

Article

Valorization of Fourth-Range Wastes: Evaluating Pyrolytic Behavior of Fresh and Digested Wastes

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Abstract: Changes in daily habits and a stressful lifestyle create modifications in consumer preferences and open opportunities to new market products. This is the case of fourth-range products in which the industrial sector generates a waste stream of high quality. Valorization of this type of waste as a single stream is desirable to avoid lowering quality with other low-grade materials. Anaerobic digestion of fourth-range wastes was studied under discontinuous and semi-continuous conditions. A high carbon content characterizes the organic material composed of fruit and vegetable wastes. The fast degradation of the substrate indicated no limitations associated with the hydrolysis stage, as observed from kinetic parameters estimated from batch assays. However, the easiness of degradation did not translate into short hydraulic retention times when operating under semi-continuous conditions. Additionally, the insufficient amount of nutrients prevented the development of a well-balanced digestion process. Specific methane production was 325 mL CH₄/g VS added at a hydraulic retention time of 30 days. However, solid accumulation was observed at the end of the experiment, indicating that conditions established did not allow for the complete conversion of the organic material. Digestate evaluation using thermal analysis under inert conditions showed a thermal profile evidencing the presence of complex components and a high tendency to char formation.

Keywords: valorizing fruit and vegetable waste; digestion performance; first-order decay model; digestate pyrolytic behavior



Citation: Martínez, E.J.; González, R.; Ellacuriaga, M.; Gómez, X.

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Fermentation **2022**, *8*, 744. <https://doi.org/10.3390/fermentation8120744>

Academic Editor: Mohammad Taherzadeh

Received: 31 October 2022

Accepted: 14 December 2022

Published: 15 December 2022

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1. Introduction

The desire for a healthier style of life and the tight schedule citizens are stuck with due to the increased size of cities have given rise to a new gamma of food products ready to eat. Fourth-range products are fresh fruit and vegetable products having minimum processing and presented in packaging ready to eat. This type of commercial product brings several advantages to our daily lifestyle, facilitating and promoting the consumption of healthy food in office and scholar hours [1,2]. The processing of this type of product, although being minimum, requires a high-quality grade material and strict quality control. Washing, drying, peeling, and cutting operations give also, as a result, a waste product needing final disposal. This material is rich in carbohydrates suffering fast degradation and acidification without proper treatment. Biological processes can transform organic rich carbohydrate wastes. Fermentation of wastes can be intended to produce ethanol, butanol, or hydrogen. In the case of ethanol, the conversion of food wastes into fermentable sugars requires additional stages involving enzymatic hydrolysis [3,4] which adds complexity to an already high-energy-demanding process. Butanol production is characterized by low titer and costly separations stages, which set relevant constraints to the feasibility of the process [5,6].

Finally, fermentative hydrogen production and anaerobic digestion are both characterized by generating a gas stream needing no extra energy demand for obtaining the desired

fuel. However, the former is still a pilot-scale process and it is considered an intermediate processing stage having an acidified stream needing further treatment as an outcome [7,8], whereas the latter is a well-known and developed technology where the conversion of substrates takes place in sequential stages; thus transforming the organic materials into biogas and a slurry product denoted digestate, containing cell biomass and components being recalcitrant to the anaerobic microflora.

The choice for valorizing organic wastes is based on economic feasibility and stability of process performance. Anaerobic digestion has been demonstrated to be a reliable process capable of treating a wide variety of substrates. Digestion is among the most environmentally friendly and economically advantageous technology [9] capable of recycling nutrient and valorizing waste streams, thus aiding in attaining the desired circular economic model [10]. The digestion of rich carbohydrates wastes is not a new subject and has been studied by several authors [11–13]. The digestion of this type of material gives rise to a fast hydrolysis stage and acidification, leading to an increase in VFA concentration which may affect fermentation pH and stable fermentation development, therefore, the application of low organic rates is recommended [14].

The addition of vegetable wastes as a co-substrate in digestion systems has proven to enhance anaerobic degradation by exerting synergistic effects, thus resulting in higher volatile solid removal, and therefore, greater methane yields [15–17]. However, the co-digestion of substrate, although presenting several benefits and environmental advantages, may not always be the best option if the further valorization of digestate is desirable for obtaining an organic matrix finding application in other biological processes.

Digestate may be used as a high-quality organic amendment or may serve as a precursor of fermentation media for the growth of microflora, as it is a lipid-based biofuel production by fungal fermentation [18], recovering nutrients to be used in ethanol fermentation [19], enzymes and biopesticide production [20,21], or active biofertilizers inoculated with root-growth-promoting bacteria [22]. The use of digestate for any of these processes requires careful analysis of the organic material and stability of the preceding digestion stage to obtain a high-quality product with a relative homogeneous composition.

Food wastes derived from the industrial processing of fourth-range products may be categorized as high-quality waste material, since contamination with other wastes can be easily prevented. However, the fermentation of this low nitrogen content waste may create digestion imbalances associated with excessive VFA build-up, endangering process performance. Although co-digestion with manures may be a solution for equilibrating nitrogen content, if the desire is to obtain a product free of animal cross-contamination, then the digestion must proceed under nutrient limitation conditions without the supplementation of any other type of animal waste. Another alternative use of digestate is the conversion of this material for producing biochar or solid fuel products. Therefore, digestate has been proposed as a raw material in pyrolysis and thermal processes [23–25].

