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Mesophilic anaerobic co-digestion of the organic fraction of municipal solid waste with the liquid fraction from hydrothermal carbonization of sewage sludge

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ABSTRACT

In the present study, the influence of substrate pre-treatment (grinding and sieving) on batch anaerobic digestion of the organic fraction of municipal solid waste (OFMSW) was first assessed, then followed by co-digestion experiments with the liquid fraction from hydrothermal carbonization (LFHTC) of dewatered sewage sludge (DSS). The methane yield of batch anaerobic digestion after grinding and sieving (20 mm diameter) the OFMSW was considerably higher (453 mL CH₄ STP·g⁻¹ VS_{added}) than that of untreated OFMSW (285 mL CH₄ STP·g⁻¹ VS_{added}). The modified Gompertz model adequately predicted process performance. The maximum methane production rate, R_m , for *ground* and *sieved* OFMSW was 2.4 times higher than that of untreated OFMSW. The anaerobic co-digestion of different mixtures of OFMSW and LFHTC of DSS did not increase the methane yield above that of the anaerobic digestion of OFMSW alone, and no synergistic effects were observed. However, the co-digestion of both

wastes at a ratio of 75% OFMSW-25% LFHTC provides a practical waste management option. The experimental results were adequately fitted to a first-order kinetic model showing a kinetic constant virtually independent of the percentage of LFHTC ($0.52\text{--}0.56\text{ d}^{-1}$) and decreasing slightly for 100% LFHTC (0.44 d^{-1}).

Keywords: Biochemical methane potential (BMP), anaerobic co-digestion, hydrothermal carbonization (HTC), organic fraction of municipal solid waste (OFMSW) pre-treatment, sewage sludge.

1. Introduction

Anaerobic digestion is a well-proven and mature technology for producing methane-rich biogas from the decomposition of organic wastes. Because of the energy efficiency of this technology, it has been used for treating biodegradable wastes, such as the organic fraction of municipal solids wastes (OFMSW), wastewater treatment biosolids, and a number of food and beverage wastes (Kim et al., 2017). Over 17,000 biogas plants have been constructed in Europe, primarily in Germany (over 10,000 plants), followed by Italy and France (EBA, 2015). The majority of the biogas plants (72%) are powered by agricultural resources, and the remainder use mainly organic waste substrates and sewage sludge (Torrijos, 2016).

Anaerobic digestion of single substrates presents some drawbacks linked to characteristics of the substrates. Anaerobic co-digestion, the simultaneous digestion of two or more substrates, is a practical option to overcome the drawbacks of mono-digestion and to improve a plant's economic feasibility (Mata-Alvarez et al., 2014). Anaerobic co-digestion has many advantages compared to digestion of wastes alone: it improves the process stability, increases organic

loading rates and methane yield, dilutes toxic compounds, and balances solid content and nutrients, all of which allow for treatment of different wastes in one facility (Khalid et al., 2011; Mata-Alvarez et al., 2011). Recently, the main use of anaerobic co-digestion has been for co-digestion of OFMSW and thickened sewage sludge (Krupp et al., 2005; Mata-Álvarez et al., 2014).

In 2013, global municipal solid waste production was approximately 1300 million t·yr⁻¹ (Hoornweg and Bhada-Tata, 2012), and it is estimated that in 2025 the production will rise to 2200 million t·yr⁻¹, with approximately 46% organic content (Al Seadi et al., 2013). OFMSW is characterized by a high C:N ratio resulting from the presence of paper materials and other carbon-rich substances (Campuzano and González-Martínez, 2016). However, sewage sludge has a relatively low C:N ratio, ranging from 6:1–13:1. Appropriate mixing ratios of sewage sludge and OFMSW can provide an optimum C:N ratio (20:1–30:1) for anaerobic digestion (Zhang et al., 2008). Sludge is also rich in other macro- and micro-nutrients that stimulate the anaerobic digestion process (Silvestre et al., 2015).

Anaerobic digestion has become the preferred option to valorize sewage sludge. In recent decades, thermal treatments (e.g., pyrolysis or gasification) that require pre-dried feedstock have also been used for treating sewage sludge. Hydrothermal carbonization (HTC) is a relatively new process for wet biomass valorization, and is usually performed at temperatures lower than 375 °C and pressures of 4–22 MPa (Tekin et al., 2014). This technology is very promising for valorizing dewatered sewage sludge (DSS), and produces hydrochar with a high heating value (Kambo and Dutta, 2015). The liquid fraction obtained is characterized by a high chemical oxygen demand (COD) (90–100 g·L⁻¹) and has a total Kjeldahl nitrogen (TKN) value of 8.7 g N·L⁻¹ with a C:N ratio of 7:1 (Villamil et al., 2018). These are similar to the values

observed for thickened sewage sludge (Zhang et al., 2008). Reports on the potential to produce methane from the liquid fraction from hydrothermal carbonization (LFHTC) are limited. Previous studies have primarily focused on the results from LFHTC of lignocellulosic residues (Erdogan et al., 2015; Wood et al., 2013). Moreover, to date, no study has investigated the co-digestion of OFMSW and LFHTC of DSS.

The aim of this work was to study anaerobic co-digestion of the LFHTC of DSS and OFMSW using different co-substrate ratios. Biochemical methane potential (BMP) tests were conducted to determine the effects of the mixture co-substrate ratio under mesophilic temperatures on methane yield. The effects of substrate pre-treatment, after grinding and sieving, on anaerobic digestion of the OFMSW are also reported.

2. Material and Methods

2.1. Inoculum source

The anaerobic inoculum was obtained from the anaerobic digestate collected from a mesophilic reactor that treats the OFMSW from a municipal solid waste treatment plant (MSWTP) located near Madrid, Spain. The main characteristics of this digested solid waste were: pH, 8.2 ± 0.1 ; total solids (TS), $136.8 \pm 0.6 \text{ g} \cdot \text{kg}^{-1}$; volatile solids (VS), $70.7 \pm 0.8 \text{ g} \cdot \text{kg}^{-1}$; and total chemical oxygen demand (TCOD), $84.2 \pm 6.5 \text{ g} \cdot \text{L}^{-1}$.

