Anaerobic Digestion - Digestate's Valorization

Beatriz Dias Fernandes

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Supervisors: Prof. Maria Amélia Nortadas
Duarte de Almeida Lemos (IST); Dr. Tiago
Barreiros Macedo de Faria (Efacec)

Examination Committee

Chairperson: Prof. Sebastião Alves
Advisor: Dr. Tiago Faria
Members of the Committee: Prof. Edgar Fernandes
Eng. Maria Sacadura

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Declaration

I declare that this document is an original work of my own authorship and that it fulfills all the requirements of the Code of Conduct and Good Practices of the Universidade de Lisboa.

Declaração

Declaro que o presente documento é um trabalho original da minha autoria e que cumpre todos os requisitos do Código de Conduta e Boas Práticas da Universidade de Lisboa.

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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

Resumo

A valorização do digerido, um subproduto da digestão anaeróbia, é fulcral de acordo com os princípios de uma economia circular. No entanto, aliada à enorme variabilidade das características do digerido, esta valorização ainda é bastante comprometida pela escassez de estudos efetuados.

Este trabalho pretendeu fornecer um conjunto de recomendações quanto à melhor estratégia de valorização do digerido produzido em Portugal a partir de RSU. Para isso, numa primeira fase foram comparadas as características do digerido fresco e das suas frações sólida e líquida com os requisitos legais para a comercialização de biofertilizantes. Numa segunda fase, foram efetuadas análises térmicas para estudar o potencial de valorização da fração sólida do digerido através de pirólise e combustão.

Os resultados sugeriram que tanto o digerido como a sua fração líquida apresentam potencial para ser comercializados em aplicações agrícolas, enquanto a fração sólida apresenta um conteúdo demasiado elevado em patogénicos.

Em relação à valorização termoquímica, a fração sólida revelou um elevado teor de humidade, cerca de 68%, o que influenciou negativamente a eficiência energética da combustão e da pirólise. Para além disso, o seu elevado teor em cinzas (52% em base seca) refletiu-se num poder calorífico bastante reduzido. A sua torrefação, tanto a 200 como a 250°C, aumentou este valor, mas não o suficiente para o tornar comercialmente atrativo como biocombustível.

Adicionalmente, foram desenvolvidos modelos cinéticos para a descrição das variações mássicas associadas à combustão e pirólise da fração sólida do digerido, que permitiram a obtenção dos parâmetros cinéticos destes processos com elevada exatidão.

Keywords: digestão anaeróbia; digerido; valorização energética de resíduos; biofertilizante

Contents

List of Tables

List of Figures

Acronyms

AD After Digestion.

BD Before Digestion.
BMW Biodegradable Municipal Waste.

CHP Combined Heat and Power.
CMC Component Material Criteria.

DM Dry matter.
DSC Differential Scanning Calorimetry.

EU European Union.

FM Fresh matter.

HHV Higher Heating Value.

IST Instituto Superior Técnico.

LF Liquid Fraction.
LHV Lower Heating Value.

MBT Mechanical and Biological Treatment.
MSW Municipal Solid Waste.

OFMSW Organic Fraction of Municipal Solid Waste.

PFC Product Function Category.

RT Room Temperature.

SF Solid Fraction.
STA Simultaneous Thermal Analysis.

TGA Thermogravimetric Analysis.

Chapter 1

Introduction

1.1 Municipal Solid Waste - Current Situation

Waste generation has been continuously increasing over the last few decades due to the rising of global population and living standards. The observed numbers have been aggravated by the historical influence of a linear economy model that promotes the use of finite and scarce raw materials combined with the disposal of the resulting waste and is still very present in today's society. As a result, countries become dependent on each other for natural resources, whose extraction is often associated with high energy consumption and carbon dioxide emissions. In addition, a large part of the waste generated ends up in landfills, which is very harmful both for the environment and human health [11][12].

Fortunately, the European Union (EU) has made a tremendous effort to revert this pattern and promote a transition to a circular economy model, characterized by a more sustainable use of resources, increasing the useful life of primary raw materials and encouraging the reuse and recovery of waste [11].

In this matter, Municipal Solid Waste (MSW)[1], despite representing less than 10% of total waste produced in the EU, is a crucial aspect as it is one of the most challenging to manage. This difficulty is due to its highly complex and unsorted composition, its direct proximity to the citizens, the great public attention it attracts, and its high negative impacts on both the environment and living species [14].

To improve this situation, in 2015, the European Commission adopted a new Circular Economy Package, establishing new and ambitious targets regarding waste management in its member states. One of the proposed goals was to reduce landfill of municipal waste below 10% by 2030 [15]. Sadly, in 2019, 5 million tons of municipal waste were produced in mainland Portugal, and 33% of them were directly sent to landfill, as seen in Fig.1.1 [3]. Besides that, regarding its final destinations, around 58% of the total MSW managed was disposed in landfills, both directly and indirectly. The difference between those numbers indicates that a significant percentage of the waste resulting from treatments is not recovered, reflecting the need to increase their efficiency to ensure that the targets are met [3].

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[1] According to the Portuguese Decree-Law nº 73/2011, the definition of MSW is ”Waste from households as well as other waste which, by its nature or composition, is similar to waste from households”[13].

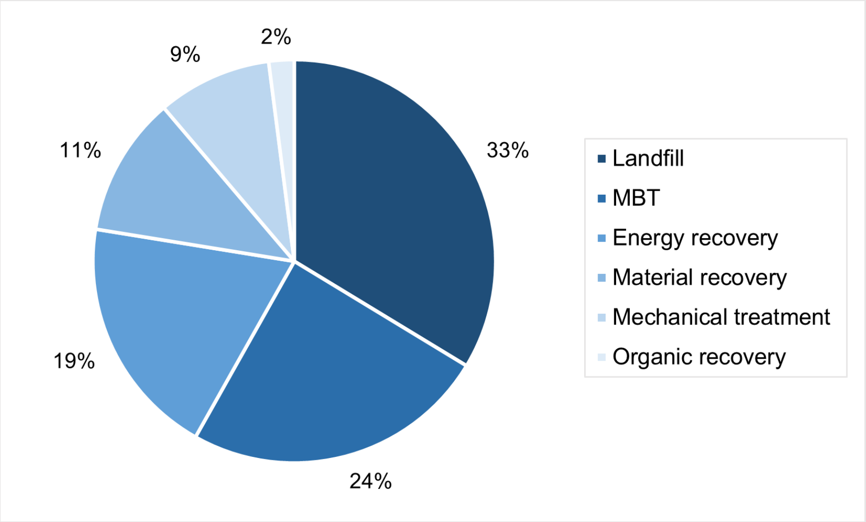

Figure 1.1: Direct destination of MSW produced in mainland Portugal in 2019. *Adapted from:* [3]

The main focus of landfill concern is biodegradable municipal waste (BMW)[2], which makes up about 55% of MSW and whose landfill rate was 43% in 2017 [17]. This decomposes, producing mainly methane, a significant greenhouse gas. Moreover, if not well managed, it represents a threat to humans and the environment, releasing unpleasant odors, attracting insects, rodents, and other disease vectors, and generating leachate that may contaminate surface and groundwater supplies [4].

In 2018, as part of the circular economy package, the Directive (EU) 2018/851 was approved. Concerning the preparation for reuse and recycling rates for Municipal Waste, it was imposed an increase to 55% by 2025, 60% by 2030, and 65% by 2035 [14]. However, in 2019, this rate was about 41% in Portugal, still far below the intended for 2025 [3]. These values reflect, once again, the difficulty in recovering waste with such a heterogeneous composition. Thus, to facilitate the achievement of the proposed targets, the Directive also established the mandatory selective collection of bio-waste[3] from 2024 - not allowed to be sent to incineration [14].

All of the above reflects Portugal's existing problem regarding waste management but also the enormous commitment that has been made by the heads of state to reverse this situation. With it, many opportunities arise in this regard, thanks to the incentives and investments proposed for this sector. However, none of this will be enough if technological development does not follow these changes. The technologies that currently exist for the energy and material recovery of urban waste still face enormous technical and financial challenges at the industrial scale and must be continuously studied and improved.

1.2 Bio-waste treatment technologies

Bio-waste's valorization consists of its transformation into value-added products, such as fuels, chemicals, and electric power. This can be achieved through several routes, with the most common being thermochemical and biological treatments.

Thermochemical processes are operated at high temperatures, using heat as the driving force to induce chemical reactions that allow the extraction of the energy from the waste or its conversion into

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[2] According to the Portuguese Decree-Law nº 152/2002, the definition of BMW is "Waste that can undergo anaerobic or aerobic decomposition, such as food and garden waste, paper and cardboard"[16].

[3] According to the Directive (EU) 2018/851, the definition of bio-waste is "biodegradable garden and park waste, food and kitchen waste from households, offices and restaurants, wholesale, canteens, caterers and retail premises and comparable waste from food processing plants" [14]. It is often mistaken for biodegradable municipal waste, but the latter also includes, in addition to bio-waste, other types of residues. In 2019, bio-waste accounted for 38,51% of the MSW generated in Portugal [3].

energy carriers. On the other hand, biological processes are carried out through the action of microorganisms at lower temperatures, which substantially reduces the external energy required. Besides that, all biological treatments occur in moisture environments, making them suitable for the treatment of high moisture waste, such as Municipal Waste, contrary to thermochemical processes. The main advantages of the latter are the shorter time required and greater stability compared to the biological.

Both routes will be addressed throughout this work, either as individual or as complementary processes, with particular focus on the technologies described in Fig.1.2.