In the present manuscript, the digestion of wastes derived from a fruit and vegetable industry were studied with the aim of obtaining a high-quality digestate free of animal-derived components. Anaerobic digestion was studied under batch and continuous conditions, evaluating digestate by the use of thermal analysis.

2. Materials and Methods

Fourth-range waste used in the present study was composed mainly by pineapple peels (40%), pineapple hearts (20%), apple peels and degraded quality apple pieces (10.5%), pumpkin peels (19.5%), and the remaining components were a mixture of mango, pepper, and cauliflower.

The mixture of inoculum and substrate was made using a volatile solid (VS) ratio of 1. The inoculum was obtained from the large-scale digester of the wastewater treatment plant (WWTP) of the city of León. This inoculum was stored in ambient conditions for a month to wait until biogas evolution was reduced to a minimum. After this period elapsed, the total solid content was 28 g/L with a VS percentage of 55%. The digestion mixture was

prepared using 200 mL of inoculum and by adding the corresponding amount of substrate to attain the desired VS ratio. Thus, the total solid (TS) content of the digestion mixtures after completing the reactor volume (250 mL) with distilled water was 35.6 g/L. The main characteristics of inoculum are shown in Table 1.

Table 1. Inoculum chemical characterization.

Parameter	Inoculum
Total solids (TS, g/L)	28.0 ± 0.6
Volatile solids (VS, g/L)	15.4 ± 0.4
Alkalinity (mg/L)	4316 ± 65
NH ₄ ⁺ (mg/L)	2376 ± 14
pH	7.2 ± 0.4
C/N	4.7

Batch fermentation assays were carried out in Erlenmeyer flasks of 250 mL in triplicate. A reactor containing inoculum as a single component was used as a blank reactor to measure the biogas background production. The biochemical methane potential (BMP) of the substrate was estimated by subtracting biogas production from the blank reactor. The digestion tests were evaluated under mesophilic conditions (35 ± 1 °C) with reactors submerged in a water bath provided with temperature control. The measurement of biogas was performed using water traps containing an acid solution to avoid the dissolution of CO₂. The liquid displacement volume was daily recorded at the beginning of the tests and every two days, close to the end of the assay when the liquid displaced was too small, to allow for daily measurements. Gas volumes were corrected to standard temperature and pressure conditions (STP, 0 °C and 100 kPa).

Methane data obtained from batch assays were fitted to a first-order model (Equation (1)). Data were fitted using OriginPro 8.0 software (Northampton, MA, USA).

$$M_{(t)} = M_{max}(1 - e^{-kt}) \quad (1)$$

where $M_{(t)}$ is the volume of methane produced at a given time, M_{max} is the maximum methane volume expected, k is the kinetic decay constant and t represents the experimental time.

Thermal behavior under an inert atmosphere was fitted to a logistic equation (S-type curve) represented by:

$$\alpha_{(T)} = \frac{A_1 - A_2}{1 + \left(\frac{T}{T_0}\right)^p} + A_2 \quad (2)$$

with $\alpha_{(T)}$ representing the conversion of the sample, A_1 and A_2 are the minimum and maximum values, T_0 represents the center of the curve, and p is the power.

The modified Gompertz model was also used for fitting data regarding the thermal behavior of the digested sample derived after six months of stabilization.

$$\alpha_{(T)} = \alpha_{max} \exp\left[-\exp\left[\frac{R_{max}e}{\alpha_{max}}(\lambda - T) + 1\right]\right] \quad (3)$$

with α_{max} representing the maximum value of conversion obtained after full thermal degradation of the sample, R_{max} is the maximum rate of mass decomposition, λ is the delay experienced prior to initiating thermal degradation of the sample, and e is 2.71.

Semi-continuous digestion was carried out using continuously stirred tank reactors (CSTR) with a working volume of 3 L. Reactors were provided with a top stirring motor using axial flow impellers. Two reactors were studied for testing the substrate at a hydraulic retention time (HRT) of 30 days. Daily feeding of the reactor was manually carried out. Thorough mixing was provided prior to withdrawing the reactor liqueur, subsequently adding an equivalent volume of substrate to the reactor. Reactors were previously adapted

to the substrate by running the digester initially inoculated with the same digestate as that used in batch BMP tests. The start-up was carried out at an initial HRT of 100 days and reduced subsequently to 30 days in a 35-day period, based on the acclimation procedure proposed by Cuetos et al. [26]. The organic loading rate was 3.8 g VS/Lr d when working at an HRT of 30 d. A nutrient solution was added to one of the reactors when failure symptoms became evident. A total of 10 mL of the NH_4Cl solution (200 g/L) was added once a week to the reactor. A total of 2 mL of the KH_2PO_4 solution (100 g/L) was also added once weekly, and for the remaining components, 1 mL of a unique solution containing concentrations listed in Table 2 was added also once weekly. At the end of the experiment, digestate was stored under ambient conditions during a six-month period and thermal analysis of the stabilized sample was performed.

Table 2. Nutrient-containing solution used as supplement for digestion of fourth-range products (fruit and vegetable wastes).

Component	Concentration (g/L)
NH_4Cl	200
KH_2PO_4	100
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$	8.83
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	0.36
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	4.03
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	0.10
ZnCl_2	10.41
H_3BO_3	0.57
$\text{Na}_2\text{MoO}_4 \cdot \text{H}_2\text{O}$	0.024
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	2.282

Analytical Techniques

Ultimate analyses were carried out using a LECO CHN-600 analyzer and following ASTM 5373; a LECO SC-132 analyzer was used for measuring sulfur content in accordance with ASTM 4239.