2.2. Substrate characteristics

2.2.1. Influence of substrate pre-treatment

The sample of OFMSW was taken from the waste reception area of the aforementioned MSWTP. Although the solid waste delivered to the plant is source-segregated at the

household level, it still contained considerable amounts of plastic, paper, cardboard, metal, and glass. About 100 kg of OFMSW was manually sorted and the non-OFMSW portion was removed. Part of the prepared sample of OFMSW (*raw OFMSW*), was ground in a mill (*ground OFMSW*). In addition, a portion of the shredded organic waste was sieved to a final particle size of < 20 mm (*ground + sieved OFMSW*), increasing the homogeneity of the substrate. A commercial sieve (Orto Alresa OASS203) was used to shred and classify the OFMSW by using a 20 mm screen mesh (Cisa, serial number 151534.2). The main characteristics of the substrates are summarized in Table 1.

2.2.2. Co-digestion of OFMSW with LFHTC of DSS

Co-substrate 1. The *ground + sieved OFMSW* used to assess the influence of substrate homogeneity was selected as the first co-substrate. A more detailed characterization of this specific fraction, than showed in Table 1, was carried out (average values of three determinations \pm standard deviations), including the elemental composition: 24.52 ± 2.89 % C, 1.64 ± 0.46 % H, 1.90 ± 0.19 % N, 0.13 ± 0.05 % S; carbohydrates, 2590.1 ± 131.2 mg \cdot L $^{-1}$; proteins, 2035.5 ± 70.1 mg \cdot L $^{-1}$; and volatile fatty acids (VFA), 2045.4 ± 38.3 mg COD \cdot L $^{-1}$.

Co-substrate 2. The LFHTC, used as co-substrate 2, was obtained from hydrothermal carbonization of DSS (85% moisture), which was collected from a full-scale membrane bioreactor that treats industrial wastewaters from a cosmetics factory. The co-substrate was maintained at -20 °C until use. HTC of 1.5 kg of DSS was performed in a ZipperClave® 316 stainless steel pressure vessel with a working volume of 4 L (127 mm of inside diameter and 312 mm of inside length) and a maximum allowable working pressure of 151 bar at 232 °C. The reactor is equipped with a Rushton impeller (diameter:

50.8 mm) and a bottom flush valve. The temperature (208 °C) and stirring rate (150 rpm) were controlled using an (IB62) Iberfluid controller. The operating temperature was reached via a heating rate of 3 °C·min⁻¹, maintained for 1 h. The reaction was stopped by cooling with an internal heat exchanger using tap water. The liquid fraction was recovered by centrifugation (3500 rpm for 1 h) and filtration (0.45 µm); then was maintained at 4 °C until anaerobic digestion tests were performed.

The main characteristics and composition of this LFHTC (average values of three determinations ± standard deviations) were: pH, 5.1 ± 0.1; soluble COD (SCOD), 109.6 ± 0.9 g·L⁻¹; TS, 55.7 ± 0.5 g·L⁻¹; VS, 46.2 ± 0.5 g·L⁻¹; total organic carbon (TOC), 42.6 ± 0.9 g·L⁻¹; TKN, 8.7 ± 0.1 g·L⁻¹; carbohydrates, 2237.3 ± 31.9 mg·L⁻¹; proteins, 5420.5 ± 116.5 mg·L⁻¹ and VFA, 2748.6 ± 57.3 mg COD·L⁻¹. Figure 1 depicts a representative GC/MS chromatogram showing its fairly complex composition (Table 2).

2.3. Batch anaerobic experiments

Experiments were conducted in an automatic methane potential test system (AMPTS), which is a laboratory-scale batch methane-potential analyzer developed by Bioprocess Control AB (Lund, Sweden) following the procedure described elsewhere (Garcia-Mancha et al., 2012; Puyol et al., 2009; Rodriguez-Chiang and Dahl, 2015). This device registered only methane flow because other gas components, such as CO₂ and H₂S, were removed by an alkaline solution. A data acquisition system was incorporated.

2.3.1. Experiment to assess the influence of substrate homogeneity

The reactors (total volume: 1 L) were maintained at 35 ± 1 °C, and initially charged with the inoculum by maintaining a concentration of 15 g VS·L⁻¹. The inoculum to substrate

ratio (ISR) was maintained at 2 (VS basis) to avoid acidification (Alzate et al., 2012; Lee et al., 2017; Raposo et al., 2011; Villamil et al., 2018), because anaerobic digestion can be inhibited by accumulation of VFA at ISR lower than 1 (Alzate et al., 2012; Lee et al., 2017; Raposo et al., 2011; Villamil et al., 2018). Therefore, 7.5 g VS·L⁻¹ of OFMSW was added to every batch reactor for the three fractions studied. Fifty milliliters of stock mineral medium solution (composition described in Villamil et al., 2018) was added, followed by distilled water, to achieve the desired working volume of 225 mL. The reactors were flushed with N₂ to establish an anaerobic condition.

2.3.2. Experiment of co-digestion of OFMSW and LFHTC

Co-digestion experiments were conducted maintaining the ISR at 2 on a VS basis (1.75 on a COD basis), using different mixing ratios of OFMSW and LFHTC, on a COD basis: 100% OFMSW, 75% OFMSW-25% LFHTC, 50% OFMSW-50% LFHTC, 25% OFMSW-75% LFTHC, and 100% LFHTC. Throughout this paper, these co-substrates are referred to as 100OFMSW, 75OFMSW-25LFHTC, 50OFMSW-50LFHTC, 25OFMSW-75LFTHC, and 100LFHTC, respectively.

To determine the composition of the biogas from the co-digestion experiment, 120 mL glass serum vials (working volume of 60 mL) were filled with the same proportion of inoculum, substrates, and basal medium. Before sealing the vials with rubber stoppers and metallic crimps, the suspensions were flushed with N₂ for 3 min to establish anaerobic conditions. The vials were maintained at a mesophilic temperature (35 ± 1 °C) using a thermostatic water bath shaker (80 rpm). All the experiments were run until no significant gas production was observed, suggesting that biodegradation was essentially completed. This was confirmed with controls of starch (≈350 mL CH₄ STP·g⁻¹ COD_{added}). Triplicate

blank samples with no substrate were run to determine the amount of background methane originating from the inoculum alone.

