Anaerobic Digestion - Digestate's Valorization

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Abstract

The valorization of digestate, a by-product of anaerobic digestion, is essential according to the principles of a circular economy. Nevertheless, it is still highly compromised by the lack of studies performed, coupled with the significant variability of digestate's characteristics. This thesis aimed to provide a set of recommendations regarding the best strategy for the valorization of the digestate produced in Portugal from MSW. In the first part, the characteristics of the fresh digestate and its liquid and solid fractions were compared with the legal requirements for the commercialization of biofertilizers. In the second part, thermal analyses were performed to assess the potential of the valorization of the solid fraction through combustion and pyrolysis. The results suggested that both the fresh digestate and its liquid fraction have the potential to be sold for agricultural purposes, while the solid fraction presents an overly high pathogen content. Regarding the thermochemical valorization, the solid fraction revealed a far too high moisture content, around 68%, which negatively influenced the energy efficiency of both combustion and pyrolysis. Besides that, its high ash content (52% on a dry basis) was reflected in a poor heating value. Its torrefaction at 200 and 250°C seemed to increase this value, but still not enough to make it commercially attractive as a solid biofuel. Additionally, kinetic models were developed to describe the mass changes associated with the combustion and pyrolysis of the solid fraction, allowing the obtention of the kinetic parameters of these processes with high accuracy.

Keywords

anaerobic digestion; digestate; waste to energy; biofertilizer

Contents

1. Introduction

In Portugal, the valorization of biowaste is performed through anaerobic digestion and composting. During anaerobic digestion, the digestate, a by-product, is produced in large quantities, and its valorization is essential to ensure the circular economy principles. However, its characteristics differ widely according to the raw material, which highly dificults this process. In Portugal, all the digestate produced from MSW passes through a solid-liquid separation, where the liquid fraction is sent to a WWTP and the solid fraction to composting to ensure its hygienization.

In other countries, such as Denmark, the digestate is sold as a fertilizer or soil amendment, without further treatment, saving a lot of money. However, in these countries, the quality of the digestate is usually higher due to the type of waste used and to the higher temperatures in digestion, which guarantee its hygienization. Besides that, the legislation is far more advanced and there is a higher acceptance of these products in the fertilizer market.

In 2019, the European regulation on the commercialization of fertilizers was revised, starting to include the digestate, and it is expected that the Portuguese legislation follows these changes soon. Besides that, from 2024, mandatory selective collection of MSW will be implemented, which will have an enormous positive impact on the quality of the digestate [1]. This way, it is expected that the commercialization of digestate for agricultural purposes gains a better public acceptance, allowing the expansion of this market.

Even though this is a significant positive step towards a circular economy, the use of these products as fertilizers may be conditioned by increasing urbanization, which will imply the reduction of the available agricultural land. This way, it is crucial to find other applications for these products that complement their use in soils [2].

In recent years, the thermochemical valorization of digestate has been gaining more interest as an alternative to composting, as it can also improve the quality of the digestate while increasing the overall energy gain.

Different experiments have been performed on a laboratory scale regarding the pyrolysis of the digestate, stating that this is a promising alternative. The main focus of the work done so far has been to investigate the agricultural properties of the pyrochar produced and its suitability to be used as a soil amendment.

Opatokun et al. (2016) studied the pyrolysis of digestate from industrial food waste achieving a solid mass yield of 60.55% at 700°C [3]. The obtained char was not attractive as a combustible due to the high ash content, which increased with the pyrolysis [3]. However, the authors noticed a positive increase in the phosphorous and potassium content, interesting from an agronomic point of view [3]. Monlau et al. (2016) performed similar work, stating that the main interest in the pyrochar was its recalcitrant carbon nature, associated with higher carbon sequestration [4]. Tayibi et al. (2020) also performed pyrolysis of solid digestate of agricultural residues at 500°C, obtaining mass yields of 37.6% in biochar, 33.7% in bio-oil, and 29.3% in syngas [5]. The syngas presented an LHV of 12.9 MJ/Nm^3 and the bio-oil an HHV of 28.4 MJ/kg after water extraction [5].

Other works have been performed regarding the combustion of digestate. Kratzeisen et al. (2010) studied the combustion of digestate from agricultural and animal waste in a biomass heating system [6]. The samples were dried and pelletized before the combustion and presented an average net calorific value of 15.4 MJ/kg and a moisture content of 9.6%, similar to the woody pellets usually used in that system [6]. More recently, in 2020, Ogwang et al. studied the fuel properties of digestate from animal and domestic waste for domestic use [7]. The samples were dried, pelletized, and pyrolyzed, revealing an HHV of 14.87 MJ/kg and an LHV of 7.88MJ/kg [7].

The present work aimed to provide a set of recommendations for the management of digestate in a national context, exploring both the fertilizing and thermochemical routes. For this purpose, in the first part, the characteristics of the digestate produced in Portugal were analyzed in the light of the national and European legislation to assess the possibility of integration in the fertilizer market without the need for composting. In a second part, the properties of the same digestate were studied through Simultaneous Thermal Analysis (STA) to evaluate the potential of using combustion and pyrolysis after anaerobic digestion to improve the overall net energy gain.

2. Methodology

2.1 Samples

The samples analyzed throughout this work were taken from a mechanical and biological treatment plant implemented by Efacec in Portugal, capable of treating around 43 000 tons of undifferentiated urban waste per year. The residues pass through a series of mechanical pre-treatments and enter the digester with a total solids content of 8%. The digestion process is wet and mesophilic, with temperatures around 35°C. The average hydraulic retention period is approximately 22 days and the daily feed is between 80 to 90m^3. In this process, more than 50% of the organic matter is converted into biogas and an average of 225 m^3 of digestate is produced. After digestion, the digestate goes through a screw press separator where two distinct fractions are obtained: a liquid with a solids content between 0.5 and 2%, and a solid with content between 30 and 35%. The former goes to wastewater treatment and the latter to composting.