TS, VS, total ammonia nitrogen (TAN) and alkalinity were measured in accordance with the American Public Health Association [27]. Samples were analyzed from a semi-continuous working reactor just prior to the feeding procedure. Volatile fatty acids (VFAs) were also analyzed for these same samples. A gas chromatograph equipped with a flame ionization detector (FID) was used for quantifying VFAs. The chromatograph was equipped with a Nukol (Supelco) capillary column. Details of the VFA measurement method are reported in González et al. (2021). Gas composition was measured by gas chromatograph equipment Varian CP-3800 provided with a thermal conductivity detector. The components separation was made by the use of a HayeSep Q 80/100 (4 m long), followed by a molecular-sieve column (1 m long). Helium was used as carrier gas and the column pressure was set at 331 kPa with a temperature of 50 °C.

Thermogravimetric analysis was performed under an inert atmosphere using nitrogen gas at a flow of 100 mL/min. A TA instrument, model Q600 was used for registering thermogravimetry (TG) and the derivative thermogravimetry (DTG) signal. A sample of approximately 5 mg was used for registering thermal behavior and a heating ramp of 10 °C/min was applied from an ambient temperature until reaching a final oven temperature of 750 °C.

3. Results and Discussions

3.1. Batch Digestion Assays

Table 3 shows the results of chemical parameters obtained from the fresh sample containing fruit and vegetable waste. The material is characterized by a high carbon content and a low nitrogen composition.

Table 3. Characteristics of fourth-range waste and model parameters obtained for describing the conversion (α) behavior under thermal degradation.

Chemical Parameter	Value
TS (g/L)	124.3 \pm 1.68
VS	116.1 \pm 0.36
C (%)	45.8 \pm 0.77
H (%)	6.1 \pm 0.52
N (%)	1.57 \pm 0.13
S (%)	0.17 \pm 0.011
pH	4.2 \pm 0.1
Model parameters	
A ₁	1.15 \pm 0.07
A ₂	79.52 \pm 0.10
To	338.54 \pm 0.31
p	11.63 \pm 0.11
R ² adj	0.99823

Figure 1a shows the cumulative methane production derived from batch assays. The average methane yield was 309 ± 11.5 mL CH₄/g VS. Cumulative methane curves show fast degradation during the first days of the digestion tests. Data were fitted to a first-order model. Values of kinetic parameters are also presented in Figure 1a. Based on this model, it is estimated that 80% of biogas production can be obtained during the first four days of the experiment. The fast degradation taking place under conditions evaluated may be a symptom of the easiness found by the microflora for transforming this substrate into biogas. However, the easiness in the degradation observed under batch digestion tests may not necessarily translate into a well-balanced process under continuous configuration. In fact, accumulation of acid intermediaries may adversely affect the production of biogas, a common claim observed during the anaerobic conversion of easily degradable wastes [28].

Studies performed by different authors reported higher methane yields regarding the digestion of a similar type of material. Koch et al. (2015) [29] obtained a value of about 450 mL CH₄/g VS when evaluating food leftovers from a canteen. A different composition regarding proteins and lipids is the main difference from the case here studied. The methane profile obtained by these authors also resembled a first-order decay model, although data were adjusted to a modified Monod-type kinetic. Similarly, Shahbaz et al. [30] studied methane yields when applying different substrate–inoculum ratios. Values in the range of 410–655 mL CH₄/g VS were reported for mixtures of municipal solid wastes and food wastes. Data reported by Keucken et al. [31] are within this same range (475 mL CH₄/g VS) when also evaluating food wastes derived from canteens. The lower value obtained in the present study was probably explained by the higher ratio of substrate–inoculum used, favoring the fast accumulation of intermediaries during the initial experimental stage, probably leading to a partial inhibitory stage. However, the second experimental stage under a semi-continuous condition would aid in obtaining reliable data from the substrate.

The kinetic parameter obtained here represents fast degradation, scarcely evidencing limitations by the hydrolysis stage. Values in the range of 0.2–0.55 were reported by Liu et al. [32] and Vavilin [33]. The kinetic constant had a value of 0.4, thus being in accordance with data found in the literature. Table 4 compiles results found in the literature regarding the anaerobic digestion of food waste. This substrate has been widely investigated, presenting a high proportion of carbohydrates, which makes the material easily degradable. However, the lack of enough nutrients to sustain an adequate development of fermentation impairs an important limitation [34].