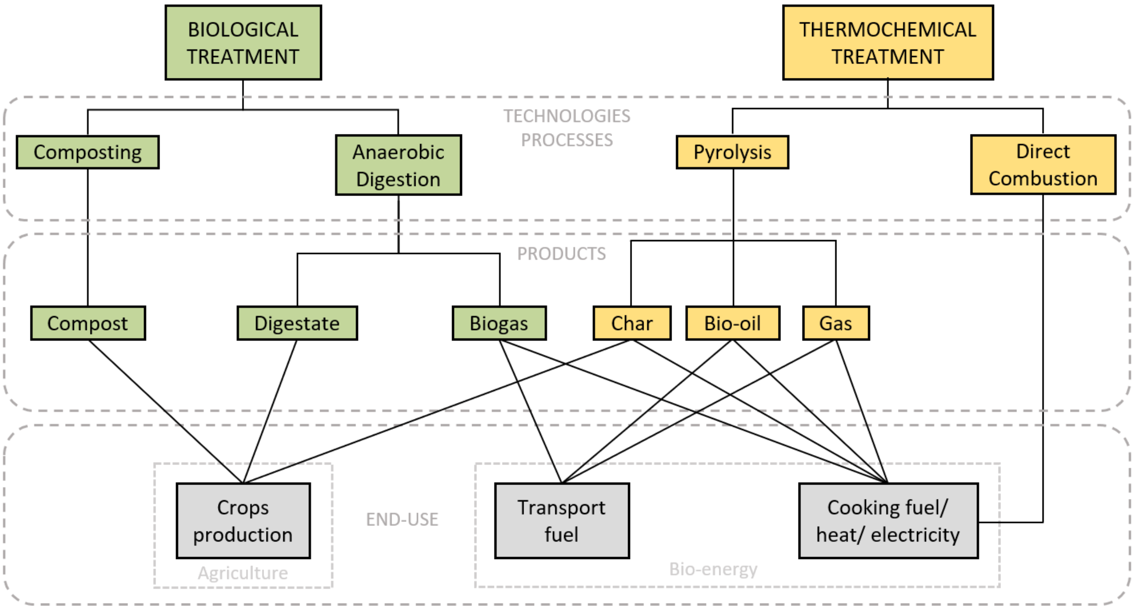

Figure 1.2: General scheme of the bio-waste treatment technologies studied throughout this work. *Adapted from:* [4]

1.2.1 Biological treatments

In Portugal, the recovery of this type of waste is performed only through biological treatments, which can be done in two different ways: anaerobic digestion (AD) and composting [18].

AD occurs in the absence of an external source of oxygen, as the bacteria can access the oxygen present in the waste itself. Through this process, the biodegradable organic matter is converted into biogas and digestate [19]. The first one is a gas mainly composed of CH_4 (55-60%) and CO_2 (35-40%) that can be directly used as a fuel in heat and power generation plants (CHP plants) or be treated to remove the CO_2 and later injected into the natural gas network [20][4]. On the other hand, digestate is the solid-liquid by-product of AD, which consists of what remains of the substrate after the extraction of its volatile components [20]. Its characteristics differ widely depending on the raw material, but it is generally rich in organic matter and nutrients, which gives it great potential as an organic fertilizer [20]. Besides the advantages of being a biological process, it is also a mature technology that reduces Municipal Waste in landfills and allows the recovery of its energy and nutrients. All of that has driven its growth in Europe a lot in recent years, with over 21 000 plants in 2019 [21].

One of the drawbacks of AD is that it is only partly able to inactivate weed seeds, bacteria, viruses, and parasites, which is extremely important if the digestate is intended to be used in agriculture. To guarantee a complete deactivation of pathogens, the process must occur at high temperatures, above 50°C, and long retention times or, as an alternative, with a post-treatment of the digestate, such as composting.

Composting is also a process of biodegradation of organic matter. However, unlike AD, it occurs in the presence of oxygen and has the drawbacks of not allowing the recovery of the energy content of the waste and requiring more space [22]. The obtained product, compost, can also be applied to the soil, presenting vital plant nutrients and being a stabilized and sanitized product, as the process can reach temperatures of 70°C [23]. For these reasons, composting is usually performed after AD [24].

In 2017, in Portugal, around 753 thousand tons of biodegradable municipal waste, corresponding to 16% of the MSW produced, were subjected to biological treatment. Of these, 60% underwent anaerobic digestion followed by composting, and the remaining 40% only composting [17].

As said, all biogas plants in Portugal compost their digestate to guarantee its hygienization and stabilization. However, this route is particularly challenging for two main reasons: i) requires large areas of treatment due to the high volume of digestate, related to its moisture content; ii) implies the loss of some of the nutrients of the waste, which are all present on the digestate.

In other countries, such as Denmark, the digestate is sold directly as a fertilizer or soil amendment without further treatment, saving a lot of money. These countries, however, benefit greatly from the fact that their waste is industrial, and therefore much less contaminated, and that the temperature of the process is much higher, 55°C compared to 35°C. Besides that, the national legislation in force regarding the commercialization of organic fertilizers is much better established than in Portugal.

The Portuguese legislation has suffered several adjustments in recent years to ensure a well-defined market for organic fertilizers that consumers can trust. According to it, there are three main possible classifications for these products [17]:

- I) the fertilizer presents maximum quality and can be used in agriculture;
- II) its quality is not the best, but it can also be used in agriculture;
- IIA) it can only be used in tree and shrub crops, namely orchards, olive groves and vineyards, as well as in forestry species.

The quality of these products depends not only on the adopted treatment but also on the origin of the waste. In 2017, 89% of fertilizers obtained from the selective collection of biodegradable municipal waste were classified as I, with the remaining 11% classified as II, mainly due to plastic contamination. Concerning the products from the undifferentiated collection, the vast majority, about 77%, were classified as IIA, and the remaining 23% were classified as II [17].

Therefore, with the implementation of mandatory selective collection from 2024, it is expected that the quality of the fertilizing products obtained from waste will increase significantly, allowing the expansion of this market. This might even imply that the digestate produced in Portugal could meet the necessary quality requirements to be sold without the need for composting and with only a few adjustments of the operating conditions of the digestion.

Although this is a significant positive step towards a circular economy, the use of these products as fertilizers may be conditioned by the increasing urbanization that has been happening, which implies 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 [21].

1.2.2 Thermochemical treatments

Besides the problems already mentioned associated with AD, the carbon conversion of the process can be very low - limited to 50% - due to the low degradation capacity that some microorganisms have for specific substrates, which implies that 50% or more of the initial organic matter remains in the digestate

[7]. Furthermore, not all the converted carbon originates methane, as typically, half of it is converted into CO_2. The energy conversion efficiency can also be only between 33-50%, which means that again more than half of the energy contained in waste remains in the digestate, making it a promising feedstock for biofuel production [25].

As an alternative to the biological treatments for digestate, the thermochemical processes have been gaining more interest as an alternative to composting, as they can also improve the quality of the digestate while increasing the overall energy gain.

The combination of the mentioned processes is still rarely used in waste treatment, despite its high potential for improving the full recovery of the waste and the economics of these systems [26][8]. With this new approach, it is possible to integrate the advantages associated with each process, combining them in a sustainable system consistent with circular economy principles [26][8].

1.3 Aim of this work

The indispensable role of anaerobic digestion in an efficient municipal waste management system is obvious. However, the challenges that this technology faces at the industrial level, namely with handling the digestate, are also evident. These obstacles can be overcome, in part, by implementing mandatory selective collection. However, to make the best use of the waste, the different existing thermochemical technologies, which still lack the proper recognition in Portugal, should also be explored as a complement to the biological processes.

By combining Efacec's vast experience in anaerobic digestion plants and academic knowledge, this work aims to provide a set of recommendations for the management of digestate in a national context.

This will be done by focusing on two distinct aspects:

- Analyze the characteristics of the digestate obtained in one of the Portuguese industrial plants, from the anaerobic digestion of undifferentiated municipal waste, in the light of national and European legislation, to assess the possibility of integration in the fertilizer market without the need for composting;
- Study the properties of this digestate through Simultaneous Thermal Analysis (STA) to evaluate the potential of using thermochemical treatments, namely combustion and pyrolysis, after anaerobic digestion to improve the overall net energy gain.

1.4 Outline

This thesis is organized into five chapters:

- Chapter 1: introduction and relevance of the theme, and presentation of the objectives of the work developed;
- Chapter 2: theoretical background and literature review of the main work developed so far by other authors on the valorization of digestate;
- Chapter 3: description of the material and equipment used throughout the work and the methodology followed;
- Chapter 4: presentation and discussion of the results obtained;
- Chapter 5: main conclusions taken and suggestions of future work.

Chapter 2

Literature Review

This chapter will discuss the current state of the art of the valorization of digestate. First, will be provided a brief description of the Anaerobic Digestion process and the characteristics of the produced digestate, followed by the main processing technologies used according to each intended final destination. Then, the different possibilities studied throughout this work - use as fertilizer, pyrolysis, and combustion - will be presented in detail, providing the information available so far, as well as the gaps in the literature. Lastly, the experimental technique used to study the digestate thermochemical properties - Simultaneous Thermal Analysis (STA) - will be presented, together with a review of the work done so far in the same field.

2.1 Anaerobic Digestion

Anaerobic digestion corresponds to the natural decomposition process of organic matter in the absence of oxygen. It is performed by different types of microorganisms that are capable of degrading a great variety of substrates [20]. One of its main limitations is that it cannot decompose lignin, one of the principal components of wood, which can be achieved through other processes such as composting or pyrolysis [20].

In a typical digester, the different stages of digestion tend to occur simultaneously [20]. However, the various bacterias responsible for them have different optimal growth conditions, which difficults the optimization of the process [20]. Therefore, it is crucial to carefully control the main parameters affecting the process, such as temperature, pH, substrate characteristics, residence time, and inhibitor concentrations, to ensure good performance [20].

Regarding the dry matter content of the substrate, the digestion can be wet if this value is below 20% or dry otherwise. In terms of temperature, digestion can be mesophilic if it happens between 35 and 50°C, or thermophilic when performed above 50°C [20]. Lower temperatures decrease the amount of external energy required [20]. However, they also slow down the speed of reactions, which implies lower biogas yields or the need to increase the retention time and, consequently, the equipment's volume [20]. Besides that, as mentioned before, for the application of digestate in lands, it is mandatory to fully inactivate harmful substances, which can only be ensured by elevated temperatures [20].

The type of waste also has a strong influence on the biogas obtained. Cellulosic residues, for example, usually produce biogas with 50% of CO_2 and 50% of CH_4 [18]. On the other hand, fats and oils generally lead to biogas with 70% of CH_4 [18].