2.4. Analytical methods

The inoculum and OFMSW were characterized by dry matter, moisture, VS, and ash according to Standard Methods 2540B and 2540E (APHA, 1998). TCOD was determined by the method proposed by Raposo et al. (2008). This analysis used 1 mL (liquid sample) or 250 mg (solid sample), 20 mL $K_2Cr_2O_7$ 1.2 N, 30 mL H_2SO_4 – Ag_2SO_4 , and the final solution was titrated with ferrous ammonium sulfate 0.5 N. Elemental analysis, was determined using a Leco CHNS-932 (Model No: 601-800-500) elemental analyzer, following the manufacturer's standard procedures.

The LFHTC of DSS was characterized by pH (using a model Crison 20 Basic pH meter), SCOD (using the closed digestion and colorimetric standard method 5220D (APHA, 1998), TOC (with an automatic analyzer TOC-VCPN, Shimadzu), and TKN (determination described in Villamil et al. (2018)). The identification of species was performed by gas chromatography/ion trap mass spectrometry (GC–MS; CP-3800/Saturn 2200) with an autosampler injector (Varian CP-8200), and a solid phase microextractor, (Carbowax/Divinylbenzene Yellow-Green). A Factor Four VF-5ms capillary column (30m long, 0.25mm diameter) was used. Sample injection was carried out with split-less at 220 °C, using He as carrier gas. The temperature program used in the GC/MS analyses ramped as follows: 40 °C for 15 min and 15 °C·min⁻¹ until 250 °C. The compounds were identified using the NIST 2008 Library.

Both co-substrates were characterized by carbohydrates and proteins by the methods

proposed by Dubois et al. (1956) and Lowry et al. (1951), respectively. Individual VFA concentrations (from acetic to heptanoic, including iso-forms) were determined by gas chromatography (GC) (Varian 430-GC) equipped with a flame ionization detector (FID) and a capillary column filled with Nukol (polyethylene glycol modified by nitroterephthalic acid). Prior to injection, 900 μL of the sample was mixed with 150 μL of H_3PO_4 (1:2 V:V) to adjust pH below 2.0 and 150 μL of a solution of crotonic acid (2000 $\text{mg}\cdot\text{L}^{-1}$) as an internal standard. This mixture was centrifuged to remove any solids and transferred to a 1500 μL gas GC vial. The sample injection volume was 1 μL . The temperatures of the injector and detector were maintained at 200 and 250 $^{\circ}\text{C}$, respectively, while the column temperature was increased from 120 to 160 $^{\circ}\text{C}$ with an increasing rate of 10 $^{\circ}\text{C}\cdot\text{min}^{-1}$.

As stated in Section 2.3.2, volumetric and manometric experiments were conducted for co-digestion assays. For the manometric method (Rozzi and Remigi, 2004), biogas production was determined by measuring the pressure increase in each vial using an electronic pressure monitor (ifm, PN 7097). This was measured daily during the first 3 d and eight more times for the remainder of the incubation period. It was expressed at standard temperature and pressure (STP: 273 K, 1 bar). Biogas was subsequently exhausted to re-establish atmospheric pressure. The gas composition (H_2 , H_2S , CO_2 , and CH_4) was determined by gas chromatography separation (Thermo Scientific Trace 1310) with an 8 ft. \times 1/8 in SS column packed with HayeSep Q 80/100 mesh and a thermal conductivity detector (TCD). The injection volume was 1 mL. The temperatures of the injector and detector were maintained at 110 and 150 $^{\circ}\text{C}$, respectively. Helium was used as the carrier at a flow rate of 30 $\text{mL}\cdot\text{min}^{-1}$. A standard gas (Praxair, S.A; composition: 7.35% H_2 ; 3.01% H_2S ; 59.84% CH_4 , and 29.8% CO_2) was used for system calibration.

3. RESULTS AND DISCUSSION

3.1. Influence of substrate pre-treatment on methane potential

Figure 2 shows variations in the accumulated methane yields ($\text{mL CH}_4 \text{ STP} \cdot \text{g}^{-1} \text{ VS}_{\text{added}}$) with time for the *raw*, *ground*, and *ground + sieved* OFMSW substrates. Lag periods of 8–14 d were observed for the three substrates tested, after which exponential increases in methane production were detected until reaching a final maximum value, which coincided with the ultimate methane yield for each case studied. These values were 285, 249, and 453 $\text{mL CH}_4 \text{ STP} \cdot \text{g}^{-1} \text{ VS}_{\text{added}}$ for *raw*, *ground*, and *ground + sieved* OFMSW substrates, respectively.

The values reported in the literature indicate that OFMSW can produce approximately 300–500 $\text{mL CH}_4 \cdot \text{g}^{-1} \text{ VS}_{\text{added}}$, with an average methane yield of 367 $\text{mL CH}_4 \cdot \text{g}^{-1} \text{ VS}_{\text{added}}$, depending on the source and type of OFMSW. Specifically, Curry and Pillay (2012) obtained methane yields in the range 310–490 $\text{NmL CH}_4 \cdot \text{g}^{-1} \text{ VS}_{\text{added}}$ with anaerobic digestion of OFMSW, while Davidsson et al. (2007) and Karnchanawong and Uparawanna (2006) achieved methane production of 300–400 $\text{NmL CH}_4 \cdot \text{g}^{-1} \text{ VS}_{\text{added}}$, respectively. More recently, Abudi et al. (2016) reported yield coefficient values of 214 $\text{mL biogas} \cdot \text{g}^{-1} \text{ VS}$ in anaerobic digestion experiments of *raw* OFMSW carried out in batch mode at a mesophilic temperature (37 °C). All these values were lower than those obtained in the present study for anaerobic digestion of *ground + sieved* OFMSW.