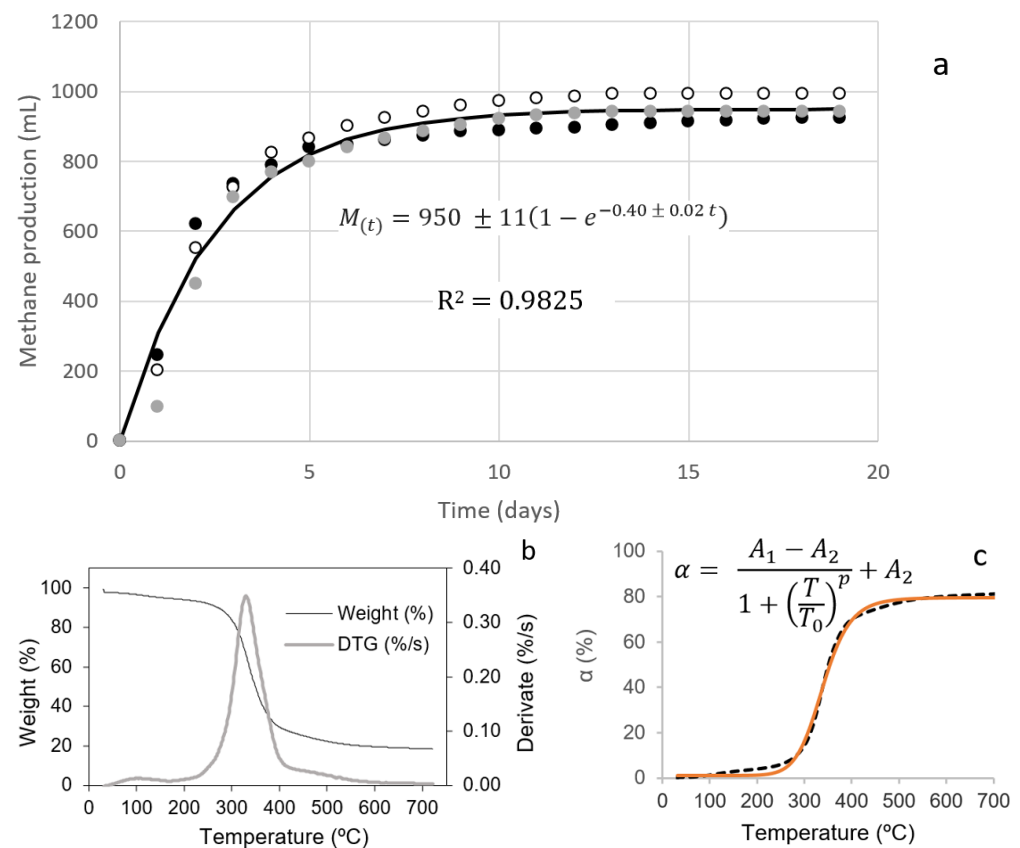


Figure 1. (a) Cumulative methane production curves derived from batch assays evaluating BMP of fourth-range products. (b) TG and DTG profiles of the fourth-range waste sample. (c) Alpha curve and curve-fitted data.

Table 4. Results reported in the literature regarding methane yields obtained from food wastes under different operating conditions.

Methane Yields (mL CH ₄ /g VS)	Main Characteristics	Reference
410	Batch experiment. Mesophilic conditions (35 °C). Food wastes containing 22.8% of fat (d.b)	[35]
347	Semi-continuous experiment. Mesophilic conditions (35 °C). OLR of 8 g VS/Lr d. Increments in OLR caused a decrease in methane yield under semi-continuous conditions	[35]
435	Batch Thermophilic conditions (50 °C). Food wastes collected from different sources: restaurants and food markets	[36]
234 ¹	Batch experiment using a 40 L reactor. Mesophilic conditions (Food wastes)	[37]
398	Large scale digestion plant. Digester volume of 900 m ³ . Mesophilic conditions (42 °C) Feed composed of a mixture of kitchen and garden wastes	[38]
527.5	Batch experiment. Mesophilic conditions (35 °C). Food wastes collected from a cafeteria	[16]
288.5	Batch experiment. Mesophilic conditions (35 °C). Food wastes collected from university campus	[39]

¹ values expressed as mL CH₄/g VSS removed, d.b.: dry basis; VSS: volatile suspended solids.

The thermal behavior of the sample is also shown in Figure 1. The mass loss curve is characterized by the presence of a main peak of high intensity centered around 338 °C. Although no relationship has been established between the biological degradation behavior of biomass samples and that under thermal degradation processes, an intrinsic relationship may be found, associated with the complexity of compounds present in the sample. On the one hand, carbohydrate-rich materials are known to experience a fast degradation, as already demonstrated by the profile obtained from cumulative methane curves and the goodness of the fit to the exponential decay model. On the other hand, the thermal degradation profile of this same type of material experiences an early devolatilization and pyrolysis taking place mainly in a single process centered around 340 °C, just as it becomes easily observed from the DTG profile characterizing this same sample. In this latter case, the conversion of the material was adjusted to an S-type profile with a steep ramp, locating the main process in the range from 250 to 450 °C.

The pyrolysis of different biomass materials has been extensively studied in the literature. Malika et al. [40] evaluated high lignin content wastes (almond shells, nut shells, among others) and reported a thermal profile characterized by three main stages. The first one is the loss of water, the second stage corresponds to devolatilization of organics due to thermal breaking and formation of low molecular weight compounds, and a third final stage is associated with the formation of char. The second stage (225–375 °C), also known as the “active pyrolysis zone” [41], is characterized in this case by a high mass release, due to the high content of cellulose and hemicellulose of the material. Syguła et al. [42] studied the thermal profiles of different wastes under pyrolytic conditions. The high cellulose and hemicellulose content of paper wastes and cotton wool also gave, as a result, a single peak where the maximum was located at around 400 °C. The increase in heating rate causes a shift in the thermal phenomenon, leading to a displacement to higher temperatures, that is, the maximum rate of mass conversion shifts to the right in the temperature scale when the heating ramp is increased. This effect is clearly shown by Jo et al. [43] who studied the thermal profile of cereals and different types of food waste under different heating rates. The pyrolysis of cereals carried out at 5 °C/min gave a maximum mass loss at around 300 °C. The increase in the heating ramp to 10 °C/min shifted this maximum to around 320 °C. In the present study, only one heating ramp was tested to approximate the thermal decomposition to a unique single empirical model.