Overall, digestion consists of four main successive steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. In the first step, the carbohydrates, proteins, and lipids that constitute the biomass are hydrolyzed into their monomers - sugars, amino acids, and fatty acids [20][18]. During the acidogenesis, the products from the previous step are converted into H_2, CO_2, and smaller fatty acids, such as propionic acid, butyric acid, and acetic acid [20][18]. Then, in the acetogenesis step, the propionic and butyric acids are further converted into acetic acid, H_2, and CO_2, through the reactions 2.1 and 2.2 [20][18].

$$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 3H_2 \tag{2.1}$$

$$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2 \tag{2.2}$$

Finally, in the last stage, the methanogenic microorganisms produce CO_2 and CH_4, the main components of biogas [20][18]. Around 70% of the methane is produced from the breaking down of volatile fatty acids (2.3) and 30% from the combination of CO_2 and H_2 (2.4) [20][18].

$$CH_3COOH + H_2O \rightarrow CH_4 + CO_2 + H_2O \tag{2.3}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{2.4}$$

2.2 Digestate

2.2.1 Digestate's characteristics

The quality and characteristics of the digestate are highly influenced by the feedstock and the type of digestion it underwent. Therefore, it is extremely difficult to define typical values for its physicochemical properties. This is particularly challenging for the digestate from MSW since the composition of this type of waste varies greatly from country to country and within the same country, depending on regions and seasons [21]. Nevertheless, extensive research is found in the literature providing the values observed for the main characteristics of digestates from different sources.

The digestate comprises a mixture of partially degraded organic matter, microbian biomass, and inorganic compounds. It is an alkaline material with pH's usually ranging between 7.7 and 8.7 for digestates from the organic fraction of MSW [21].

Its content in lignin, hemicellulose, and cellulose are excellent indicators of the success of the digestion [27]. During the process, the easily degradable compounds, such as cellulose and hemicellulose, are mostly degraded, increasing the stability of the remaining organic matter compared to the raw material. For that reason, when the cellulose content is high and the lignin is low, the digestate should be returned to the digester for further biogas extraction [27]. Otherwise, when the lignin content is excessive, the residues might need a pre-treatment to enhance the digestion performance [27]. Correa et al. (2017) analyzed a digestate from corn and grass silage and manure, with contents in cellulose, hemicellulose, and lignin of 35.8, 3.95, and 24.9%, respectively [28]. Cao et al. (2019) reported values of 19.9% in cellulose, 5.6% in hemicellulose, and 21.9% in lignin for a digestate from kitchen and green waste [29]. The authors also investigated digestate from manure and found 31.2% in cellulose, 15.5% in hemicellulose, and 20.1% in lignin [29].

Since digestion's purpose is to extract the carbon compounds from the residues in the form of biogas, the carbon content in the digestate is a reflection of the recalcitrance nature of the waste used in the process [27]. Wang et al. (2021) found that the values present in the literature for the carbon contents in digestates from different sources ranged from 15 to 55% on a dry basis [27]. High values, over 50%, are very common for feedstocks with an excess of lignocellulosic biomass such as maize silage or grass silage [27]. Nevertheless, when these values are found in digestates from easily degradable types of waste such as animal manure, MSW, or sewage sludge, it might indicate poor digestion performance [27]. Different values were found in the literature for digestates from food waste, all below 50%: 42.1% (Opatokun et al. (2017)), 45.95% (Akarsu et al. (2019)), 43.5% (Luo et al. (2020)), and 19.8% (Li et al. (2020)) [30][31][32][33]. For MSW digestate, Pawlak et al. (2020) reported a content of 16.25%, Parmar and Ross (2019), a value of 24.1%, and Nistico et al. (2019) a surprisingly superior content of 54.5% [34][35][36].

Regarding its moisture content, it is determined by whether the digestion is dry or wet. In general, dry digestion of the organic fraction of municipal solid waste leads to a digestate with a solids content between 30 to 40% [6]. However, the temperature can also influence these parameters. Usually, thermophilic conditions lead to higher destruction of solids inside the digester and consequently a higher moisture content [6]. On the other hand, the digestate usually presents more than 90% of moisture content when the digestion is wet. Logan and Visvanathan (2018) claimed that the different moisture values found in the literature for MSW digestate ranged from 48.8 to 99.3% [6]. Opatokun et al. (2017) reported a moisture content of 90.8% for a food waste digestate produced at mesophilic wet conditions [30]. Li et al. (2020) also determined a 90% moisture content for food waste digestate [33]. Conversely, Reza et al. (2016) analyzed digestate samples from dry digestion of MSW and determined a moisture content of 74% [37].

The nutrients present in the substrate are conserved throughout the digestion, being only converted to a more organic form [6]. This way, the nutrient content present in the digestate corresponds to the value found in the residue from which it originated [6]. The digestate contains macronutrients (N, P, K, Ca, S, and Mg) and micronutrients (B, Cl, Mn, Fe, Zn, Cu, Mo, and Ni) [6]. The main nutrients found are nitrogen, phosphorous, and potassium [6].

The nitrogen present in the residues entering the digestor is usually in the form of ammonium or organic nitrogen [6]. Ammonium is not degraded during digestion, and the organic nitrogen is converted into ammonium mainly due to the degradation of proteins [6]. Because of that, nitrogen content in the form of ammonium is always higher in the digestate than its raw material [6]. According to Logan and Visvanathan (2018), the ammonium content in digestate is usually 60-80% of all the nitrogen [6]. Wang et al. (2021) reviewed the values found in the literature [27]. They observed that, in general, the nitrogen content is between 1-3% (on a dry basis) for digestates from animal manure, food waste, and sewage sludge [27]. Opatokun et al. (2017) reported a higher value - 5.81% - for food waste digestate [30]. Pawlak et al. (2020) observed a content of 0.74% for MSW digestate, and Parmar and Ross (2019) claimed 1.5% [34][35].

The phosphorous present in the residues is also not degraded during digestion. However, a part can be converted into ortho-phosphorous, a soluble form [6]. Under thermophilic conditions, Zhang et al. (2020) observed a phosphorous content of 0.17% for cattail digestate, and Parmar and Ross (2019) a value of 0.7% for MSW digestate [38][35]. Zhao et al. (2018) reported a content of 1.35% for digestate from silage and manure [39].

Regarding other inorganic compounds, Parmar and Ross (2019) determined contents of 0.9% in Na, 1.4% in Mg, 1.6% in K, 10.4% in Ca, 3.2% in Fe, and 10.2% in Si (on a dry basis) for an MSW digestate from thermophilic digestion [35].

2.2.2 Digestate processing

As the characteristics and applications of the digestate vary greatly, so does the type of treatment it can undergo.

The most common and simplest use for the digestate is its direct application in agricultural soils due to its fertilizing properties. However, as mentioned before, this application carries some inconvenients. Besides the ones already presented, the extremely high content in nitrogen can represent an environmental danger when the digestate is not correctly managed, either due to nitrate leakage to the soils and waters or through ammonia emissions [6]. Besides that, as most of the nitrogen is in the form of ammonia, which is easily accessible for plants, most countries adopt restricted regulations limiting the quantities applied per unit of agricultural land [6]. Because of that, the soils close to the biogas plants are usually insufficient to apply all digestate produced, which increases the need to store it for long periods or transport it for long distances.

As the digestate usually comprises more than 90% of moisture, it presents a large volume, leading to high transport and storage costs and a low marketing value.

For the mentioned reasons, the digestate is usually treated through a series of different technologies, commonly designated as digestate processing, before any further type of valorization. These intend to increase the digestate marketing value, reducing the dependency on on-site land application [6]. Such is accomplished by reducing the digestate volume and concentrating its nutrients. In most cases, it increases the revenues of the biogas plant. However, as it comprises expensive technologies, each case should be intensively studied to better adequate the treatment to the characteristics of the digestate in question and the intended final destination.

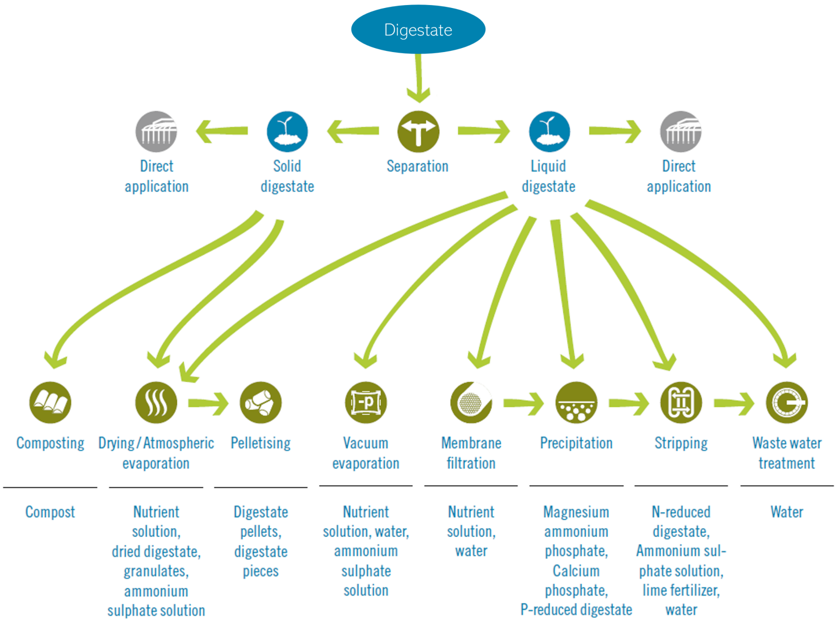

Figure 2.1: Most commonly applied technologies for the processing of digestate. *Adapted:* [5]

Solid-liquid separation

The first step of any treatment is the solid-liquid separation, also designated as mechanical dewatering. This results in two distinct fractions, a solid and a liquid, which can then be used or valorized in different ways. The solid and fibrous fraction usually presents 20-40% of dry matter and is rich in carbon and phosphorous. On the other hand, the liquid fraction presents a high moisture content of more than 92% and comprises most of the nitrogen and potassium of the raw digestate. Thus, better management of the nutrients is achieved through this treatment, allowing the use of each fraction according to the soil's needs [6].

There are different technologies available for this separation. The most commonly used at full scale are the screw press separators and decanter centrifuges. The centrifuges allow for more efficient separations but are more expensive and cannot perform well for very fibrous materials. They are commonly used in agricultural, industrial, and MSW treatment plants, while the screw press separators are mostly used for digestates from energy crops, which have higher contents in fiber [40].