There is wide variability in the BMP from OFMSW, depending on the separation operations carried out on this substrate. The highest methane production was achieved

when the waste was more homogeneous, that is, when the waste was subjected to grinding and sieving. This type of mechanical pretreatment reduces the particle size and increases the specific surface area available to the anaerobic microorganisms. This improves solubilization and allows the process rate to increase. In addition, this pretreatment generally facilitates the release of carbon from the organic matter contained in the substrate, increasing its biodegradability, and thereby resulting in higher yields (Agencia Andaluza de la Energía, 2011). These results agree with those obtained by Hajji and Raji (2013), who evaluated particles of 10, 20, 30, and 100 mm diameter in anaerobic digestion of OFMSW under mesophilic conditions (40 °C) with retention time of 21 d. The results showed a correlation between particle size and biogas production, with optimum production recorded for smaller particle sizes, and improvement in the biogas yield of approximately 20% for 10 mm particles.

Similarly, after efficient mechanical sorting of OFMSW, a reduction of biodegradable organics in particles < 10 mm, and removal of any remaining glass, it was demonstrated that the composition of the resulting sorted waste was close to a source-sorted organic fraction. The methane yields obtained for the last waste samples were comparable to that from raw biodegradable organics (De Laclos et al., 2013). In this sense, pretreatment of OFMSW based on a prototype optical sorter, a wet-crusher, and a hydrocyclone-decanter (which uses near-infrared spectroscopy) could increase the organic matter content from 40 to 60% in a more efficient and less energy-demanding way than methods used in conventional systems (Romero-Güiza et al., 2014). After this pre-treatment, methane yields of 480–560 mL CH₄·g⁻¹ VS were obtained, which were somewhat higher than those obtained in the present work. For other solid substrates such as two-phase olive pomace, for which mechanical pre-treatment by milling was used to obtain grain size of 3 mm in

diameter, there was an increase in the maximum methane production rate from 6.99 (untreated waste) to 11.25 mL CH₄·(g VS·d)⁻¹ (pre-treated waste) (Donoso-Bravo et al., 2016).

The modified Gompertz kinetic model is a sigmoid function that is used as a mathematical model for a time series, where growth is the slowest at the beginning and at the end of a given time period (Amiri et al., 2016). It is one of the best functions for predicting the biogas production in batch-mode anaerobic digestion processes. Many researchers have studied the application of first-order and second-order kinetic models, and other models, and found that the modified Gompertz model has one of the best fits to data pertaining to biogas or methane production as a function of time under anaerobic processes conducted in batch mode. In addition, the modified Gompertz model was calibrated and examined using many experimental data (Amiri et al., 2016; Donoso-Bravo et al., 2010; Donoso-Bravo et al., 2016; Li et al., 2011). Li et al. (2011) used the modified Gompertz model to study the effects of the feedstock-to-inoculum ratio and substrate concentration on the batch mesophilic anaerobic digestion of OFMSW. This was done using a single-factor experiment and uniform-design multi-factor experiments. The results showed that substrate concentration had a greater influence on the maximum biogas yield and maximum biogas production rate, while the feedstock-to-inoculum ratio had a lesser or non-existent effect on those parameters.

In the modified Gompertz model, the cumulative methane production is related to the digestion time through the following equation:

$$B = B_m \cdot \exp[-\exp[(R_m \cdot e/B_m) \cdot (\lambda - t) + 1]] \quad (1)$$

where:

B is the cumulative methane production at time t (mL CH₄ STP·g⁻¹ VS_{added}), B_m is the maximum methane production or methane yield potential (mL CH₄ STP·g⁻¹ VS_{added}), R_m is maximum methane production rate (mL CH₄·g⁻¹ VS_{added}·d⁻¹), λ is the lag time (d), t is the digestion time (d) at which the cumulative methane production is calculated, and e is the $\exp(1) = 2.7183$.

The parameters B_m , R_m , and λ were calculated for each of the runs using the non-linear regression approach with SigmaPlot 11.0 software. Table 3 shows the values of the model parameters obtained from the modified Gompertz model for the three substrates assayed. Similar to the results of the experimental maximum methane production values, and relative to the B_m value obtained for *raw* OFMSW, the theoretical B_m value decreased by 17.6% and increased by 57.5% for *ground* and *ground + sieved* OFMSW, respectively. Therefore, a considerable increase in the biodegradability of the substrate was observed when the substrate was homogenized and sieved to achieve lower particle sizes (Abudi et al., 2016). In addition, the difference between the measured and predicted methane yields were found to be only 6.3, 3.6, and 4.5% for *raw*, *ground*, and *ground + sieved* OFMSW substrates, respectively, which demonstrated a good fit of the experimental results to the proposed model. The high values of the determination coefficients (R^2) and the low values of the standard errors of the estimate (Table 3) also showed the excellent fit of the experimental results to the modified Gompertz model.

The maximum methane production rate, R_m , for *ground* and *ground + sieved* OFMSW was 1.1 and 2.4 times higher, respectively, than the values obtained for *raw* OFMSW. Therefore, the homogenization and screening of this substrate to particle sizes less than 20 mm increased the rate of anaerobic digestion of OFMSW, and accelerated the methane

production rate. This high R_m value ($39.1 \text{ mL CH}_4 \cdot \text{g}^{-1} \text{VS} \cdot \text{d}^{-1}$) exceeded the one reported by Abudi et al. (2016) in the batch anaerobic digestion of untreated OFMSW ($27.7 \text{ mL CH}_4 \cdot \text{g}^{-1} \text{VS} \cdot \text{d}^{-1}$). The results obtained in the present work agree with those obtained by Donoso-Bravo et al. (2016) for the anaerobic digestion of two-phase olive pomace, for which the R_m value was $1.6 \text{ mL CH}_4 \cdot \text{g}^{-1} \text{VS} \cdot \text{d}^{-1}$ higher than that for the untreated waste, when the substrate was milled to a particle size of less than 3 mm. The pre-treatment of grinding and sieving reduces the particle size, increasing the specific surface area available to the anaerobic microorganisms and, at the same time, the methane production rate.