3.2. Semi-Continuous Digestion Assays

The digestion process was also evaluated under semi-continuous conditions, after an initial acclimation stage where the HRT was decreased from 100 to 30 days, reaching an average organic loading rate of 3.8 g VS/Lr d. This procedure for adapting the reactor to the substrate was based on results reported by Cuetos et al. [26] when studying the digestion performance of slaughterhouse wastes. The progressive increase in OLR allows for enough time for microflora to adapt to new digester conditions. In the present case, the rich carbohydrate waste shows fast acidification, which may cause pH disruption and accumulation of acid compounds. During the acclimation phase, the methane production increased linearly from 75 mL/g VS until reaching a value of 250 mL/g VS, which is coincident with specific methane production (SMP) values obtained at the beginning of the evaluation period.

Figure 2a shows SMP data obtained from the reactor working under set conditions. In this case, an increase in SMP is observed from data obtained at the beginning of the evaluation period (HRT of 30 days). Two reactors were run under the same conditions experiencing similar performance until day 35 of the experiment. From that day onwards, the performance was disturbed—a phenomenon observed by the difference in biogas production. Once analyses of the liquor phase were available, the decision was to supplement one of the reactors with a nutrient solution on day 43. The non-supplemented reactor experienced a total process failure due to inadequate nutrient balance, as observed in Figure 2b. Therefore, the continuous performance of this type of substrate is conditioned to

a suitable balance of nutrients or availability of a nitrogen-rich co-substrate. The nutrient-supplemented reactor kept presenting disturbances, indicating that recovery of the process was delayed until the assimilation of nutrients took place by the anaerobic microflora. A 15-day period was observed, where biogas production was completely irregular. Afterward, values recorded for SMP were higher, which initially seemed to be explained by the presence of essential nutrients in the reactor liqueur. However, this first appreciation proved erroneous, as demonstrated by other chemical parameters evaluated, which will be subsequently commented on.

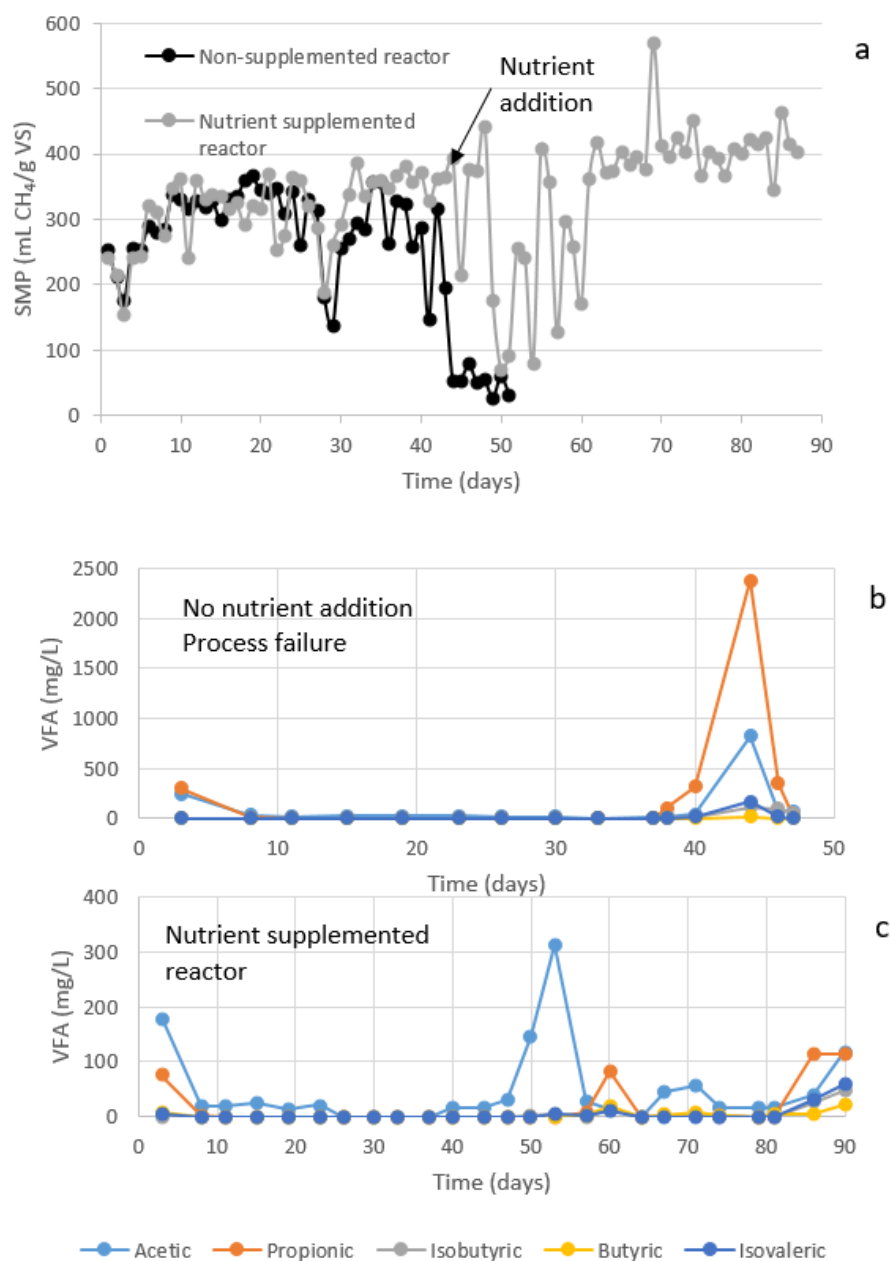


Figure 2. (a) Specific methane production (SMP) from reactors treating fourth-range wastes. Two reactors shown, one with nutrient supplementation and the other one lacking nutrient addition (failure system). (b) Volatile fatty acid (VFA) evolution for failure system. (c) VFA evolution for nutrient-supplemented reactor.