Each fraction can be directly applied to the soil as a fertilizer or can undergo further treatments [21]. The solid fraction can be composted, dried and pelletized, used for industrial production of added value products, or sent to thermal treatments, such as incineration, for energy recovery [6]. Regarding the liquid fraction, if it is not used as a fertilizer, it can be treated with two distinct goals. The first one is the recovery of its nutrients for individual commercialization and is usually achieved with membrane treatments. The second one is the elimination of its nutrients to obtain a liquid effluent with enough purity to be treated in wastewater treatment plants. When this is the goal, aerobic biological treatments are usually employed.

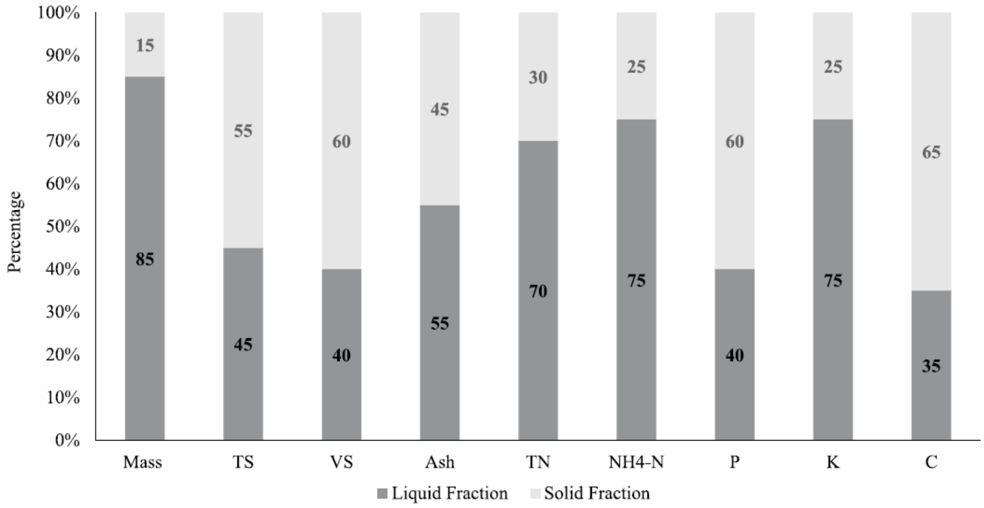

Figure 2.2: Typical distribution of the main components of digestate after solid-liquid separation. *Source:* [6]

Solid fraction processing

After the solid-liquid separation, the solid fraction is usually dried to evaporate its water content and reduce its volume. Different technologies are available in the market, such as belt, drum, or solar dryers.

With these, it is possible to achieve a total solids content of up to more than 90%, stabilizing the material and facilitating its transport and storage [6][40]. The drying is usually applied to the solid fraction but can also be performed to the whole digestate without solid-liquid separation. However, in this case, very high energy consumption is required, resulting in enormous costs.

After drying, the digestate might need to be further compacted to avoid dust emissions and spontaneous combustion. This can be achieved through pelletizing, which can increase the digestate bulk density from an average of 250-350kg/m^3 to around 700-750kg/m^3 [5]. For that to be possible, the digestate must possess a total solids content superior to 85%. Under those conditions, the process usually requires an energy consumption of around 30-50kWh/ ton [5].

Besides drying and pelletizing, the solid fraction of the digestate can also be sent to composting, as it was already mentioned, or be valorized through thermochemical processes, which will be discussed in detail in Chapter 2.4.

Liquid fraction processing

When the primary goal of the liquid fraction treatment is to reduce its volume, the most applied technologies are evaporation and membranes, which can achieve reductions of up to 50% [5].

The **evaporation** consists of the heating up of the material under normal pressures (atmospheric evaporation) or negative pressures (vacuum evaporation) [5]. The first one can be applied to the raw digestate and both of its fractions. Conversely, the vacuum evaporation can only be performed to the liquid fraction, being necessary to guarantee a prior efficient solids removal to prevent clogging of the equipment [6]. Besides that, in both cases, it is necessary to add a sulphuric acid solution to prevent ammonia evaporation [6].

The evaporation results in a concentrated solution rich in nitrogen and a condensate which usually still contains some small quantities of nitrogen. According to Al Seadi (2013), the nitrogen concentration in the liquid fraction can increase from 3.1g/kg to 9g/kg in the concentrate [40]. The condensate can be further treated either through membranes or scrubbers to obtain a purified water that meets the discharge levels requirements [41].

Besides the initial investment, the main costs of this technology are related to the sulphuric acid solution and the high energy requirements [41]. For atmospheric evaporation, the heat consumption is usually around 1000-1500kWh/m^3 of evaporated water [5]. For single-stage vacuum evaporation, the power requirement is about 10-13kWh/m^3 and the heat requirement is 600-1000kWh/m^3. For this reason, evaporation is only an attractive solution for plants with an excess of heat available [5].

Membrane technology consists of a filter with extremely fine pores, capable of separating solutes and particles from any liquid on a molecular scale [40]. There are different types of membranes according to their pore size. Generally, several steps with different membranes are needed to achieve the purity desired for the liquid digestate, starting with Ultrafiltration (0.01-0.05 μm) and ending with Reverse Osmosis (0.0005-0.005 μm) [5]. In each step, the particles larger than the membrane pores are retained, forming the concentrate, and the rest of them passes through the membrane along with water, resulting in the permeate [6]. The concentrate can be sold as an enriched nitrogen fertilizer and the permeate can be discharged in water bodies or the sewage system [5].

One of the downsides of the membranes is that only a limited amount of digestate produces purified water - around 50% of it is accumulated as by-products. Besides that, it is an extremely expensive and sensitive technology, with a power consumption of between 10-30kWh/m^3 of input [40][5].

There are other technologies available when the purpose is to recuperate and concentrate each nutrient individually to be sold as mineral fertilizers or to the chemical industry [5]. The most common one is **Ammonia Stripping**, which reduces the ammonium nitrogen concentration in the liquid digestate [40]. The process involves adding a chemical agent to enhance the separation and then scrubbing with sulphuric acid. One of the products formed is ammonium sulfate, an inorganic salt that can be sold as a fertilizer, increasing the plant revenues [41]. The main costs are the initial investment and buying of chemical products, but it requires much less heat than drying or evaporation [41].

An alternative to the discussed technologies is the **biological treatments** performed by bacterias to remove nitrogen from the digestate. Essentially, they consist of two steps: 1) nitrification - aerobic conversion of ammonium into dinitrogen; 2) denitrification - anaerobic conversion of nitrate into dinitrogen [40]. This way, the nitrogen is no longer available as a nutrient but can be released to the atmosphere, and the purified water can be discharged in receiving water bodies [5]. With the excess of nutrients in agriculture compared to the soils available for their application, this process has been gaining more interest, even though it is often seen as a waste of nutrients as it leads to their elimination [40].

2.3 Use as a fertilizer

Agriculture is one of the fundamental sectors of any country. In future years, with the expected growth of the global population, its efficiency will have to continuously increase to cover all people's food needs while searching for more environmentally sustainable options [5]. The fertilizers used play a vital role in this aspect.

Conventional mineral fertilizers consist of nutrients in the form of inorganic salts obtained from mineral extraction or chemical and physical industrial processes. Their main advantage over the most common biofertilizers, such as animal manure, is the high nutrient availability to plants. This happens since they are mineralized, unlike with manure, where they are bound to organic compounds and not so easily absorbed by plants [40].

During anaerobic digestion, the nutrients present in the waste in the form of organic compounds are partially mineralized, giving excellent fertilizing properties to the digestate, making it capable of substituting mineral fertilizers [42]. This substitution represents a decrease in costs for farmers and several environmental advantages. First, it ensures the reuse of the nutrients present in the waste whose natural reserves are finite and increasingly scarce, especially phosphorus [5][42]. Secondly, it represents drastic decreases in greenhouse gas emissions and energy consumption associated with mineral extraction [5][42].

The digestate also represents several advantages over the direct application of raw manure in the soils:

- Since the easily degradable carbon compounds are extracted from the residues during digestion, the carbon remaining in the digestate presents high recalcitrance levels. This increases the concentration of humic-like substances in the soils and, consequently, its structure and water holding capacity [5][43];

- Due to the destruction of substances such as volatile acids, phenols, and phenol derivatives, there is a significant decrease in the release of unpleasant odors [40];
- There is a destruction of almost all pathogenic substances, which increases safety in its application for farmers and reduces health risks for the population [40];
- The destruction of organic acids during digestion drastically decreases the risk of leaf burn during digestate application on the soils [5].

Besides all the benefits, there are still some challenges regarding the use of digestate as a fertilizer. One of those is the extremely high content of ammonium, which can result in significant losses through ammonia emissions [5]. Another difficulty is that the nitrogen is present in digestate in different forms - organic, ammoniacal, nitrate/nitrite - which means its total content does not correspond to the total amount directly available to plants [5]. Throughout the vegetative season, the organic fraction is mineralized, changing its availability for the plants, which should be taken into account by the farmers [5].

Other problems are related to the high moisture content in the digestate. Guilayn et al. (2019) observed that the raw digestate had a total solids content so low that it could not be classified as an organic fertilizer according to the legislation [43]. Kataki et al. (2017) assessed the use of cow dung digestate as a fertilizer. The authors claimed that the solid fraction presented a much higher potential due to the increased concentration of organic matter and nutrients [27].

Finally, the variable composition of the digestate, as well as the possible presence of impurities (especially when the origin is MSW), hinders its public acceptance and the legislation in this regard.

The legal framework that a product must meet to be classified as a fertilizer can be established at a national level if it is intended to be marketed only inside the country, or at the EU level if it is intended to be commercialized between different member states [5]. The legislation concerning fertilizer marketing in the EU has recently been revised to include organic fertilizers, such as digestate. Currently, the Regulation (EU) 2019/100 is in force. Regarding the Portuguese legislation, the DL 103/2015 applies, which has not yet been revised after the EU alterations.

2.3.1 Regulation (EU) 2019/1009

The Regulation (EU) 2019/1009 establishes eleven Component Material Criteria (CMC) that define what the fertilizer can be made of. The only relevant category for this work is the CMC5 - Digestate other than fresh crop digestate. It also defines seven Product Function Categories (PFC) with different requirements. The digestate could be used as a PFC1(A) - Organic fertilizer (solid or liquid), PFC3(A) - Organic soil improver, PFC4 - Growing medium, or PFC6(B) - Non-microbial plant biostimulant, according to its characteristics.