For this work, samples were taken to the digestate exiting the digester, and to the solid and liquid fractions right after the separation.

2.2 Analysis of agronomic properties

To assess the agricultural properties of digestate, a set of different analyses were requested to the Portuguese laboratory ALS Life Sciences. These were based on the requirements of the Regulation (EU) 2019/1009 and the DL 103/2015, responsible for the commercialization of fertilizers in the European Union and Portugal, respectively.

The analyses were performed in duplicate for the different samples, and the medium value was considered.

Due to the samples' characteristics, the laboratory could not perform some of the analysis requested, and since Efacec already had some analyses performed previously, those were also considered when needed.

2.3 Simultaneous Thermal Analysis

For the simultaneous thermal analysis, only the sample of the solid fraction was analyzed since the other two presented a far too high moisture content. The material was stored for several days in a laboratory fridge at Instituto Superior Técnico, and samples with weights between 57 and 122 mg were used without any pre-treatment.

The experiments were performed in an STA 6000 PerkinElmer, placing the samples in an alumina crucible.

The first two trials, one under air and one with nitrogen, were conducted with an empty crucible. These blank trials were performed to assess any possible interferences due to the crucible that could influence the samples' results.

After that, experiments were performed under dynamic and isothermal temperature profiles, with a gas flow rate of 20ml/min. Two dynamic trials were performed, one with air to evaluate the sample's behavior under combustion, and the second with nitrogen to assess the behavior under pyrolysis. Both presented the following temperature profile: 1) hold for 10 min at 40°C; 2) heat from 40 to 900°C at 10°C/min; 3) hold for 10 min at 900°C; 4) cool from 900 to 40°C at 50°C/min. After the pyrolysis test, the remaining solid was subjected to a combustion trial with the same temperature profile.

The subsequent tests were performed in isothermal conditions under a nitrogen atmosphere to simulate the torrefaction of the sample at different temperatures. For that, the following temperature profile was used: 1) hold for 10min at 40°C; 2) heat from 40°C to the torrefaction temperature at 10°C/min; 3) hold 60min at the torrefaction temperature; 4) cool from the torrefaction temperature to 40°C at 50°C/min. Four torrefaction temperatures were tested: 200, 250, 300, and 350°C. After each experiment, the torrefied obtained was combusted to assess its combustible properties and compare them with the raw digestate. The temperature profile used for the combustion was the same as in the first test performed.

The mass values provided by the program as a function of time and temperature were used to plot the TG curve. From these values, the derivative of mass as a function of time was calculated, which allowed the construction of the DTG curve. The heat flow values were used to plot the DSC curve, where the positive values correspond to heat consumption (endothermic transitions) and the negative values correspond to heat releases (exothermic transitions). The amount of energy absorbed or released during a specific period was calculated by numeric integration of the curve using the Trapezoidal Rule.

2.4 Model development

Based on the experimental results from the TGA, first-order kinetic models were developed to describe the weight loss inherent to the decomposition of digestate.

These models estimate the kinetic parameters of the reactions involved in the process (kinetic constant and activation energy), which are extremely useful when designing, for example, a pyrolysis reactor.

Due to the considerable number of components that constitute the digestate, a pseudo-components model was used. This assumes that the total mass of the sample at a given time, w_t, corresponds to the sum of the mass of the different components at that same time, $w_{i,t}$.

$$w_t = \sum_{i=1}^{n} w_{i,t} \tag{1}$$

This type of model allowed the estimation of the initial fraction of each major component in the sample, leading to a better understanding of the composition of the digestate.

As the number of components, n, was unknown, it had to be assumed. To simplify the calculations, this was done by always trying to reach the closest solution to the experimental results, with the smallest number of components possible.

Thus, knowing the initial experimental value of the sample weight, $w_{exp,t=0}$, and assuming the fractions of each component, x_i, the first estimate of each component's initial mass was made using Equation 2.

$$w_{i,t=0} = w_{exp,t=0} \times x_i \tag{2}$$

This way, it was possible to estimate the mass of each component and, consequently, the mass of the sample throughout time using Euler's method, where the mass derivative as a function of time was calculated in the following way:

$$\frac{dw_{i,t}}{dt} = -k_i(T) \times w_{i,t} \tag{3}$$

The kinetic constant of each component, k_i, depends on the temperature and can be obtained through the Arrhenius equation:

$$k_i(T) = k_i(T_{ref}) \times exp\left(-\frac{Ea_i}{R} \times \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) \tag{4}$$

where Ea_i corresponds to the activation energy of each component, R to the universal gas constant ($8.314 J \cdot mol^{-1} \cdot K^{-1}$), and T_{ref} to the assumed reference temperature (523K).

For the initial estimate, in addition to arbitrating the fractions of each component, their kinetic parameters - pre-exponential factor and activation energy - were also arbitrated.

After obtaining all the mass values from the model as a function of time, those were compared with the experimental values. For that, the quadratic residues of each point, R, were calculated in the following way:

$$R = (w_{exp,t} - w_t)^2 \tag{5}$$

Then, using the solver excel tool and manual adjustment, each component's kinetic parameters and mass fractions were optimized to decrease the sum of the residues of all points.