The present study intended to understand the valorization of this material as a single substrate. However, the reactor performance proved unfeasible. Figure 2a also shows a general increasing trend in SMP. Reactors presented a value of around 244.2 mL CH₄/g

VS during the first five days, at an HRT of 30 days. However, prior to experiencing severe process imbalance, the SMP reached a value of 439 mL CH₄/g VS, which was much higher than that obtained under BMP tests.

The evolution of the VFA profile is also shown in Figure 2b,c. The reactor that was not supplemented with nutrients experienced a complete failure. A rise in propionic acid to values above 2000 mg/L was observed along with acetic acid increasing to 823 mg/L (Figure 2b). However, its homologous system supplemented with nutrients, kept a stable performance, although a small peak of acetic acid was measured on day 53, which was consistent with gas instabilities observed between days 50 and 60 of the experiment (Figure 2c).

The increase in acetic acid experienced by the reactor receiving nutrient supplementation did not seem to be high enough to cause such a severe disruption. However, this type of fermentation took place at a very limited condition of ammonia concentration. Digestion proceeded at mean pH values of 7.2 units for both reactors. However, alkalinity and ammonia levels in the fermenter liquor experienced a decreasing trend, as observed from Figure 3. Average ammonium levels at the end of the experiment were 20 mg/L for the reactor supplemented with nutrients, and alkalinity kept showing unstable evolution.

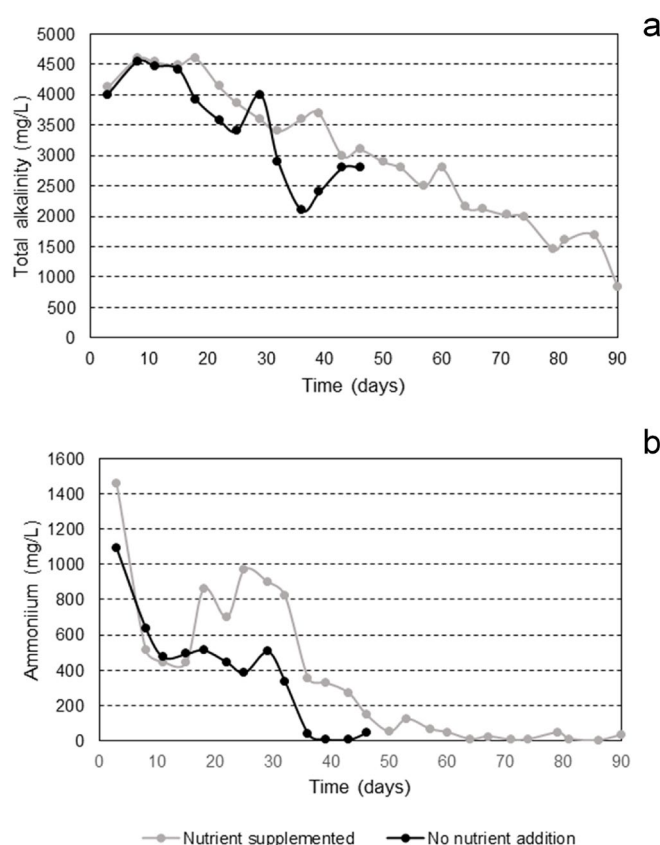


Figure 3. (a) Total alkalinity and (b) ammonium measurements from the reactor liquor during digestion of fourth-range wastes. Systems studied were supplemented with nutrients in one case and lacked nutrient addition in the other case.

The evolution of performance parameters indicated that even though the gas profile seems to reach a quasi-steady state, the liquid phase measurements evidenced process unbalances. Figure 4 shows the appearance of digestate right at the end of the experiment (left image) and after a stabilization period of six months at ambient conditions (right image). The average values of TS and VS measured from samples withdrawn from sample ports were 23.3 and 16.8 g/L. This translates into a VS removal of 85% calculated from data derived from sampling aliquots. However, the reactor content at the end of the experiment showed accumulation of organic material, as observed in the image. Measurements of TS content of the reactor liqueur after homogenizing such material gave a mean value of

40.2 g/L TS, corroborating the cumulative behavior. The fast degradation experienced under batch assays did not translate into a balanced performance under a semi-continuous operation at an HRT of 30 days. This retention time should be, in principle, considered as suitable since batch tests reported that about 80% of total gas production was obtained in 4 days. However, in the present experiment, evaluating digestion at a high retention time (30 d) resulted in poor stabilization.



Figure 4. Images of digestate obtained right at the end of the experiment (nutrient-supplemented reactor) and digestate after six months of storage at ambient conditions.