To be classified as an EU fertilizer, the digestate should meet the requirements for its corresponding CMC and the relevant PFC. Those values are presented in Tables 2.1 and 2.2.

Table 2.1: Requirements that the digestate should meet to be classified as CMC5 according to Regulation (UE) 2019/1009 [1].

Parameters	**Unit**	**CMC5**
PAH_{16}	mg/kg DM	≤ 6
Each macroscopic impurity with $>$2mm	g/kg DM	≤ 3
Sum of all macroscopic impurities with $>$2mm	g/kg DM	≤ 5

DM - Dry matter

In order to be inserted into CMC5, the digestate not only has to meet the requirements of Table 2.1 but also must have been produced in a digestion with one of the following time-temperature profiles:

1. Thermophilic digestion (55°C) for, at least, 24h, followed by a Hydraulic Retention Time of, at least, 20 days;
2. Thermophilic digestion (55°C), followed by a treatment that involves pasteurization (70°C);
3. Thermophilic digestion (55°C), followed by composting with one of the following time-temperature profiles:
   - (a) 70°C and three days;
   - (b) 65°C and five days;
   - (c) 60°C and seven days;
   - (d) 55°C and fourteen days;
4. Mesophilic digestion (37°C), followed by a treatment that involves pasteurization (70°C);
5. Mesophilic digestion (37-40°C), followed by composting with one of the following time-temperature profiles:
   - (a) 70°C and three days;
   - (b) 65°C and five days;
   - (c) 60°C and seven days;
   - (d) 55°C and fourteen days;

To guarantee an acceptable level of organic matter stability, both the solid and liquid fractions of digestate must meet one of the following stability criteria:

1. Oxygen uptake rate (indicator of the extent to which biodegradable organic matter is being broken down within a specified time period): $\leq$ 25mmol O_2/kg of organic matter/h;
2. Residual biogas potential (indicator of the gas released from the digestate during 28 days, measured as a function of the volatile solids contained in the sample): $\leq$ 0.25 l biogas/g volatile solids.

Table 2.2: Requirements for possible PFCs for digestate according to Regulation (UE) 2019/1009 (FM - Fresh matter; DM - Dry matter) [1].

		PFC1(A)		**PFC3(A)**	**PFC4**	**PFC6**
Parameters	**Unit**	**(I): solid**	**(II): liquid**			
N	wt % FM	≥ 2.5 or 1^*	≥ 2 or 1^*	-	-	-
P_2O_5	wt % FM	≥ 2 or 1^*	≥ 1 or 1^*	-	-	-
K_2O	wt % FM	≥ 2 or 1^*	≥ 1 or 1^*	-	-	-
$N+P_2O_5+K_2O$	wt % FM	≥ 4	≥ 3	-	-	-
C-org	wt % FM	≥ 15	≥ 5	$\geq 7{,}5$	-	-
Cd	mg/kg DM	≤ 1.5		≤ 2	$\leq 1{,}5$	≤ 1.5
Cr VI	mg/kg DM	≤ 2		≤ 2	≤ 2	≤ 2
Hg	mg/kg DM	≤ 1		≤ 1	≤ 1	≤ 1
Ni	mg/kg DM	≤ 50		≤ 50	≤ 50	≤ 50
Pb	mg/kg DM	≤ 120		≤ 120	≤ 120	≤ 120
As-inorg	mg/kg DM	≤ 40		≤ 40	≤ 40	≤ 40
Biuret	mg/kg DM	0		-	-	-
Cu	mg/kg DM	≤ 300		≤ 300	≤ 200	≤ 600
Zn	mg/kg DM	≤ 800		≤ 800	≤ 500	≤ 1500
Salmonella spp.	in 25g or 25ml FM	0		0	0	0
Escherichia coli	UFC in 1g or 1ml FM	≤ 1000		≤ 1000	≤ 1000	≤ 1000
Phosphonate	wt %	≤ 0.5		≤ 0.5	≤ 0.5	≤ 0.5
Dry matter	wt %	-		≥ 20	-	-

* If the product contains only one declared primary nutrient, that nutrient should meet the first value. If the product contains more than one declared primary nutrient, those nutrient contents should meet the second value.

2.3.2 DL 103/2015

The DL 103/2015 establishes the quality criteria for the fertilizers produced from residues and biodegradable organic matter to be commercialized in Portugal. It also defines the end of waste status for the products that meet those criteria.

In Appendix I of the Regulation, the different types of fertilizing materials are defined. The groups into which the digestate may be placed are Group 2 - Organic fertilizers and Group 5 - Organic correctives [2].

Group 2 - Organic fertilizers

Group 2 requires that the material to be commercialized is entirely produced from products or by-products of animal and/or vegetable origin. This is not exactly the case of digestate of MSW, as the biodegradable organic fraction of these products includes, for example, paper and card. However, it is expected that in the near future the Portuguese legislation follows the recent changes in the European legislation, starting to also include the digestates of this origin. In addition, the imposition of the mandatory selective collection will further facilitate its acceptance process. For that reason, group 2 was also considered in this work.

In order to be recognized as an organic fertilizer, the material must have the minimum nutrient and organic matter content of one or more of the categories presented in Table 2.3 [2]. Besides that, at least 85% of it should pass through a sieve with a mesh opening of 10mm.

Table 2.3: Minimum contents of organic matter and macronutrients in a product to be classified as organic fertilizer according to DL 103/2015 [2].

	N-org (wt %)	**Organic matter (wt %)**	**P_2O_5 (wt %)**	**K_2O (wt %)**	**$N+P_2O_5+K_2O$ (wt %)**	**$N+P_2O_5$ (wt %)**	**$N+K_2O$ (wt %)**
N-fertilizer	3	50	-	-	-	-	-
NPK-fertilizer	2	50	2	2	10	-	-
NP-fertilizer	2	50	3	-	-	6	-
NK-fertilizer	3	50	-	6	-	-	10

Group 5 - Organic correctives

According to DL 103/2015, the digestate should meet the criteria defined in Table 2.4 to be classified as an organic corrective. Besides that, 99% of the material should pass through a 25mm square mesh sieve, and it has to show an absence of fitoxicity.

Table 2.4: Requirements that the digestate should meet to be classified as a Group 5 - Organic corrective according to DL 103/2015 [2].

Parameters	**Unit**	**Group 5**
pH	-	5.5 - 9
Moisture	wt % FM	$<$40
Organic matter	wt % DM	$>$30
Salmonella spp.	in 25g of FM	0
Escherichia coli	UFC/g of FM	$<$1000
Weed seeds and propagules	Active units/L	$<$3

To guarantee the hygienization of the digestate, the digestion should obey one of the following profiles:

1. Average retention time in the digester of more than 20 days at temperatures superior than 53°C;
2. If it does not obey the previous profile, one of the following options should be performed:
   (a) composting after digestion for i) more than two weeks at more than 50°C, or ii) more than one week at more than 60°C;
   (b) treatment of the residues for one hour at more than 70°C before entering the digester.

Depending on its content in heavy metals and inert materials, the digestate inserted into Group 5 can be classified into four different classes. Its application depends on the class attributed:

- Class I and II - Agriculture;
- Class IIA - Agricultural tree and shrub crops, including orchards, olive groves, and vineyards. Forestry species;
- Class III - Soil where there are no intended crops for human and animal feeding:
  - Final cover of landfills and dumps, quarries and mines, aiming at restoring the landscape;
  - Covering ditches and slopes, in the case of road construction (landscape integration);
  - Fertilization of soils intended for forestry (species whose fruit is not used in human or animal food);

- Bioenergy crops;
- Gardening; flower production (edible crops are excluded);
- Football and golf courses.

The maximum values allowed for each class are presented in Table 2.5.

Table 2.5: Maximum values allowed for the total content of heavy metals and inert materials for each class of Group 5 according to DL 103/2015 [2].

Parameter	Unit	I	II	IIA	III
Cd	(mg/kg DM)	0.7	1.5	3.0	5.0
Pb	(mg/kg DM)	100	150	300	500
Cu	(mg/kg DM)	100	200	400	600
Cr	(mg/kg DM)	100	150	300	400
Hg	(mg/kg DM)	0.7	1.5	3.0	5.0
Ni	(mg/kg DM)	50	100	200	200
Zn	(mg/kg DM)	200	500	1000	1500
Glass, metals, and plastics >2mm	(wt % DM)	0.5	1.0	2.0	3.0
Stones >5mm	(wt % DM)	5.0	5.0	5.0	-

2.4 Thermochemical applications

2.4.1 Pyrolysis

Pyrolysis principles

Pyrolysis is the heating up of biomass or any organic material up to temperatures between 400-900°C under an inert atmosphere [44]. Since it occurs in the absence of oxygen, it does not trigger the combustion of the material, only its thermochemical decomposition [45].

The mechanism of this process is highly complex due to the number of intermediate products formed and the diversity of substrates. Different reactions occur simultaneously or sequentially, such as dehydration, dehydroxylation, decarboxylation, and decarbonization [4]. Overall, four main stages can be identified. The first one usually corresponds to the drying of biomass, where the moisture content is reduced to a maximum, which occurs until approximately 100°C [4]. Then, between 100-300°C, dehydration reactions occur, where the water molecules resulting from reactions between the different components are eliminated, along with other volatiles such as CO, CO_2, and H_2 [4]. At around 200°C, primary pyrolysis occurs, where the larger molecules break down into char and condensable and non-condensable gases [4]. Finally, between 300-900°C, happens the secondary cracking of the volatiles into char and non-condensable gases [4].

Even though it is a process that can treat a great variety of substrates, it usually requires them to be dried until at least 10-15% of moisture to guarantee high energy efficiency.

In terms of products, three distinctive ones can be obtained: a solid, commonly known as pyrochar; a liquid called bio-oil; and a combustible gas[45].