The lag time (λ) value for *ground + sieved* OFMSW substrate (1.36 d) was 44% lower than that obtained for raw OFMSW substrate (2.42 d), which also demonstrates the advantage and benefit of the pre-treatment of this waste prior to treatment with anaerobic digestion. The lag value obtained for *raw* OFMSW was higher than that obtained by Amiri et al. (2016) for the batch anaerobic co-digestion of OFMSW, leachate, and sludge (0.2–0.5 d).

3.2. Mesophilic anaerobic co-digestion of OFMSW with LFHTC of DSS

A study of the anaerobic co-digestion of different mixtures of OFMSW and LFHTC of DSS (75OFMSW-25LFHTC, 50OFMSW-50LFHTC, and 25OFMSW-75LFHTC), as well as of the corresponding single substrates (100OFMSW) and 100LFHTC) was conducted. Figure 3 shows the time course of the cumulative methane production (expressed as $\text{mL CH}_4 \text{ STP} \cdot \text{g}^{-1} \text{COD}_{\text{added}}$) with digestion time for the five experimental series conducted and discussed above. Experimental methane yield values of 194 ± 1 , 188 ± 1 , 161 ± 1 , 142 ± 10 , and $124 \pm 9 \text{ mL CH}_4 \text{ STP} \cdot \text{g}^{-1} \text{COD}_{\text{added}}$ were obtained for the

substrates 100OFMSW, 75OFMSW-25LFHTC, 50OFMSW-50LFHTC, 25OFMSW-75LFHTC, and 100LFHTC, respectively. Therefore, an increase in the LFHTC content in the mixture brought about a decrease in the methane yield. In addition, the co-digestion of OFMSW and LFHTC of DSS did not improve the experimental methane yield compared to the anaerobic digestion of OFMSW alone. The theoretical methane yield of the mixtures 75OFMSW-25LFHTC, 50OFMSW-50LFHTC and 25OFMSW-75LFHTC calculated from the yield of mono-digestion data were found to be 176, 159 and 142 mL CH₄ STP·g⁻¹ COD_{added}, respectively. By comparing these theoretical values with the experimental ones, only the mixture 75OFMSW-25LFHTC showed a low synergistic effect, with a 6% increase in the experimental methane yield value compared to the theoretical one. Moreover, by using ratios with more OFMSW (e.g., 75OFMSW-25LFHTC), LFHTC, a residue difficult to degrade, could be managed and output. This is known because the methane yield obtained with this ratio was very similar to that obtained by digestion of OFMSW alone.

The experimental methane yield values obtained in all cases were consistently lower than the theoretical methane yield value (350 mL CH₄ STP·g⁻¹ COD) (Raposo et al., 2011), which was also obtained experimentally using control reactors with starch as a substrate. This finding agrees with data reported in the literature, which indicate that the experimental methane yield achieved in an anaerobic reactor is always lower than the theoretical one because part of the organic matter is inaccessible to microorganisms owing to the bonding among particles or to the presence of rigid structures. In addition, some organic compounds are difficult to biodegrade anaerobically, and part of the resources from the substrate is used for cell growth and maintenance.

The following efficiencies were obtained by comparing the experimental methane production obtained in this work with the above mentioned theoretical value (350 mL CH₄ STP·g⁻¹ COD): 55% for 100OFMSW, 54% for 75OFMSW-25LFHTC, 46% for 50OFMSW-50LFHTC, 41% for 25OFMSW-75LFHTC, and 35% for 100LFHTC. The highest biomethanation efficiencies were achieved for the substrates with the highest percentages of OFMSW (100OFMSW and 75OFMSW-25LFHTC), while the lowest efficiency was found for the substrates with higher percentages of LFHTC. The lowest efficiency occurred with 100LFHTC. This is because the OFMSW usually contains high concentrations of organic matter, such as carbohydrates, lipids, and proteins, which are easily degradable by the anaerobic microorganisms, resulting in a greater methane-production potential. In contrast, the LFHTC of DSS is composed of alkenes, oxygen- and nitrogen-bearing aromatics, and phenolic compounds (Table 2), which are more difficult to degrade through anaerobic digestion, resulting in lower methane yields, (Danso-Boateng et al., 2015, Reza et al., 2014; Villamil et al., 2018). The above-mentioned compounds and other organic acids (e.g., propionic, butyric, valeric, phenylacetic) are products resulting from the hydrolytic stage of sludge decomposition, as well as from dewatering, decarboxylation, condensation, polymerization, and aromatization reactions (Danso-Boateng et al., 2015).

None of the studies in the literature describe the anaerobic co-digestion of OFMSW and liquid fraction from HTC of DSS, although there are several studies of anaerobic co-digestion of OFMSW with other substrates such as cow and pig manure, slaughterhouse wastewater, and wastes with high fat content (Cabbai et al., 2013; Castrillon et al., 2013; Martín-Gonzalez et al., 2010). Cabbai et al. (2013) observed an increase in methane production of 18% and 47% in the co-digestion mixtures of source selected OFMSW

(from canteens and restaurants) and waste activated sludge (WAS) at ratios of 0.23 g $VS_{OFMSW} \cdot g^{-1} VS_{WAS}$ and 2.09 g $VS_{OFMSW} \cdot g^{-1} VS_{WAS}$, respectively, compared with the anaerobic mono-digestion of WAS. This was attributed to the high content of easily biodegradable carbohydrates and the appropriate ISR selected (2). In addition, Martín-Gonzalez et al. (2010) achieved an increase in biogas production from 0.38 to 0.55 L $g^{-1} VS_{feed}$ when the OFMSW was co-digested in 5 L continuous reactor with high fat, oil and grease content waste (FOGW) at mixtures of 1:7 (g $VS_{OFMSW} : g VS_{FOGW}$), compared to the single digestion of OFMSW.

The methane yield obtained for 100LFHTC in the present study was very similar to that reported by Danso-Boateng et al. (2015) in the anaerobic digestion of the LFHTC of primary sludge carbonized at 200 °C. However, Fernández-Cegrí et al. (2012) reported a methane yield of 250 mL $CH_4 \cdot g^{-1} COD_{added}$ in the anaerobic digestion of sunflower oil cake after a hydrothermal treatment at 200 °C, giving a methane yield higher than that obtained in the present study.