The performance of reactors under conditions tested showed incomplete degradation, which is observed by the increase in SMP values represented in Figure 2a and corroborated at the end of the experiment by the higher concentration of TS measured in the reactor liqueur. The methane potential obtained from batch tests was 309 mL CH₄/g VS. However, the evolution of continuous systems provided an average value of 405 mL CH₄/g VS as an outcome during the last HRT after nutrient supplementation. The cumulative loading and methane evolution are graphically represented in Figure 5.

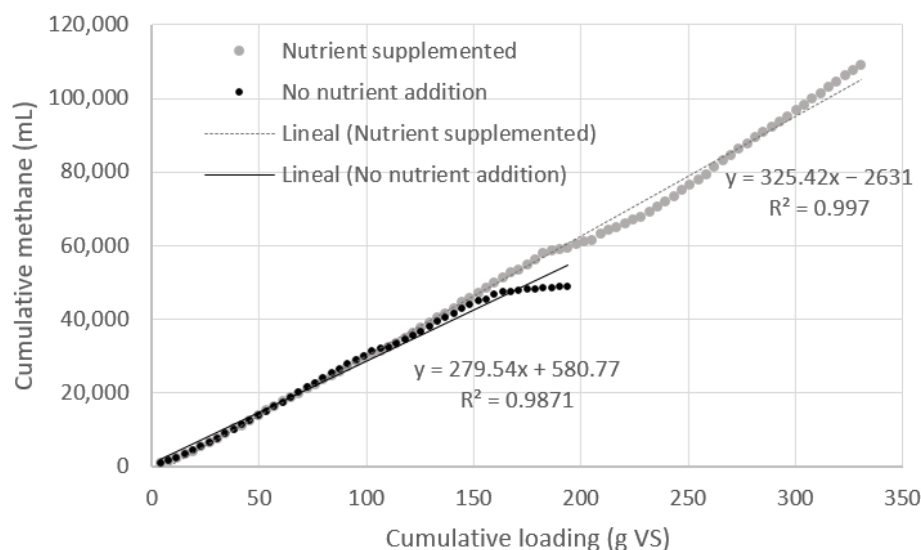


Figure 5. Cumulative evolution of methane production for semi-continuous operating reactors.

A linear relationship is established between cumulative organic loading and methane evolution. The slope of this line represents the mean SMP value obtained for the whole experiment. Therefore, the reactor lacking nutrient supplementation showed an SMP value lower than that derived from batch tests, whereas the reactor supplemented with nutrients had a value 5% higher, explained by the solid build-up experienced. Results here obtained indicate that a direct extrapolation of performance from batch to continuous conditions is inadequate given the different dynamic behaviors of these systems.

Figure 6 shows the thermal behavior of the digested sample after the six-month stabilization period. The pyrolytic performance indicated a high yield of char material

as observed from the residual amount of mass at the end of the heating procedure, when temperature approached 750 °C. The thermal profile is now characterized by a lower intensity in the DTG signal, with a maximum centered at about the same temperature (332 °C) of that for the fresh sample, but a distinctive shoulder is now visualized at the temperature range 400–500 °C. The high mineral content of the digestate is explained by the decomposition of volatile solids into biogas during digestion. This feature leads to a material prone to char formation during the pyrolysis procedure.

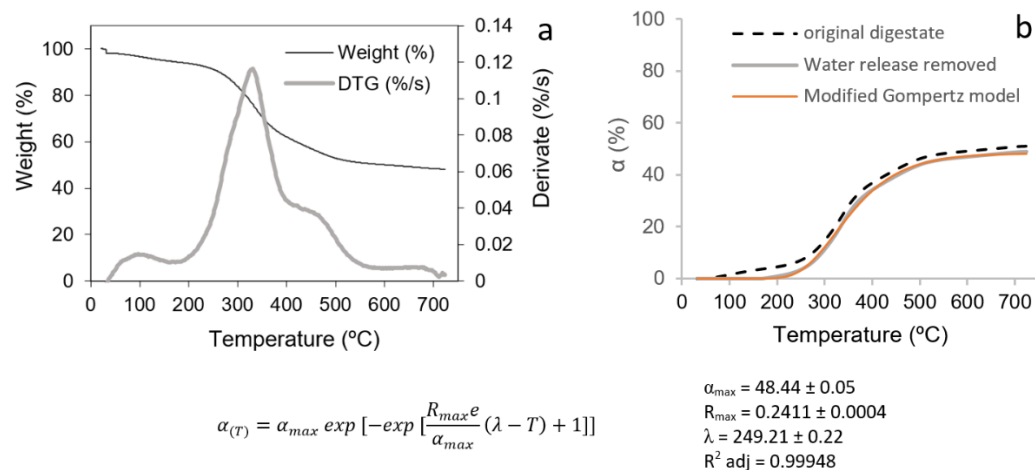


Figure 6. (a) TG and DTG profile of the digested sample after a six-month stabilization period at an ambient temperature. (b) Conversion profile derived from TG sample. Data were fitted using the modified Gompertz model after removing the effect of water release.

Figure 6 also shows the conversion curve derived from the TG analysis. In this case, two curves were represented. One corresponded to the thermal profile of the whole sample, considering the release of water which takes place from the beginning of the experiment until a temperature of about 170 °C is reached. Water release is clearly observable in the DTG profile. In the present sample, this feature has an adverse effect in fitting conversion data since this final value for digestate is low, scarcely reaching 50%. Data were corrected to remove the effect of water loss by the increase in the temperature of the sample, thus, a normalization of data was carried out, considering the point at which water release ceases as the new 100% value. A new set of data was obtained where water loss was eliminated, with the α parameters now exclusively representing the thermal degradation of the sample.