Pyrochar, which mainly consists of carbon (>85%), generally has a low ash content and may contain some amounts of oxygen and hydrogen [46]. On one hand, it can be used in agriculture, being an

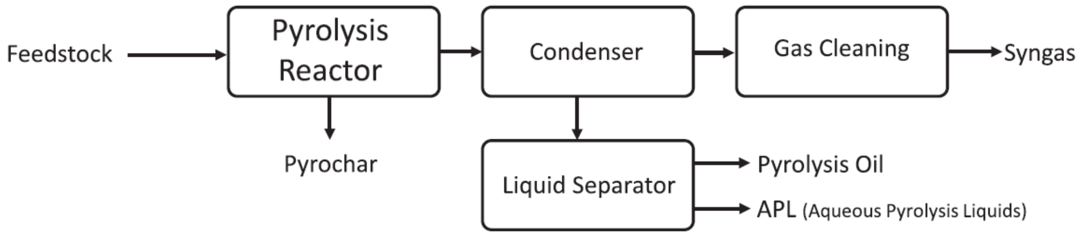

Figure 2.3: General scheme for the process of pyrolysis. *Source:* [7]

excellent soil amendment due to its high capacity to retain water, nutrients, and agricultural chemicals [45]. This way, it not only increases the soil's retention capacity but also minimizes water contamination and soil erosion [45]. In addition, it is also capable of sequestering significant amounts of carbon, which is a major benefit to the environment [45]. On the other hand, the calorific value of biochar is much greater than the biomass from which it originated, so it can easily be commercialized as a solid biofuel [46]. Furthermore, it can also be used as a feedstock in other processes for the production of chemicals [46].

Bio-oil, on the other hand, is a black liquid consisting of a dense mixture of different oxygenated organic compounds (about 25-50% by weight) and some water (15-30%) [46]. Thanks to its composition, it is usually unstable, corrosive, and immiscible with petroleum compounds [46]. However, its density ($>$1kg/L), much greater than the biomass, facilitates its transport and storage [45]. One of its main applications is its use as a liquid biofuel, usually presenting about 50-70% of the fuel value of petroleum-based products, with the great advantage of allowing considerable savings in GHG emissions, superior to other biofuels [45]. In addition, it is not produced from food products, so it does not compete with the food chain. It can also be stored for long periods, being available whenever needed, and can complement other intermittent renewable sources such as solar or wind [46]. Finally, it can also be used to manufacture chemicals or to produce heat and electricity in turbines or boilers [46][45].

The gas produced consists of a mixture of several volatile and combustible compounds, such as CO, CO_2, and H_2 [45]. Its applications are similar to bio-oil, being used to produce electricity, heat, chemicals, or in the synthesis of liquid biofuels for transportation [46].

Several factors influence the yield obtained in each product. The main ones are the composition of the raw material, the final temperature reached, the residence time in the reactor, and the heating rate [45]. In terms of time, the faster the process is, the greater the amount of water and organic compounds in the final product, and the less the amount of char formed [46]. Regarding the temperature, the lower it is, the greater the amount of carbon and water in the product, and the lower the number of volatile compounds [46]. This way, when it is intended to favor char production, a low heating rate, low temperature, and high residence time should be chosen. In turn, to maximize gas production, a high heating rate, high temperature, and low residence time are preferred. Finally, when the desired product is bio-oil, high heating rates, intermediate temperatures, and low residence times should be selected. For example, when the temperature is around 500°C, and the heating rate is high - 10°C/s - the following distribution in product yield is generally obtained: 60-70% in bio-oil, 15-25% in gas, and the remaining 10-15% in char [45].

Therefore, there are three main variations of the pyrolysis process:

1. Slow pyrolysis: with residence times in the order of minutes, a heating rate of approximately 0.1 to 1°C/s and final temperatures up to 600°C, it is used to produce mainly gas and biochar [47][46];
2. Torrefaction: corresponds to the slow heating of biomass up to low temperatures - between 200-300°C - and with high residence times [47][48]. During this process, the moisture content is reduced to a maximum and some volatile components are released. The product obtained, known as vegetable coal, is mainly char with a much reduced size and no biological activity, which facilitates its storage and transport [46][48]. Besides that, it presents a higher energy density than the biomass due to a lower O/C ratio, being a solid that is generally more suitable for energy production [46][48];
3. Fast pyrolysis: characterized by high heating rates - 10-200°C/s - and short residence times (in the order of seconds) [47]. It can either be flash pyrolysis or ultra-rapid pyrolysis. The first one is operated between 450-600°C and can obtain yields in bio-oil up to 75% by weight on a dry basis. The second one, which can go up to 1000°C, maximizes gas production [46].

The diversity of products obtained and, consequently, of possible applications gives pyrolysis great interest as a technology for biomass valorization, either as an individual process or as an intermediate one [44]. However, in general, pyrolysis is not self-sufficient and requires an external heat supply, unlike other processes [46].

Digestate pyrolysis

Different experiments have been performed on a laboratory scale regarding the pyrolysis of the digestate. All results indicate that this is a promising alternative. However, extending the studies to a pilot scale is still necessary before introducing them at an industrial level.

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.

In 2016, Opatokun et al. studied the pyrolysis of digestate from industrial food waste to compare the agronomic properties of the raw digestate and the pyrochar obtained [30]. After drying the digestate, the pyrolysis was performed in a fixed bed horizontal tubular reactor, for 4 hours, at a heating rate of 10°C/min [30]. Different temperatures were tested, between 300-700°C, and, as expected, it was found that an increase in temperature decreased the solid yield [30]. The best result obtained was 60.55% at 300°C, with the worst being 35.03% at 700°C [30]. One of the issues found was that the amount of ashes increased with the pyrolysis, especially at higher temperatures [30]. The ash content of the digestate was 25.6%, increasing to 35.7% at 300°C and 60.2% at 700°C [30].

Regarding the agronomic properties of pyrochar, Opatokun et al. (2016) noticed a positive increase in phosphorus, potassium, and other micronutrients and a slight decrease in nitrogen, accentuated by increased temperature [30]. One of the downsides of pyrolysis was that the char presented a lower water holding capacity, making it unsuitable for soils that need a higher water availability for plants [30]. However, it showed great potential as a liming agent for acidic soils and positive effects in seed germination and toxicity, unlike digestate [30]. All of that indicated that the pyrolysis of the digestate has excellent potential, as it allows greater energy extraction from the waste while maintaining its agricultural potential.

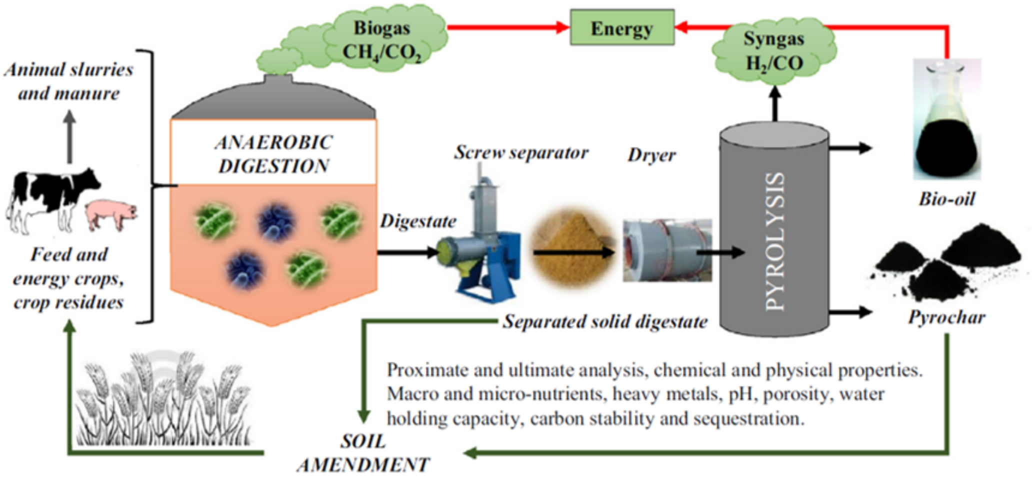

Figure 2.4: General scheme for the experiments performed by Monlau et al (2016). *Source:* [8]

Other similar works were also performed [8][49]. In 2016, Monlau et al. performed the pyrolysis of digestate from animal and plant waste with the same intents [8]. The experiments were done to the solid fraction of digestate after its drying and dehydration in a screw separator [8]. A quartz rotary kiln reactor was used, at 600°C, with a heating rate of 20°C/min and a residence time of 10 min at the maximum temperature [8]. The average yields obtained at this temperature were: 12% for syngas, 34% for pyrochar, and 54% for bio-oil [8]. The changes observed in micronutrients, pH, and ashes were similar to those in Opatokun et al. (2016) [30][8]. However, the pyrochar presented a higher water holding capacity than the digestate, preventing nutrient leaching and soil erosion [8].

Monlau et al. (2016) stated that the main interest in the pyrochar was its recalcitrant carbon nature, associated with higher carbon sequestration and thus helping to decrease global climate changes [8]. Its main conclusions were that the coupling of Pyrolysis and AD is a technologically efficient solution and that both the digestate and pyrochar have good but complementary properties as soil amendments [8]. While pyrochar has the qualities already mentioned, the digestate favors the microbiological processes of the soil due to its higher content in degradable organic matter [8].

In 2015, Opatokun et al. characterized food waste and its digestate as potential substrates for pyrolysis [26]. The digestate was dried and pelletized, and the experiments were performed in a fixed bed horizontal tubular reactor, at 10°C/min, testing temperatures between 300-700°C [26]. At 500°C, the yields obtained from the digestate were: 5.3% in gas, 42.5% in char, and 52.5% in bio-oil [26]. The same values from the raw food waste were: 7.4% in gas, 32.3% in char, and 60.3% in bio-oil [26]. The heats of combustion of both gases and liquids were similar for the digestate and waste: 16.5MJ/kg for gas and 12.4MJ/kg for oil [26]. However, the heat of combustion of the char obtained from the untreated waste, 24.8 MJ/kg, was almost double the one from digestate [26].

The observations of Opatokun et al. (2015) related to the solid obtained were in agreement with other works. There was an increase in ash content with pyrolysis, which is particularly challenging in the case of the digestate, as it already has a high value [26]. There was also an increase in fixed carbon and a decrease in the volatile matter, oxygen, hydrogen, and nitrogen [26].

In 2015, Wiśniewski et al. studied the pyrolysis of the digestate produced from agricultural waste with a moisture content of 7.85% in a batch reactor at 500°C [50]. The mass yield verified for the solid product was 43.3% and the energy yield was 52.5% [50]. There was a slight increase in the carbon content in the char and significant decreases in terms of hydrogen and oxygen, suggesting an increase in fuel properties [50]. However, in agreement with other works, there was a significant problem with ash accumulation, with an increase of 86% [50].