For a more accurate analysis of the model fit, its standard deviation from the experimental values was calculated as follows:

$$\frac{\sqrt{\frac{R}{N}}}{\overline{w}_{exp}} \tag{6}$$

where R corresponds to the sum of all the quadratic residues, N to the number of points, and $\overline{w}_{exp}$ to the average of the experimental mass values.

3. Results and Discussion

3.1 Analysis of the agronomic properties

European commercialization

To be commercialized within the European Union, the digestate should firstly meet the requirements of the Component Criteria Material 5 (CMC5), which are presented in Table 1 together with the results obtained from the laboratory [8]. Unfortunately, the analyses of most of those parameters were not performed due to the samples' characteristics.

Table 1. Requirements that the digestate should meet to be classified as CMC5 according to Regulation (UE) 2019/1009, and results obtained for those parameters for the samples after digestion (AD) and the solid (SF) and liquid (LF) fractions [8].

	Limit	AD	SF	LF
PAH_{16} (mg/kg DM)	<6	-	3.18	0.23
Each impurity >2mm (g/kg DM)	<3	-	-	-
All impurities >2mm (g/kg DM)	<5	-	3.75	-
OUR ($mmolO_2$/kg OM/h)	<25	-	-	-

FM - fresh matter; DM - dry matter; OUR - oxygen uptake rate.

Regarding the content in PAH_{16}, related to chemical toxicity, both the solid and liquid fractions of digestate meet this requirement. Concerning the physical impurities, it is not expected that the liquid fraction presents any problems, and the results revealed that the solid fraction is also within the allowed limit.

Finally, the oxygen uptake rate is required to measure the stability of digestate, directly related to the organic matter. After the solid-liquid separation, most of the organic matter remains in the solid fraction. Although it is not possible to affirm that this sample meets the defined value, it was subjected to a maturity level test, obtaining a level V as a result, corresponding to the level of greater stability, associated with mature compounds.

Thus, even without access to further results, it is plausible to conclude that both the solid and liquid fractions should meet the required parameters for CMC5.

After meeting the CMC5 requirements, the digestate should also meet the specifications of the Product Function Category (PFC) for which it is intended. The values demanded for each PFC are shown in Table 3 together with the results from the laboratory.

According to the results, both the fresh digestate and the liquid fraction cannot be classified as PFC1 (organic fertilizer) or PFC3 (organic soil improver) as they do not meet the minimum contents in nutrients, organic matter, and dry matter. This could be resolved through a drying process, which would increase these concentrations, but due to the high moisture content of these samples, that could be extremely expensive.

Regarding the remaining categories, both the fresh digestate and the liquid fraction meet the requirements for all the parameters analyzed. This way, they have the potential to be sold on an European level as PFC4 (growing medium) or PFC6 (non-microbial plant biostimulant).

On the contrary, the solid fraction does not satisfy the maximum content allowed for pathogens for all categories, so it could never be commercialized as a European fertilizer without further treatment such as composting or pyrolysis.

National commercialization

According to the DL 103/2015, the digestate might be classified as an organic fertilizer (group 2) or organic corrective (group 5) [9].

Group 2 establishes the minimum contents in nutrients and organic matter presented in Table 2 together with the results from the laboratory.

From the results, it is possible to conclude that both the fresh digestate and the liquid fraction do not meet the minimum contents in macronutrients to be classified as organic fertilizers. The solid fraction also fails to meet all the required minimum contents. However, it is much closer to these values, so it would probably be more justifiable to dry it.

Table 2. Minimum contents of organic matter and macronutrients to be classified as an organic fertilizer according to DL 103/2015, and the results obtained for those parameters for the samples after digestion (AD) and the solid (SF) and liquid (LF) fractions [9].

	Minimum allowed				**Results**		
	N	**NPK**	**NP**	**NK**	**AD**	**SF**	**LF**
N_{org} (wt %)	3	2	2	3	0.26	2.08	0.14
OM (wt %)	50	50	50	50	-	49	-
P_2O_5 (wt %)	-	2	3	-	0.01	0.09	0.00
K_2O (wt %)	-	2	-	6	0.17	0.87	0.16
$N+P_2O_5+K_2O$ (wt %)	-	10	-	-	0.44	3.03	0.30
$N+P_2O_5$ (wt %)	-	-	6	-	0.27	2.17	0.14
$N+K_2O$ (wt %)	-	-	-	10	0.42	2.94	0.30

The classification as group 5 presents considerably more requirements than group 2, as seen in Table 4.

From the results, it was possible to conclude that, once again, none of the samples meet the minimum content in moisture.

Regarding the fresh digestate, the results obey the maximum limits for Escherichia coli and all the heavy metals. However, previous analyses revealed that it did not meet the requirements of class I for Zn and Cu, and of class II for Cu. Thus, further analyses need to be performed to assess the national commercialization of digestate, but apparently, it could only be sold as an organic corrective for the purposes of classes IIA and III, if previously dried.

The liquid fraction meets the limits for pH, Escherichia coli, and heavy metals, except class I for Hg.

The solid fraction, once again, does not meet the maximum limits for pathogens, Cu, and Zn, so it does not seem promising for national commercialization as a fertilizer.

3.2 Simultaneous Thermal Analysis

Blank trials

The device used in this study to perform the thermal analysis presented a deviated endothermic baseline, so the expected results for the blank trials were a horizontal straight line on the DSC curve with a positive ordinate.

This way, after obtaining the results from the combustion and pyrolysis trials, the blank trial in the corresponding atmosphere should have been subtracted from the heat flow values to annulate this interference.

However, contrary to the expected, the blank trials revealed an increasing endothermic behavior from 500°C.