Taking into account the shape of the curves of methane production with time (Figure 3) a first-order kinetic model was used to analyze the performance of the anaerobic co-digestion of OFMSW and LFHTC of DSS:

$$G = G_m \cdot [1 - \exp(-k \cdot t)] \quad (2)$$

where:

G is the cumulative specific methane production (mL CH_4 STP $\cdot g^{-1} COD_{added}$), G_m is the ultimate methane production (mL CH_4 STP $\cdot g^{-1} COD_{added}$), k is the specific rate constant (d^{-1}), and t is the digestion time (d). This kinetic model is normally applied to assess the

kinetics of batch anaerobic digestion of different types of easily biodegradable substrates (Li et al., 2012).

Table 4 summarizes the kinetic parameters obtained from Eq. (2) for the different co-digestion mixtures and for the substrates alone. Deviations between the experimental G_m values (Figure 3) and the theoretical values (Table 4) were lower than 1% for all the cases studied, except for 100LFHTC, which had a 5% deviation. Therefore, the low values of the standard deviations and the high determination coefficient values prove an appropriate fit of the experimental results to the proposed model. The value of the kinetic constant for 100OFMSW and 75OFMSW-25LFHTC was identical (0.52 d^{-1}), while for 50OFMSW-50LFHTC and 25OFMSW-75LFHTC, the value increased slightly to 0.54 and 0.56 d^{-1} , respectively. This demonstrates that the process kinetics did not significantly vary at increasing concentrations of LFHTC of DSS. The k value diminished 15% for 100LFHTC compared with that obtained for 100OFMSW and 75OFMSW-25LFHTC which is primarily due to its high content of aromatic and phenolic compounds (Table 2).

The kinetic constant values obtained for 100OFMSW and different mixtures of OFMSW-LFHTC were higher than those obtained for mechanically selected OFMSW, which had values ranging between 0.37 and 0.43 d^{-1} (Cecchi et al., 1991). These kinetic constant values were also much higher than those reported for batch anaerobic digestion of secondary sewage sludge alone (0.22 d^{-1}) (Donoso-Bravo et al., 2010).

3.3. CH₄ and CO₂ composition in the biogas during the anaerobic co-digestion of OFMSW and LFHTC of DSS

The composition of CH₄ and CO₂ in the biogas and their variation over time, were analyzed using gas chromatography, which allowed for comparison of these values with the corresponding values reported in the literature. The typical composition of the biogas obtained during anaerobic digestion of OFMSW comprised CH₄ (50–70%), CO₂ (30–50%), trace gases such as H₂ (0–2%), H₂S (0–8%), and NH₃ (0–1%) (Campuzano and González-Martínez, 2016).

Figure 4A shows the evolution of methane percentages in the biogas during the anaerobic co-digestion of OFMSW and LFHTC of DSS. The trend in the variation of methane content with time was very similar for all the mixtures assayed. In all cases, the increase in the proportion of methane was significantly pronounced and rapid. In the first 5–7 d, values around 52–55% were achieved, and at the end of the experiments concentrations higher than 60% were observed, which is within the normal percentage range of production by an anaerobic digestion process at equilibrium (Campuzano and Gonzalez-Martinez, 2016; Esteban et al., 2014). This same trend was also observed in the anaerobic digestion of other organic wastes under different operative conditions (Carotenuto et al., 2016).

Figure 4B shows the variation of the CO₂ content in the biogas with digestion time for all the anaerobic co-digestion mixtures. The trend in the evolution of CO₂ was very similar for all the mixtures and for the two substrates alone. The increase in the CO₂ content in the biogas with time was not as rapid as the increase in CH₄ content. In addition, a higher fraction of CO₂ was observed for 100OFMSW, while the percentage of CO₂ decreased with increasing amounts of LFHTC. The lowest CO₂ values were consistently obtained for 100LFHTC. The substrates 100OFMSW and 75OFMSW-25LFHTC achieved almost

the maximum CO₂ percentages (30–35%) after 9–10 d of digestion, while the other substrates (50OFMSW-50LFHTC, 25OFMSW-75LFHTC, and 100LFHTC) reached the maximum CO₂ levels, typical of an anaerobic process at equilibrium, only at the end of the digestion time (Esteban et al., 2014).

4. Conclusions

The pre-treatment of the OFMSW after grinding and sieving (20 mm diameter) produced a higher methane yield from batch anaerobic digestion than that from untreated OFMSW. The experimental data (methane production and time) fit adequately to the modified Gompertz model, which predicted process performance. The maximum methane production rate, R_m , for *ground + sieved* OFMSW was 2.4 times higher than the value for untreated OFMSW.

The anaerobic co-digestion of different mixtures of OFMSW and the LFHTC of DSS did not improve the methane yield with respect to the anaerobic digestion of OFMSW alone, and no synergistic effects were observed. However, a mixture of 75OFMSW-25LFHTC provided a similar methane yield to that obtained with 100OFMSW; thereby providing an alternative by which a waste that is very difficult to biodegrade, such as LFHTC, could be managed and treated by co-digestion with OFMSW. A first-order kinetic model demonstrated that the kinetic constant is virtually independent of the percentage of LFHTC as co-substrate, and decreased slightly for 100LFHTC alone.

The percentages of CH₄ and CO₂ in the biogas for the above-mentioned mixtures increased significantly and rapidly with time, reaching 55–60% and 30–35%, respectively.