Few studies have focused on the bio-oil obtained. Opatokun et al. (2015) claimed that the bio-oil produced from the digestate presented a lower concentration of phenols, esters, and hydrocarbon derivatives than the one produced from raw waste [26]. Monlau et al. (2016) observed that the produced bio-oil in its experiments presented a water content of 45%, higher than the maximum allowed in CHP engines (30%), requiring some previous upgrade for this application [8].

Regarding the gas produced, Opatokun et al. (2015) verified that, at a rate of 10°C/min, gas release started at around 200°C, with CO_2 as the main component, followed by H_2 [26]. For a heating rate of 60°C/min, the release started around 500°C, with H_2 as the most abundant, followed by CO_2 and CH_4 [26]. Wiśniewski et al.(2015) obtained a gas with a calorific value of 3700kJ/Nm^3 and the following composition: CO_2 (24%), CO (10%), CH_4 (8%), H_2 (2%) [50].

Besides the high interest shown in the agricultural properties of pyrochar, the coupling of these two processes has also proven to be very advantageous from an energy point of view [51].

Monlau et al. (2015) investigated the coupling of pyrolysis and anaerobic digestion to increase the energy recovery of agricultural waste [51]. For that, pyrolysis was performed on a laboratory scale reactor at 500°C, obtaining yields of 8.8% in syngas, 32.8% in char, and 58.4% in bio-oil [51]. The char was assumed to be used in agriculture, while the syngas and bio-oil could be used as fuels [51]. The syngas presented an LHV of 15.7MJ/Nm^3, while the bio-oil had an HHV of 23.5MJ/kg after water extraction [51]. It was claimed that the conversion of biogas into heat and power in CHP plants usually implies huge losses of energy, especially as heat [51]. The results showed that the energy surplus from the biogas was enough to cover the drying and pelletization of the solid digestate [51]. Besides that, by using both syngas and bio-oil as fuels in CHP engines, it was possible to increase the energy production of the plant by 42% when compared to the stand-alone AD plant [51].

Tayibi et al. (2020) followed a similar approach by performing pyrolysis of solid digestate of agricultural residues at 500°C, for 1 hour, at 10°C/min [52]. The yields of the products were 37.6% in biochar, 33.7% in bio-oil, and 29.3% in syngas [52]. 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 [52].

Other works were performed regarding the pre-treatment of digestate with torrefaction to increase its fuel properties [38][53].

Zhang et al. (2018) compared wet and dry torrefaction for the treatment of dried corn stalk digestate [38]. Both processes enhanced its fuel properties [38]. There was a decrease in the volatile matter, which increases combustion efficiency and reduces harmful emissions [38]. There was also a positive increase in fixed carbon and HHV [38]. The process was done for 30 min, between 220-280°C for dry treatment and 180-240°C for wet [38]. In both cases, the yields in mass and energy decreased with a temperature increase [38]. The best results were obtained for the dry treatment at 220°C, with a mass yield of 85.02% [38].

Swiechowski et al. (2020) performed the torrefaction of the digestate at temperatures between 200-300°C and residence times between 20-60 min [53]. It was also verified an increase in the HHV of the digestate up to 11%, with the best result at 300°C and 30 min [53]. A downside effect of the process was an increase in the ash content up to 22% [53].

Table 2.6: Summary of the data found in literature about the pyrolysis of the digestate.

	Pyrolysis			**Gas**		**Bio-oil**		**Char**		**Reference**
Type of waste	**T (°C)**	**Time (h)**	**Heating Rate (°C/min)**	**Yield (%)**	**LHV (MJ/Nm3)**	**Yield (%)**	**HHV (MJ/kg)**	**Yield (%)**	**HHV (MJ/kg)**	
Industrial food	300	4.0	10	—	—	—	—	61	—	[30]
Animal and plant	600	0.2	20	12	—	54	—	34	—	[8]
Food	500	—	10	5	—	52	—	43	—	[26]
Agricultural	500	0.6	—	—	3.7	—	—	43	—	[50]
Agricultural	500	0.2	20	9	15.7	58	23.5	33	—	[51]
Agricultural	500	1.0	10	29	28.4	34	28.4	38	—	[52]
Corn Stalk	220	0.5	—	—	—	—	—	85	16	[38]
MSW and plant	300	0.5	50	—	—	—	—	—	20	[53]

2.4.2 Combustion

Combustion principles

Combustion is a highly exothermic process in which a fuel reacts with oxygen, releasing large amounts of heat [54]. It has a variety of applications, being highly used both in households and in industry [54].

The amount of heat released depends on several factors, one of the most significant being the characteristics of the substrate [55]. A good fuel should have less than 20% of humidity and be rich in hydrogen and carbon [55]. Although still widely used, the combustion of fossil fuels has been partially replaced by biomass due to higher environmental awareness.

For the process to occur, it is necessary to guarantee an excess of oxygen at high temperatures, between 700-1400°C [56]. Under these conditions, hydrocarbons are completely oxidized. This means that all carbon is converted into CO_2 and all hydrogen into water vapor [57]. With biomass, the amount of carbon dioxide released corresponds to the same amount absorbed by its metabolic processes [57]. This way, it is considered a neutral process regarding carbon emissions, not contributing to climate changes, unlike the burning of fossil fuels [57]. Regarding the remaining pollutants emitted, biomass has less sulfur than fossil fuels, representing a decrease in SO_X emissions [57]. However, the amount of nitrogen and chlorine, which are responsible for the emission of NO_X and HCl, varies widely depending on the type of material [57].

One of the downsides of biomass is that it has much less carbon and more oxygen than coal, which results in a lower heating value [57]. In addition, especially in municipal waste, the highly variable composition and the high moisture and ash content still represent significant challenges to its efficiency at the industrial level [57]. Ash generally has a lower melting point which can cause a lot of fouling and slagging problems [57].

For these reasons, it is complicated to fully replace fossil fuels with biomass in existing power plants without impairing their performance [58][59]. A common practice is co-firing, i.e., simultaneously burning fuels from different sources, such as coal and biomass [58][59]. This allows renewable energy production at a low capital cost, taking advantage of the existing power plants [58][59].

A way to simplify this process is by using torrefied biomass since its properties are much more similar to mineral coal[1] [58]. In Portugal, the Pego Power Station, the only coal-fired power plant operating in the country, will start to produce energy exclusively from vegetable coal in 2021 [60][61].

From a chemical point of view, combustion is a complex process that involves several reactions in series and parallel [56][54]. At relatively low temperatures, the first step is drying, which is an endothermic process that removes all moisture content as water vapor [56][54]. Then, as the material is heated, its thermal degradation in the form of pyrolysis begins, and its volatile components are released. At very high temperatures, gasification starts to occur, consisting in the incomplete combustion of the chars, releasing CO and H_2 [56][54]. Finally, when there is enough oxygen, complete combustion occurs, releasing CO_2 and H_2O [56][54].

Digestate combustion

Few published articles were found regarding the combustion of raw digestate.

Kratzeisen et al. (2010) studied the combustion of digestate from agricultural and animal waste in a biomass heating system which usually handled woody materials [62]. 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% [62]. The results were very positive, as the pellets produced from pinewood usually present 12% of moisture with a calorific value of 16.3 MJ/kg [62]. The nominal power of the system was 49kW, and wood pellets typically achieve efficiencies higher than 90% [62]. The combustion of digestate pellets achieved a power of 44kW, representing an efficiency of 85% [62].

Compared to pinewood as a feedstock, the downside was the significantly higher nitrogen, sulfur, and chlorine values [62]. That represented higher pollutant emissions than woody pellets but still below the thresholds established by the German regulation [62]. The average emission concentration of CO and NO_X were 190 and 366 mg/m^3, respectively [62]. The average dust emission was around 103 mg/m^3 but was easily reduced to 40 mg/m^3 with an electric filter [62].

The ash content of the digestate pellets was on average 16.5%, with a softening temperature at around 1100°C, lower than the typical woody biomass, 1430°C [62]. However, it was possible to avoid slagging problems by water cooling the combustion chamber [62]. The main components found in the ashes were calcium, phosphorus, silicon, and potassium, which indicated a potential value for agriculture applications [62].

Overall, Kratzeisen et al. (2010) concluded that digestate pellets have similar fuel properties as woody pellets, presenting as an excellent alternative that can be used in already existing systems [62].

Pedrazzi et al. (2015) performed work with similar intents but with negative results [63]. Firstly, a dried and pelletized sample of digestate was burned in a domestic air furnace, which failed due to slagging problems related to ash melting [63]. Then, the combustion of 50% of digestate pellets and 50% of woody certified pellets was performed [63]. The latter had less than 1% of humidity and an HHV of 19 MJ/kg, which increased the combustion performance but still presented slagging issues [63]. Finally, the mixture of wood residues and digestate before pelletization was tested, resulting in a superior HHV and fewer ash problems [63]. However, the emissions were significantly higher than with woody pellets [63].

More recently, in 2020, Ogwang et al. also studied the fuel properties of digestate from animal

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[1] Torrefaction process is described in previous Chapter 2.4.1.

and domestic waste for domestic use [64]. Different samples were taken from the digestor at different residence times and were dried, pelletized, and pyrolyzed [64]. The briquettes obtained presented humidity up to 8.9% and ash contents up to 76.4% [64]. Due to the pre-treatment, they presented less volatiles, more carbon, and less hydrogen, oxygen, and nitrogen [64]. Results showed that the ignition time was 5.35s, with a burning rate of 0.16g/min, and water boiling time of 31.1min [64]. The HHV and LHV were 14.87 and 7.88MJ/kg, respectively [64]. The conclusions were that the digestate could be used as a fuel for domestic applications [64].

2.5 Simultaneous Thermal Analysis (STA)

2.5.1 STA principles

There are several techniques to study the thermal behavior of a material. In this work, the one chosen was Simultaneous Thermal Analysis (STA), which combines two different techniques: Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC).

By coupling these two analyses, the measurements are taken on a single sample at the same time. This way, it is possible to obtain the same information in less time than with individual measurements. Furthermore, since both the sample and the experimental conditions are the same, it is possible to directly correlate the results obtained from both techniques, leading to more accurate conclusions [65].

