as well as for F10F. However, when the PW co-digested at 10% with FW was obtained from GPW (F10GP), the methane production was reduced to 355 mL  $\text{CH}_4$  STP/g  $\text{VS}_{\text{added}}$ . This is corresponded to the lowest TVFA/SCOD ratio observed in this trial, suggesting that the difference in the SCOD must have been due to the presence of other non-biodegradable soluble compounds affecting the final methane production. Villamil et al. (2019) also found that an increase in the ratio of PW in the mixture co-digesting the liquid fraction of the HTT treatment of secondary sludge with primary sewage led to a decreased methane production. Therefore, no synergistic effects in terms of methane production were observed when AcoD (FW and PW) and AD (FW as bare substrate) were compared.

The AcoD treatments performed with GPW achieved higher methane productions than those performed with the raw residue (140 mL  $\text{CH}_4$  STP/g  $\text{VS}_{\text{added}}$  for GP10F and 107 mL  $\text{CH}_4$  STP/g  $\text{VS}_{\text{added}}$  for GP5F versus 96 mL  $\text{CH}_4$  STP/g  $\text{VS}_{\text{added}}$ ). However, these methane productions were 3-times lower than those obtained with FW, suggesting that neither AD nor AcoD are suitable processes for GPW energy recovery. As shown in Table S1, the experimental results of the cumulative methane production during the AcoD of raw BW and the PW of HTT were accurately fitted by the modified Gompertz model ( $R^2 > 0.98$ ). The apparent kinetic parameters confirmed these results.

The PW obtained from the HTT treatment of BW contained high



**Fig. 4.** Experimental and simulated cumulative methane productions for the anaerobic co-digestion of FW or GPW with the process water of the HTT of GPW or FW.

molecular weight species with low biodegradability, such as different acids (Mosier et al., 2005), cyclic, nitrogenous, aromatic, phenolic (from degradation of lignin (Monlau et al., 2014)) and alkyl compounds produced by the degradation of proteins, sugars (Simangunsong et al., 2020) and Maillard's reactions (Fig. S1). Furans, amines, and several acids, were removed after AD (Fig. S2). The degradation of acids was probably due to the high reactivity of the carbonyl group (C=O) and O–H bond, which can be oxidized by the action of anaerobic microorganisms. However, long-chain alkyl compounds (glutaraldehyde, oleyl alcohol, 1-undecanol, and sorbic acid) and O- and N-heterocyclic compounds (cyclohexene, 1-methyl-4-(1-methylethylidene)-, and aniline) were detected at the end of the digestion process. Methyl-1H-indole, which is degradable by methanogenic microorganisms, was detected in all treatments. Additionally, other refractory species (e.g., 2,5-cyclohexadiene-1,4-dione dioxime) that were not found in the PW were detected in all tests at similar abundances. The presence of these refractory species may have affected the methane production by limiting the efficiency of the biological process (De la Rubia, et al., 2018a, 2018b; Moreno et al., 2019).

### 3.4. Energy recovery

Fig. 5 shows the energy recovered per kilogram of dry feedstock from the SF obtained from the HTT treatment, AD of raw FW and GPW, and AcoD of BW with and without PW. The HHVs of raw BWs (19.3 MJ/kg<sub>dry feedstock</sub> for GPW and 18.9 MJ/kg<sub>dry feedstock</sub> for FW) were considered as the total amount of energy stored in those feedstocks (Table 1). Direct combustion of GPW is not suitable for industrial purposes because of its high VM content (76.5%).

For FW, AD allowed the recovery of 97.3% of the energy contained in the feedstock (22.5% higher than that from combusting the SF of FW); hence, AD is the most attractive technology for the management of FW. The combustion of the SF of GPW allowed the recovery of 16 MJ/kg of dry feedstock, corresponding to 83% of the amount stored in the starting feedstock, while the AD of GPW had a low energy recovery performance (20.7%). The SF of GPW met the quality standards for T2 solid fuels produced from thermally treated biomass (VM <75%). On the other hand, when evaluating the AcoD of these BWs, it was observed that an increase in the FW content in the mixture led to a higher energy recovery compared to the AD of GPW only (56.1%, 29.9%, and 16.8% for 75FW, 50FW, and 25FW respectively). The AcoD of GPW with PW (GP5F and GP10F) increased the energy recovery (2.6% and 9.6%, respectively) compared to the AD of GPW. Energy recovery was scarcely affected in the assays performed with FW and PW, except when the percentage of PW was increased to 10% (~83.1%) because of the higher concentration of non-biodegradable recalcitrant compounds.

### 4. Conclusions

The work addresses the implementation of an integrated waste management concept in a circular economy framework, combining hydrothermal treatment of GPW and biological treatment (AcoD) of the PW generated with the raw FW, improving the overall recovery of the energy stored in the GPW. Hydrothermal treatment proved to be the most attractive technology for GPW, obtaining a SF with high higher heating value and a liquid byproduct with high organic matter content. AcoD of 95% FW and 5% PW (on a COD basis) improved process stability by balancing the C/N ratio and achieved similar results in terms of energy recovery from AD of raw FW.

### Author contribution statement

**Eneko Suarez:** Investigation, Writing – original draft. **Angel F. Mohedano:** Conceptualization, Funding acquisition, Resources, Writing – review & editing, Supervision, Project administration. **Montserrat Tobajas:** Conceptualization, Validation, Methodology, Resources,

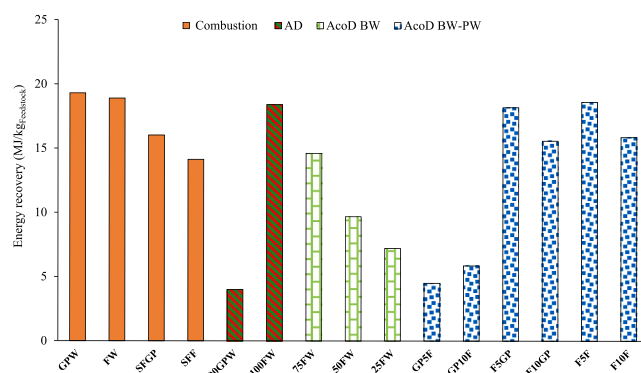


Fig. 5. Energy recovery through BW combustion, SF combustion, AD and AcoD of feedstocks, and AcoD of feedstocks with PW from HTT.

Writing – review & editing, Supervision. **M. Angeles de la Rubia:** Conceptualization, Validation, Funding acquisition, Methodology, Resources, Writing – review & editing, Supervision, Project administration.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2022.134223>.

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