This behavior was verified for the three blank trials performed, showing a quite similar pattern, suggesting that, despite being odd, they might be correct. To draw definite conclusions regarding the veracity of the blank trials it would be necessary to perform further tests, which was not possible due to lack of time.

Table 3. Requirements for possible PFCs for digestate according to Regulation (UE) 2019/1009, and results obtained for those parameters for the samples after digestion (AD) and the solid (SF) and liquid (LF) fractions [8].

	PFC1 (A I)	PFC1 (A II)	PFC3 (A)	PFC4	PFC6	AD	SF	LF
N (wt % FM)	>1	>1	-	-	-	0.28	2.10	0.16
P_2O_5 (wt % FM)	>1	>1	-	-	-	0.01	0.09	0.00
K_2O (wt % FM)	>1	>1	-	-	-	0.20	0.87	0.16
$N+P_2O_5+K_2O$ (wt % FM)	>4	>3	-	-	-	0.49	3.06	0.32
C_{org} (wt % FM)	≥15	≥5	≥7.5	-	-	0.06	-	-
Cd (mg/kg DM)	≤1.5		≤2	≤1.5	≤1.5	0.02	2.08	0.06
Cr VI (mg/kg DM)	≤2		≤2	≤2	≤2	-	<0.06	-
Hg (mg/kg DM)	≤1		≤1	≤1	≤1	<0.20	1.28	1.22
Ni (mg/kg DM)	≤50		≤50	≤50	≤50	0.94	124	3.12
Pb (mg/kg DM)	≤120		≤120	≤120	≤120	2.12	347	0.82
As_{inorg} (mg/kg DM)	≤40		≤40	≤40	≤40	<1.52	<26.08	<9.09
Biuret (mg/kg DM)	0		-	-	-	-	-	-
Cu (mg Cu/kg DM)	≤300		≤300	≤200	≤600	3.50	1 030	2.48
Zn (mg/kg DM)	≤800		≤800	≤500	≤1 500	14.11	2 402	5.43
Salmonella (/25g FM)	0		0	0	0	-	-	-
Escherichia (UFC/g FM)	≤1000		≤1 000	≤1 000	≤1 000	22	48 108	30
P_2O_5 (wt %)	≤0.5		≤0.5	≤0.5	≤0.5	-	-	-
Dry matter (wt %)	-		≥20	-	-	5.25	26.65	0.82

Table 4. Requirements to be classified as an organic corrective (group 5) according to DL 103/2015, and the results obtained for those parameters for the samples after digestion (AD) and the solid (SF) and liquid (LF) fractions [9].

	Requirements				**Results**		
	I	**II**	**IIA**	**III**	**AD**	**SF**	**LF**
Fitotoxicity	0				-	0	-
pH	5.5-9				-	8.4	7.7
Moisture (wt % FM)	<40				95	73	99
OM (wt % DM)	>30				-	-	-
Samonella spp. (in 25g of FM)	0				-	-	-
Escherichia coli (UFC/g of FM)	<1 000				22	48 108	30
Weed seeds and propagules (active units/L)	<3				-	-	-
Cd (mg/kg DM)	<0.7	<1.5	<3	<5	0.0	2.1	0.1
Pb (mg/kg DM)	<100	<150	<300	<500	2.1	347	0.8
Cu (mg/kg DM)	<100	<200	<400	<600	3.5	1030	2.5
Cr (mg/kg DM)	<100	<150	<300	<400	0.5	272	1.0
Hg (mg/kg DM)	<0.7	<1.5	<3	<5	0.2	1.3	1.2
Ni (mg/kg DM)	<50	<100	<200	<200	0.9	124	3.1
Zn (mg/kg DM)	<200	<500	<1000	<1 500	14.1	2 402	5.4
Glass, metals, plastics >2mm (wt % DM)	<0.5	<1	<2	<3	-	<0.4	-
Stones >5mm (wt % DM)	<5	<5	<5	-	-	<0.4	-

Thus, it was decided to analyze the results of the different trials without correcting the baseline, with the awareness that they might be miscalculated, especially from 500°C.

Combustion

By observing the TG/DTG curves represented in Figure 1, the degradation of the digestate under an oxidative atmosphere seems to occur in five stages.

The first and most significant weight loss step occurs from the beginning, at 37°C, until 168°C. It corresponds to a weight loss of 68% mainly associated with the moisture content and some lighter volatiles. The maximum weight loss rate occurs during this stage, at around 116°C. The DSC curve, represented in Figure 2, shows in this interval the only endothermic peak of the process, with a consumption of approximately

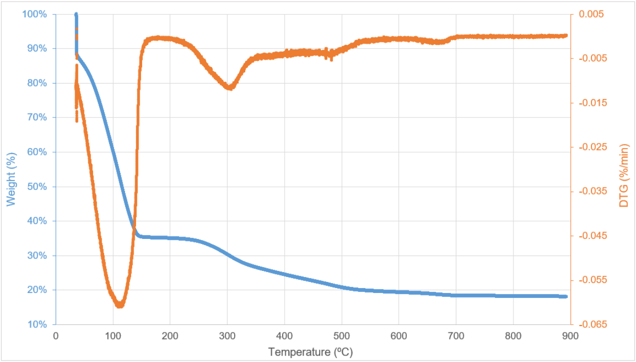

Figure 1. Experimental TG and DTG curves for the first combustion trial.

1026kJ/kg of fresh sample, corresponding to the energy required for drying.

The second stage occurs between 224-345°C, and presents a DTG peak at around 309°C. It is associated with a weight loss of about 5% due to cellulose and hemicellulose degradation [4].