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Table 1. Main characteristics of the OFMSW substrates: *raw*, *ground* and *ground + sieved*

Substrate	TS (g·kg⁻¹)	VS (g·kg⁻¹)	COD (mg O₂·g⁻¹ TS)
<i>Raw</i>	498.7±6.9	288.9±5.7	-
<i>Ground</i>	443.7±1.7	281.8±9.8	-
<i>Ground + Sieved</i>	466.5±3.0	279.9±13.3	1163±7

Table 2. Species identified by GC/MS in the liquid fraction from hydrothermal carbonization of dehydrated sewage sludge (see Figure 1 for peaks)

Compound	Peak number	Total peak area (%)
<i>Aldehydes</i>		
4-Methoxycinnamaldehyde	16	6.5
<i>Nitrogenated compounds</i>		
4-Pentyloxyaniline	2	5.1
1H-Pyrrole-2-carboxaldehyde, 1-methyl-	3	5.2
Pyrazine, 2-ethyl-5-methyl-	4	3.6
Benzenamine, 3-methoxy-	5	11.8
4,5-Dimethyl-ortho-phenylenediamine	6	10.8
2,3-Diethylpyrazine	7	1.5
Pyrazine, 2,5-dimethyl-3-propyl-	11	5.2
2(1H)-Quinoxalinone	13	0.9
1-Butanamine	14	1.2
<i>Oxygenated aromatics</i>		
Furan, 2,5-dimethyl-	1	1.4
Benzene, 1,2,4,5-tetramethyl-	8	2.0
Phenol, 2,3,5,6-tetramethyl-	9	0.9
Benzoic acid, 4-formyl-	10	2.1
Phenol, 2-methyl-6-(2-propenyl)-	12	4.4
Phenol, 2-methyl-5-(1-methylethyl)-	15	5.4
Benzophenone	17	4.2

Table 3. Parameters of the modified Gompertz model for the three substrates studied (*Raw*, *Ground* and *Ground + Sieved* OFMSW)

Substrate	B_m (mL CH ₄ ·g ⁻¹ VS)	R_m (mL CH ₄ ·g ⁻¹ VS·d ⁻¹)	λ (d)	R ²	S.E.E.
<i>Raw</i>	302.3±1.7	15.7±0.1	2.42±0.06	0.983	12.3
<i>Ground</i>	248.9±0.8	17.3±0.1	2.30±0.05	0.985	10.6
<i>Ground + Sieved</i>	476.1±3.0	39.1±0.3	1.36±0.04	0.989	14.8

R²: coefficient of determination; S.E.E.: Standard error of estimate;

Table 4. Kinetic parameters obtained from the first-order kinetic model in the batch anaerobic co-digestion experiments

Experiment	Gm (mL CH ₄ ·g ⁻¹ COD _{added})	k (d ⁻¹)	R ²	S.E.E.
100OFMSW	196±0	0.52±0.01	0.996	2.951
75OFMSW-25LFHTC	186±1	0.52±0.01	0.998	2.281
50OFMSW-50LFHTC	161±1	0.54±0.01	0.998	2.278
25OFMSW-75LFHTC	141±0	0.56±0.01	0.999	1.995
100LFHTC	118±1	0.44±0.01	0.995	2.721

R²: coefficient of determination; S.E.E.: Standard error of estimate.

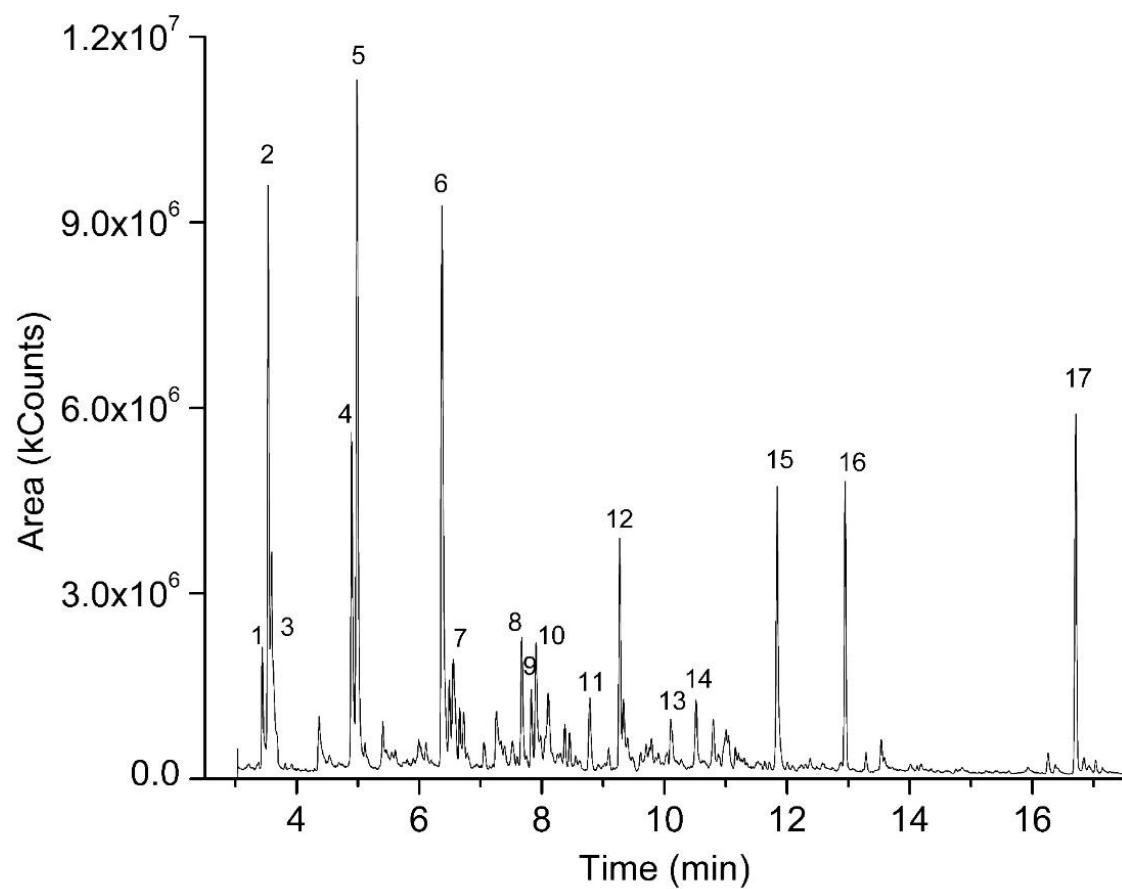


Figure 1. GC/MS of the liquid fraction from hydrothermal carbonization of dewatered sewage sludge