The modified Gompertz model was used to fit thermal data after removing the effect of water loss. It is observed, by the high quality of the adjustment (R^2_{adj} close to unit), that the pyrolytic behavior of digestate can be modelled by this approximation. Digestate presents a significant amount of complex material which experiences thermal degradation between 400 and 500 °C, but it was missing in the original fresh sample. The value of λ can be interpreted as the onset of thermal degradation. The sample experienced thermal decomposition, giving rise to volatile compounds which are swept away by the nitrogen flow applied during experimental conditions, whereas heavier compounds with high molecular weight remain in the crucible and end as part of the char fraction.

A comparative of the fresh and digested sample is presented in Figure 7. The difference in intensity of mass loss due to the lower values reached in DTG profiles for the digestate sample is clearly observed. Anaerobic digestion causes the mineralization of organic matter, transforming its components into biogas and cellular material. As a consequence, an increase in minerals and complex compounds is observed in the remaining slurry once the digestion ends. The use of thermal analysis can clearly identify these phenomena. The thermal degradation of samples allows for a rapid identification of the complexity of the different components by peak location and mineralization attained by peak intensity. Thus, the complex is the structure of the organic compounds; at higher temperatures, the mass

loss peak is located. The lower content in volatiles (high mineral content) is associated with low-intensity DTG curves.

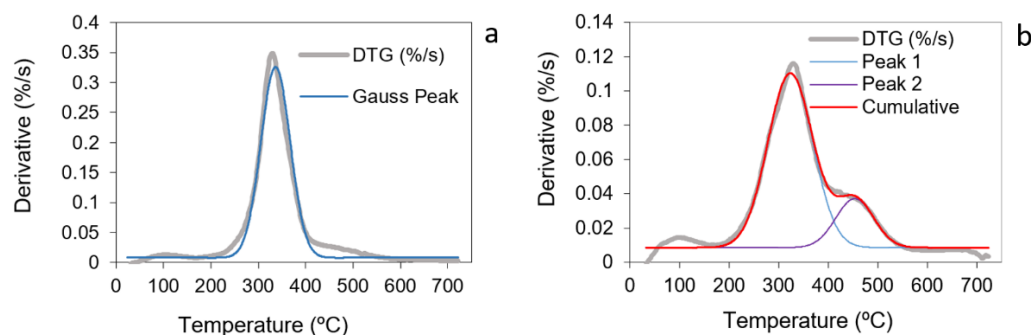


Figure 7. DTG profiles derived from thermal analysis under inert conditions for the (a) fresh and (b) digested sample after a six-month stabilization period.

Multi-peak fitting to a Gaussian behavior is also represented in Figure 7. Digestate clearly evidences the contribution of complex compounds with a peak denoted in Figure 7b as peak 2. The deconvolution procedure disregards water loss, thus giving an approximation of the thermal profile by resembling the degradation into two well-defined processes. One centered around 330–340 °C just as the one registered for the fresh waste sample, whereas the other one is centered at about 460 °C. Although, digestion of the fresh material presented process unbalances due to the lack of nutrients which adversely affected microbial performance, storage of the slurry at ambient conditions allowed further stabilization leading to an organic material dark colored presenting low thermal degradation under pyrolysis. The material remaining at the end of pyrolysis was 18% for the fresh sample, whereas this value increased to 48% for the digested sample.

Digestion and pyrolysis have been proposed as treatment alternatives for the valorization of different wastes. The integration of digestion as a first stage and pyrolysis as a subsequent stage may be a feasible energetic option as proposed by different authors [17,44–46]. However, the mineralization occurred during the biological degradation will affect the performance of the pyrolysis process due to the catalytic effect of minerals contained in the sample [47]. The increase in char formation obtained after digestion indicates that pyrolysis of digestate should be carried out at conditions that allow obtaining a high quality char with use as adsorbent, rather than a solid fuel due to the high mineral content to be expected.

4. Conclusions

The digestion of fourth-range waste was evaluated under batch and semi-continuous conditions. The degradation of the material under the batch condition was proven to be successful, with 80% of biogas obtained in just 4 days. However, the process presented unbalances when digestion was tested under semi-continuous conditions. An organic loading rate (OLR) of 3.8 g VS/Lr d was applied to the digestion system with a hydraulic retention time of 30 d. The lack of nutrients seems to be the main cause for poor performance. Average methane specific production was 325 mL CH₄/g VS under semi-continuous conditions. Accumulation of solids inside the reactor was observed, although the biological batch degradation of the substrate could be performed in a short time (80% biogas was produced in the first four days).

The study of the thermal behavior of fresh and digested samples indicated a significant increase in char formation after digestion. The pyrolysis of fresh material was characterized by steep mass loss, whereas the digested material exhibited the presence of complex components not originally discernible in the fresh sample. Integration of digestion and pyrolysis should be performed by carefully considering the effect of mineralization undertaken during anaerobic digestion.

Author Contributions: Conceptualization, E.J.M. and X.G.; methodology, E.J.M. and R.G.; software, X.G.; validation, M.E. and R.G.; formal analysis, R.G.; investigation, E.J.M.; resources, X.G.; data curation, M.E.; writing—original draft preparation, X.G. and E.J.M.; writing—review and editing, X.G.; visualization, M.E.; supervision, X.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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