Then, between 350-450°C, there is a degradation stage where the weight loss rate is practically constant, appearing as an almost horizontal straight line in the DTG curve.

After that, the fourth stage happens until 523°C, with a weight loss of 7% and a slight peak in the DTG curve at 484°C, probably associated with lignin degradation [4].

At around 672°C, there is a small peak in the DTG curve, corresponding to a weight loss of 2%, which might be related to the decomposition of calcium carbonate formed during the decomposition of calcium-containing organic compounds [10].

From 680°C, there is no longer a significant mass decrease, obtaining a solid residue of 18%, which should correspond to the ash content.

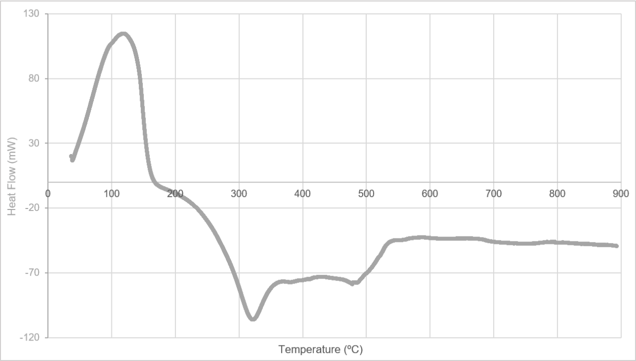

Figure 2. Experimental DSC curve for the first combustion trial.

The most significant heat release due to the combustion occurs between 168-540°C. This corresponds to a total heat release of 1346kJ/kg of fresh sample, superior to the heat required for drying, resulting in a positive energy balance of 320kJ/kg.

The heat value of the digestate, corresponding to the heat released during its combustion, is approximately 4.20MJ/kg of DM.

Pyrolysis

The thermal degradation of the digestate under an inert atmosphere seems to also occur in five steps, with similar behavior in terms of weight loss as it happens under combustion.

The first step, as in combustion, corresponds to the loss of moisture (around 66%). The drying process started at the beginning of the experience and ended at around 204°C, with the maximum weight loss rate at around 124°C. The endothermic peak associated presented a consumption of 1097kJ/kg.

The second and third peaks observed in the DTG curve, corresponding to cellulose, hemicellulose, and lignin degradation occurred at around 337 and 429°C. After that, between 495-660°C, there was a stage where the weight loss rate was practically constant. Then, once again, there was a peak in the DTG curve at around 729°C, related to the degradation of calcium carbonate.

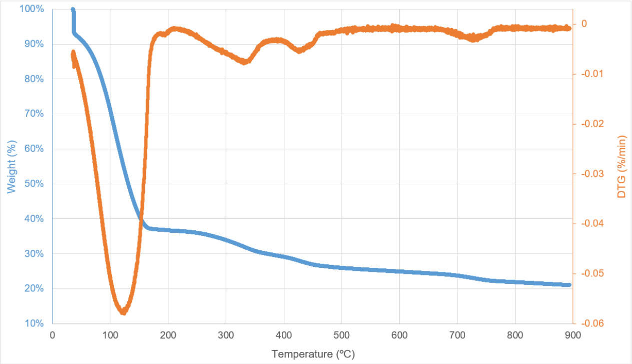

Figure 3. Experimental TG and DTG curves for the pyrolysis trial.

At the end of the process, a solid residue with 19% of the initial mass was obtained.

The behavior observed in the DSC curve (Figure 4) is quite different from the first experiment. After drying, there is a slowly increasing exothermic behavior, without significant peaks of heat release. This behavior, however, could be much more exothermic if the blank trials were subtracted. Thus, no significant conclusions could be taken regarding this process. Nevertheless, one of the main interests in the pyrolysis of the digestate would be to obtain products with a higher calorific value or to obtain a pyrochar with better agronomic properties, which was not analyzed throughout this work.

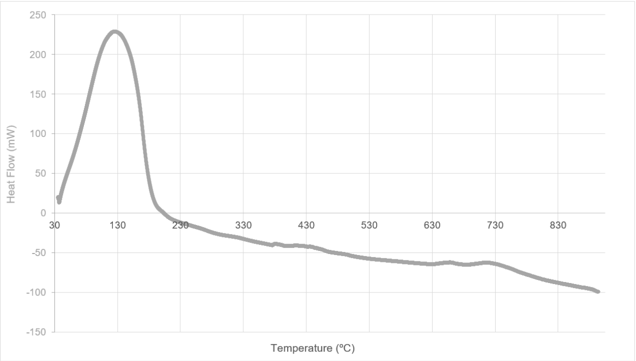

Figure 4. Experimental DSC curve for the pyrolysis trial.

The solid residue from pyrolysis was burned in an oxidative atmosphere, and the results can be seen in Figures 5 and 6.

The weight loss during combustion was only 6% compared to the mass of digestate that remained after pyrolysis. The most significant loss was verified between 400 and 600°C, resulting from the combustion of the material.

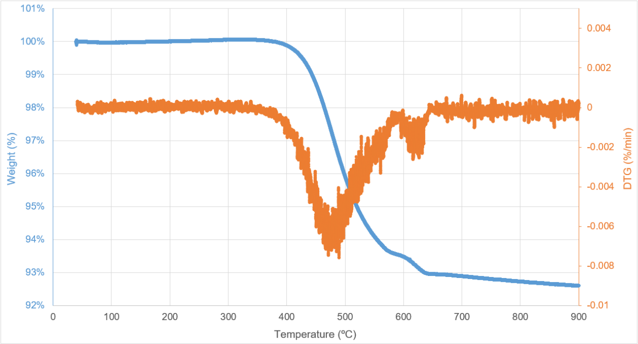

Figure 5. Experimental TG and DTG curves for the combustion of the pyrolysis residue.