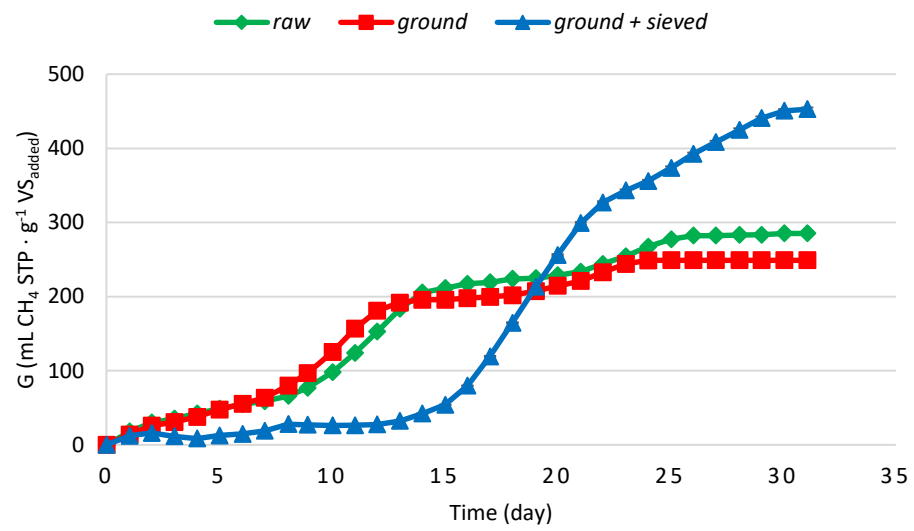


Figure 2. Time course of methane yield for *raw*, *ground* and *ground + sieved* OFMSW substrates

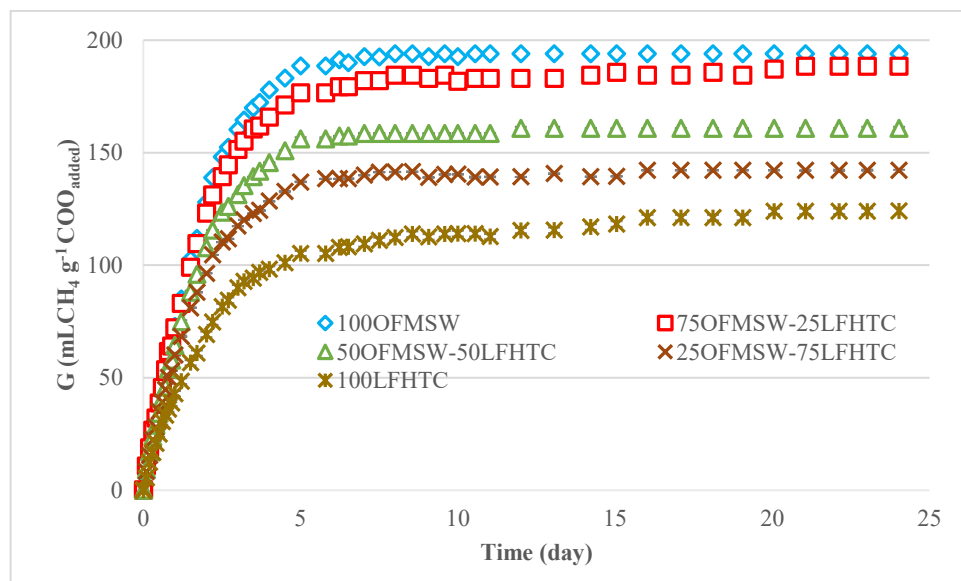


Figure 3. Time course of cumulative methane yield for different OFMSW to LFHTC ratios

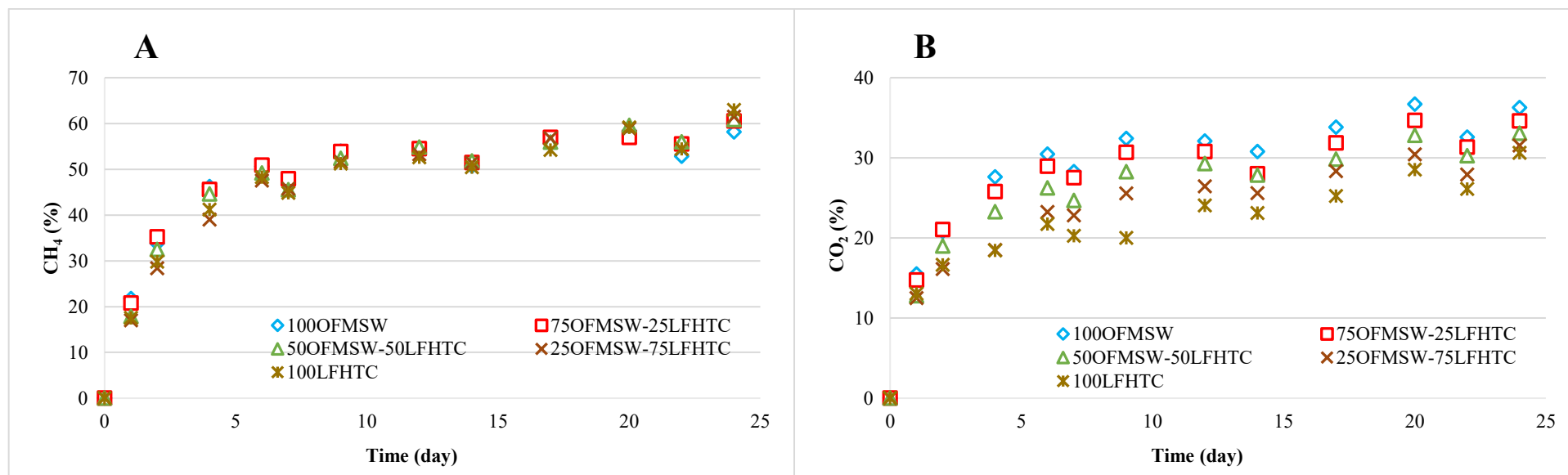


Figure 4. Timecourse of methane (A) and carbon dioxide (B) percentages for different OFMSW to LFHTC ratios