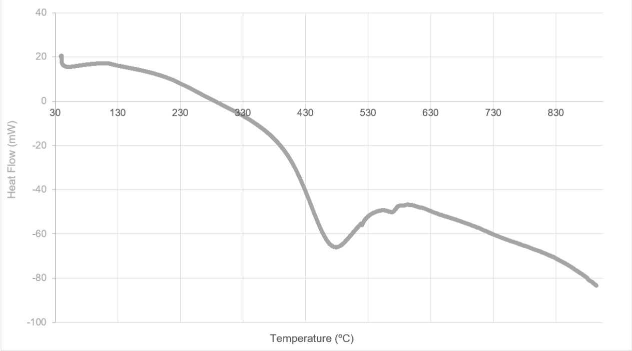

Figure 6. Experimental DSC curve for the combustion of the pyrolysis residue.

During the combustion, the pyrolysis residue released about 992kJ/kg, corresponding to only 186kJ/kg of fresh digestate sample. That last value is inferior to the amount of heat required for the drying of the digestate, resulting in an overall negative energy balance of -911kJ/kg of fresh sample. However, once again, this poor result may be much better in reality, given the lack of baseline correction.

With the results of these trials, the following proximate analysis was obtained, on a fresh matter basis: 66% of moisture, 15% of volatile matter, 1% of fixed carbon, and 18% of ashes. The moisture content is extremely high for any material intended to go through thermochemical valorization. Such an elevated moisture content requires a significant amount of energy in its drying. Therefore, it is preferable to find alternative drying sources that do not require the heat released from the digestate, in order to increase the sustainability of the process. Such alternatives could be, for example, solar drying or the use of surplus heat from CHP units.

The high ash content (around 52% on a dry basis) is also a significant concern for thermochemical processes, as it corresponds to inorganic material without any energetic content. Furthermore, due to the low melting point of ashes, they can melt, causing the clogging of the equipment, as reported by several authors.

The volatile matter and the fixed carbon correspond to the interesting fraction from the thermochemical valorization point of view. The fixed carbon content is considerably low but easily increased through a torrefaction process. Regarding the volatile matter, although this analysis does not allow the determination of its components, those are generally hydrocarbons. Therefore, this fraction is usually highly combustible and very interesting in terms of energy content. Besides that, in the context of a biorefinery, it can be promising as it allows the production of several organic compounds generally obtained from fossil sources.

Torrefactions

The results obtained in all the torrefaction experiments were quite similar. All the torrefactions present a significant peak of weight loss at around 115°C, correspondent to the loss of moisture content (69% on average). Alongside, the DSC curve shows the corresponding endothermic peak, which starts at the beginning of the experience until approximately 200°C, with an average heat consumption of 1377kJ/kg of fresh sample.

After that step, for the torrefactions at 200 and 250°C, both the mass and the heat flow stay relatively constant, with the DSC curves presenting a horizontal exothermic line. For the torrefactions at 300 and 350°C, there is an additional small peak of weight loss in the DTG curve during the isothermal stage. The DSC curve for those trials also presents a constant exothermic behavior. For all four trials, the exothermic phase does not seem significant, but it is important to mention that, once again, it is miscalculated due to the uncertainties of the baseline.

The mass yields of the process, i.e., the mass of torrefied obtained compared to the initial dry mass of digestate, were also calculated. It was possible to conclude that the increase in temperature resulted in smaller yields, with the best result being 98.5%, on a dry basis, at 200°C.

The DTG curves obtained from the combustion of the torrefied materials can be seen in Figure 7.

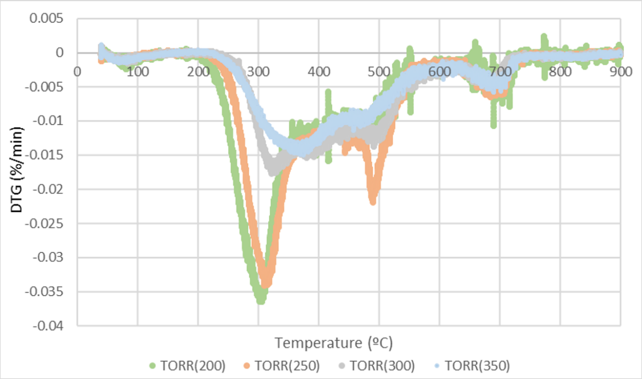

Figure 7. Experimental DTG curve for the combustion of the torrefied materials.

Despite some differences, all the materials present three prominent weight loss peaks in the DTG curve, as it happened to the combustion of digestate after drying. The first and most significant occurs between 300-400°C, with the maximum weight loss temperature increasing with the torrefaction temperature and the weight loss rate decreasing. Then, between 450-500°C, there is a smaller peak whose maximum weight loss temperature does not correlate with the torrefaction temperature. Finally, between 650-700°C, there is a third peak, also not correlated with the torrefaction temperature.

The most significant weight loss is verified between 200-550°C, with the most significant heat releases occurring between 190-605°C for all the materials.

At the end of each experiment, the remaining solid residue is more than 50%. This content increases with the torrefaction temperature, being almost 70% for the torrefied produced at 350°C, which has a tremendous negative impact on the combustion.

After all the trials were concluded, it was possible to compare the different alternatives studied.

There are two main aspects to consider when addressing the thermal valorization of digestate to produce a solid biofuel. The first is the overall energy balance of the process, i.e., the difference between the heat released during the material's combustion and the heat consumed in its production. The second is the heat value of the material, i.e., the heat released per mass unit. Both are displayed in Table 5.

The energy balance is an important aspect when the intention is to use the digestate as a fuel in the biogas plant itself. In those cases, the balance should be as high as possible so that the heat produced, not only covers the demand in its production, as it also produces an interesting surplus. This way, for the E1 trial, correspondent to the heating up of the digestate under air atmosphere, the heat consumption corresponds to the endothermic part of the process and the heat release to the exothermic. For the other trials, the heat consumption corresponds to the heat consumed during the torrefaction process and the heat release to the combustion of the torrefied produced. Both values are presented per mass unit of the initial mass of the digestate's sample.

Table 5. Main conclusions regarding the combustible properties of the raw digestate and its torrefied materials.

	COMB	T200	T250	T300	T350
Heat value (MJ/kg DM)	4.20	4.71	4.84	3.99	3.64
Heat consumption (kJ/kg FM)	1 026	1 442	1 323	1 347	1 396
Heat release (kJ/kg FM)	1 346	1 424	1 533	1 003	893
Energy balance (kJ/kg FM)	320	-18	210	-344	-503

DM - dry matter; FM - fresh matter.

On the other hand, if the goal is the commercialization as a solid biofuel, the most important parameter is the heat value. This should be analyzed as the amount of energy obtained per mass unit of the sold material. In the case of the raw digestate, it would never be commercialized without previous drying. Thus, the value presented for the E1 trial is per mass unit of dry digestate. For the torrefaction trials, the heat value was presented per mass unit of the torrefied produced, which does not contain any moisture.

Regarding the energetic balance, based on these values, the torrefactions at 200, 300, and 350°C present a negative value, which means that the burning of the produced material is not even enough to cover the energetic requirements of the drying, therefore seeming unviable processes from an energetic point of view.

In the case of the raw digestate and the torrefied produced at 250°C, the balance is positive, which means that the burning of the material covers the energetic requirements of the drying and further allows the obtainment of an energy surplus in the value of 210kJ/kg for the digestate and 320kJ/kg for the torrefied.

Even though those values are positive, they are not elevated due to the extremely high energy consumption involved in the drying. Thus, practically speaking, the process would only be interesting if an excess heat source, that could be used in the drying, was available (e.g. solar energy or energy produced in CHP plants). In that case, the energetic balance would no longer matter since all the heat released during combustion could be used.

Regarding the heat value, the first relevant observation is that the torrefactions performed at 300 and 350°C decrease the heat value of the digestate, not being interesting alternatives from an energetic point of view. In turn, the torrefactions at 200 and 250°C increase the heat value of the digestate by 12 and 15%, respectively. Despite that, the calorific values of both the digestate and the chars produced are very small and not interesting for commercialization. For comparison, the heat value of animal manure ranges between 10-15MJ/kg, while firewood usually presents a heat value of around 16MJ/kg, and fossil coal can reach 34MJ/kg. This way, it would be extremely difficult to sell the digestate as a solid biofuel.

Despite that, these results do not entirely exclude torrefaction as a viable thermochemical valorization route for digestate since these processes are often used to obtain a pyrochar with better agronomic properties. This way, its commercialization could be considered in this sense if further studies were carried out.

Finally, it is important to emphasize, once again, that the processes were not optimized and that there is uncertainty regarding the results obtained due to the lack of correction of the baseline. If, in fact, the blank trials were correct, their subtraction would decrease the heat consumption of the processes studied and increase the heat releases, since they present an endothermic behavior. This could lead to different conclusions, favorable to the thermochemical valorization of digestate.

3.3 Kinetic models

Combustion

The model developed to describe digestate's behavior under combustion is shown in Figure 8, together with the experimental data of the respective trial.

The fitting was obtained considering 4 pseudo-components.

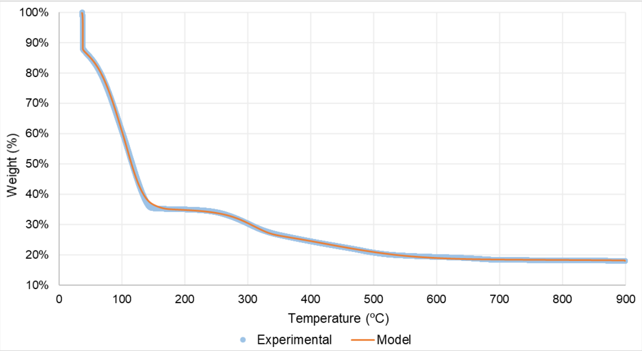

Figure 8. Model fitting of the combustion trial of raw digestate.

The adjustment was quite successful, with an error of 0.55%, which means that the model developed correctly describes the degradation and that the kinetic parameters obtained, presented in Table 6, are very close to the real ones.

Table 6. Kinetic parameters of the combustion of raw digestate, according to the developed model.

	1	**2**	**3**	**4**	**Deviation (%)**
x_i	0.65	0.05	0.11	0.19	0.55
$k_{250^\circ C}$ (s^{-1})	9.52	0.04	0.02	2.29E-05	
Ea (J/mol)	39 303	109 535	27 148	28 416	

Pyrolysis

The model developed to describe the pyrolysis of the raw digestate under dynamic conditions, seen in Figure 9, was also achieved by considering four pseudo-components. Once again, a good fitting was achieved, with a deviation of only 0.43%.

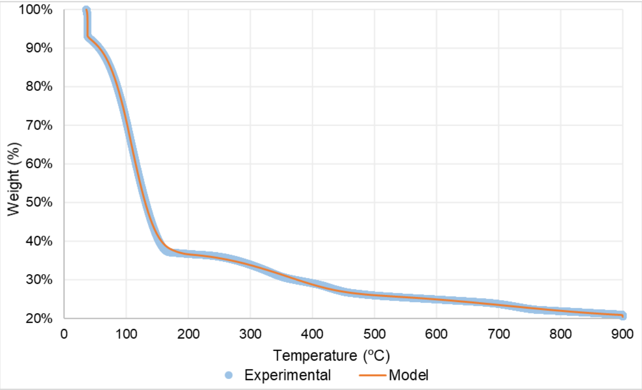

Figure 9. Model fitting of the pyrolysis trial of raw digestate.

Table 7. Kinetic parameters of the pyrolysis of raw digestate, according to the developed model.

	1	**2**	**3**	**4**	**Deviation (%)**
x_i	0.63	0.11	0.06	0.20	0.43
$k_{250^\circ C}$ (s^{-1})	6.419	0.030	0.001	2.237E-09	
Ea (J/mol)	40 425	36 686	41 004	34 829	

Torrefactions

The parameters obtained for the model of the dynamic pyrolysis were tested under the conditions of the different torrefactions to see if they correctly described the behavior of the samples under pyrolysis with different operational conditions. For the same kinetic parameters and mass fractions of Table 7, the model described the weight loss during the torrefactions with deviations up to 11.46%. These quite elevated errors can be justified by the great variability of the samples and the fact that some of the components decompose at temperatures above the torrefactions' intervals, which leads to high errors when the four pseudo-components of dynamic pyrolysis are assumed.

Thus, to achieve better results, the fractions of each component were optimized for the four torrefactions, while maintaining the values of the kinetic constants and activation energies obtained for dynamic pyrolysis. The values of the optimized fractions and the deviations obtained are presented in Table 8.

As can be seen, the fittings improved substantially with quite acceptable errors. Thus, it can be stated that the modeling was successful and that the obtained values for the kinetic constants and activation energy correctly describe the mass behavior of digestate under different pyrolysis conditions.

Table 8. Optimized mass fractions for the adjustment of the dynamic pyrolysis model to the different torrefactions.

	x_1	**x_2**	**x_3**	**x_4**	**Deviation (%)**
TORR (200)	0.69	0.00	0.00	0.31	0.85
TORR (250)	0.68	0.00	0.09	0.23	2.07
TORR (300)	0.70	0.05	0.00	0.25	0.67
TORR (350)	0.68	0.07	0.00	0.25	1.03

4. Conclusions

The main goal of the work developed in this thesis was to access different possible valorization routes for the digestate produced during anaerobic digestion of MSW in Portugal.

Regarding the analysis of the potential of digestate for agricultural purposes, it was not possible to analyze all parameters required by legislation, and only two samples from each zone of the process were taken, which was a huge limitation. To ensure more accurate conclusions, in future works, all parameters should be analyzed using a larger number of samples, preferably taken at different times.

This way, even though it was not possible to affirm in which categories the digestate could be sold, it was possible to exclude some.

The fresh digestate showed the potential to be commercialized at an European level as a growing medium (PFC4) or a non-microbial plant biostimulant (PFC6). If dried, it could also be sold as an organic fertilizer (PFC1) or organic soil improver (PFC3). At a national level, it could only be commercialized as an organic corrective in categories IIA and III.

The liquid fraction presents a moisture content so high that its drying is probably not justified. Thus, it only shows potential to be sold at a European level as a PFC4 or PFC6.

Lastly, the solid fraction does not meet the pathogens requirements of both national and European legislations, so it could never be sold for agricultural purposes without additional treatments, such as composting or pyrolysis.

This solid fraction was analyzed through thermal analysis but, unfortunately, the results of those experiments were also biased due to the impossibility of assuring a correct baseline, so they should also be repeated to ensure the veracity of the conclusions.

The analysis of the solid fraction under an oxidant atmosphere revealed a heat consumption of 1 026kJ/kg during the drying phase and a heat release of 1 346kJ/kg during combustion. Those values represented an overall positive energy balance of 320kJ/kg. Besides that, the calculated heat value of the material was 4.2MJ/kg of DM. Despite positives, those data are not enough to confer marketing value to the digestate as a biofuel, due to the high moisture content and low energetic density.

Different torrefactions trials were performed to the samples in an attempt to increase their commercial value. The torrefieds produced were burned, and only the one obtained at 250°C presented an overall positive energy balance. Still, that value was so low that the process would only be interesting if there was an excess heat source available for drying, which would allow the use of all the heat released in the combustion. Finally, the torrefieds produced at 200 and 250°C presented a higher calorific value than the raw digestate. However, it was still quite low compared to other biofuels. This way, purely based on these results, the commercialization of digestate or its torrefied materials as solid biofuels did not seem interesting. The main interest in the torrefaction of the digestate could be in the production of biochar with better agronomic properties, which should be studied in future works.

Another process studied was the pyrolysis of digestate under dynamic conditions and the burning of its residue. Unfortunately, the problems regarding the correction of the baseline did not allow definitive conclusions regarding the energetic behavior of the process. However, studies performed by other authors suggested that the main interest in the pyrolysis of digestate would be the obtention of products with higher energetic contents, who were not analyzed in this work.

Finally, with the experimental data from the thermal analyses, kinetic models were also developed to describe the mass evolution during these processes. Overall, both the model for the combustion and pyrolysis of digestate presented good fitting to the experimental data.

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