In a typical STA system, a small sample of the material is placed inside a furnace connected to a microbalance. Then, both the temperature and atmosphere of the experience are programmed as a function of time. Throughout the experiment, as the temperature changes, all the variations of mass and enthalpy are recorded.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis records the change in mass experienced by a sample when subjected to a programmed temperature profile in a controlled atmosphere [66]. The choice of the operating conditions depends on the type of information desired. The temperature program can include heating, cooling, and/or isothermal steps. The atmosphere selected may be oxidative, using air, for example, or inert, using nitrogen.

The results obtained are usually organized in a graph, where the vertical axis corresponds to the mass, usually expressed in mg or %, and the horizontal axis to time or temperature. These graphs, called TG curves, usually have a similar appearance to the green curve in Figure 2.5. Their descending shape is due to the loss of mass that occurs throughout the experiment, resulting from the release of components in the form of gases. The more complex the material is, the greater the number of degradation steps seen on the curve. Their slopes depend on the speed of the reactions and their heights on the amount of mass lost. Sometimes it may also be helpful to plot the derivative of the TG curve - DTG - which gives the rate of mass change, in mg/min or %/min. This has a similar shape to the blue curve in Figure 2.5, where the highest peak corresponds to the temperature at which the mass loss rate is maximum.

The different steps seen on the TG curve can occur due to different physical and chemical phenomena, including [66]:

- drying;
- evaporation of volatile components;
- adsorption/desorption;
- oxidative decomposition of organic substances in the presence of oxygen;
- thermal decomposition with the formation of gaseous products under an inert atmosphere.

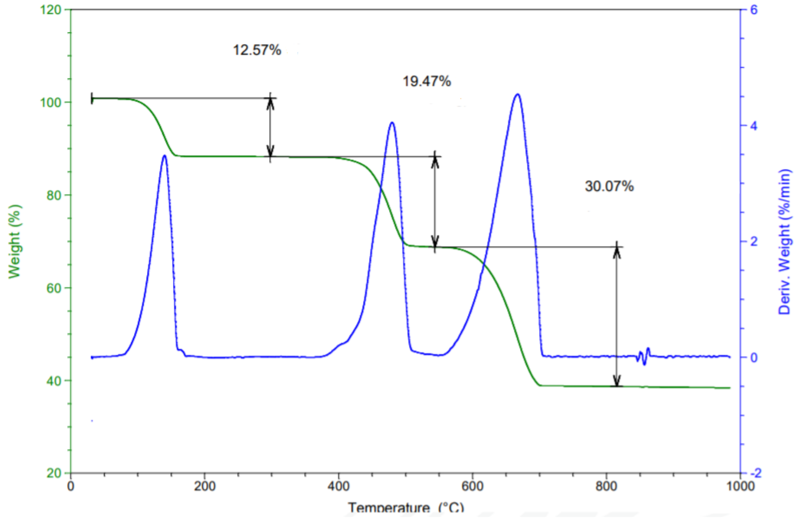

Figure 2.5: Example of the representation of the TG and DTG curves. *Adapted from:* [9]

Differential Scanning Calorimetry (DSC)

Differential Scanning Calorimetry works similarly to the previous technique. However, in this case, the measured variable corresponds to the energy exchanges that occur when the sample undergoes a temperature change [66]. The results obtained can also be represented in a graph, where the y-axis is the heat flow, usually in mW, and the x-axis is the temperature or time.

This way, by applying this technique simultaneously with TGA, it is possible to identify which energy variations correspond to mass changes and which ones correspond only to a phase change [66].

Figure 2.6 represents a typical DSC curve. In it, it is possible to distinguish two types of transitions [66]:

- 1^{st} order: correspond to enthalpy changes, which can be endothermic or exothermic, and appear in the form of peaks. Depending on the program used, positive peaks may correspond to endothermic and negative peaks to exothermic variations or vice versa;
- 2^{nd} order: these correspond to variations in heat capacity without enthalpy changes and appear as shifts from the baseline.

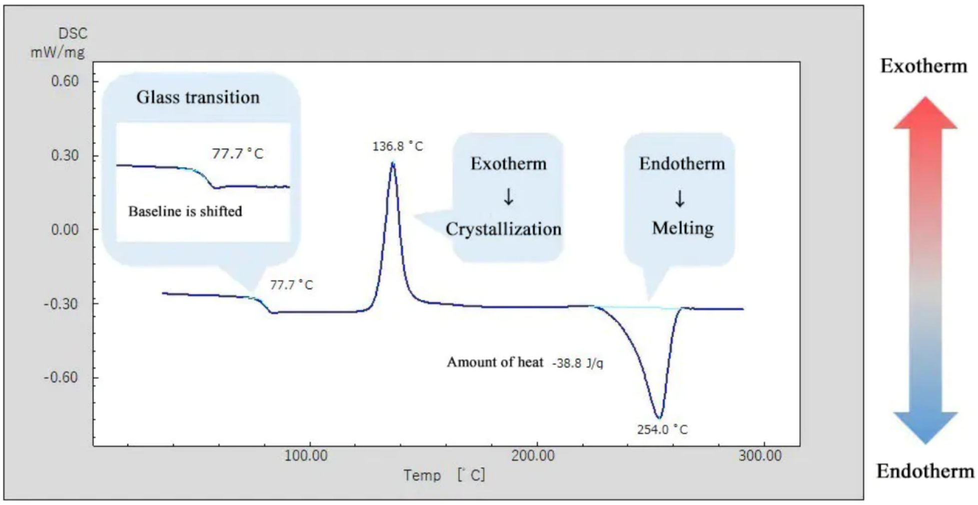

Figure 2.6: Example of the representation of the DSC curve. *Source:* [10]

2.5.2 Thermal analysis of the digestate

Different studies have been performed on the thermal degradation of digestate from different sources. The main observations of some of those studies can be found in Table 2.7.

Various authors conducted experiments under an atmosphere of N_2, most of which concluded that the thermal decomposition of digestate included three main stages [49][67]. Liu et al. (2020), who performed their experiments on food waste digestate, stated that the first stage is associated with the loss of moisture and some lighter volatiles, being a small step as the samples had already been dried [49]. In the second stage, there was a major weight loss due to devolatilization [49]. That step appeared with three peaks in the DTG curve associated with the degradation of different components: 1^{st}) hemicellulose and extractives (proteins, starches, lipids, and sugars); 2^{nd}) cellulose; 3^{rd}) lignin [49]. The third stage was a slight weight loss linked with the degradation of carbonaceous materials retained in the waste [49]. It was also noted a small peak in the range of 630-680°C due to the decomposition of calcium carbonate resulting from the decomposition of calcium-containing organic compounds present in the waste [49].

Li et al. (2017) had similar conclusions by performing analysis on dried digestates from different sources [67]. They stated that the first stage, associated with moisture, appeared between 50-180°C, with weight losses between 7-17% [67]. The second stage corresponded to the highest mass losses (28-64%), between 180-550°C, resulting from the decomposition of proteins, hemicellulose, and cellulose [67]. The last stage, between 550-900°C, with minor weight losses (3-12%), was attributed to the decomposition of calcium carbonate, lignin, and other heavy compounds [67].

Opatokun et al. (2016) also verified three main stages in the DTG, attributed to the same components as the other studies [30]. The first peak was observed at around 66°C, the second one at 273°C, and the last one at 400°C [30]. After 540°C, the mass stabilized. The authors performed the pyrolysis of the digestate at around 500°C and analyzed the pyrochar obtained [30]. It showed only two degradation peaks, one at 66°C and a small one at 550°C, which stabilized at around 657°C [30]. The pyrochar is much more thermally stable than the digestate as it presented a total weight loss of only 9% compared to 59% [30].

Petrovic et al. (2020) also verified the same stages of degradation: 1st) until 150°C, with a weight loss of only 3% as the sample had been dried; 2nd) between 200-550°C, with a major weight loss of 39%; 3rd) between 550-800°C, losing 13% [68].

Opatokun et al. (2015) compared the thermal decomposition of food waste and its digestate [26]. The experiments were carried out using N_2 and revealed that the waste decomposes in three stages but the digestate only in two [26]. The first peak observed in the DTG curve of both samples appeared between 80 and 120°C and was attributed to the loss of moisture [26]. It was a small peak as the samples had been previously dried [26]. The second peak observed for the waste was associated with the loss of water strongly bounded and the decomposition of weaker hydroxyl bonds [26]. It did not appear on the digestate curve as those bonds were already broken during the anaerobic digestion [26]. The third peak corresponded to the most significant mass loss due to primary decomposition reactions and the release of volatiles [26]. For the waste, it appeared between 250 and 400°C, with a maximum weight loss of 0.6%/°C and left a solid residue of 25% [26]. For the digestate, it was between 200 and 500°C, with a maximum weight loss of 0.3%/°C and a residue of 35% [26].

Swiechowski et al. (2020) verified a total weight loss of 63% when heating a sample to 850°C in an N_2 atmosphere [53]. The decomposition started at around 265°C, with the principal weight loss between 350 and 550°C [53]. The authors also performed a DSC analysis which showed two transformations [53]. The first one appeared between 36-168°C and was endothermic. The second one, between 285-351°C, was exothermic [53]. The energy required for the endothermic reaction was 115J/g, and the energy released from the exothermic reaction was 39.84J/g [53]. It was not possible to link the DSC results with the DTG since the temperatures did not coincide, which was attributed to imprecisions in the equipment [53].

Different authors concluded that a higher heating rate slows down the pyrolysis reactions, reflected in curves shifted to higher temperatures [26][49][68]. Petrovic et al. also claimed that a higher heating rate resulted in a decrease in weight loss [68].

Regarding thermal analysis under an oxidative atmosphere, some studies were also performed with air to evaluate the thermal behavior of digestate during combustion [8][47]. Monlau et al. (2016) found similar behavior to the one observed under an inert atmosphere [8]. The authors stated a stage until 105°C related to dehydration, a peak around 277°C due to hemicellulose and cellulose decomposition, and a final peak at 429°C associated with lignin [8]. The principal weight loss occurred between 200-400°C (65%), and at 600°C, the digestate had already lost 90% of its initial mass [8]. The pyrochars produced from that digestate were also analyzed and did not revealed the peak associated with hemicellulose as it is completely degraded during pyrolysis [8].

Szwaja et al. (2019) also studied the combustion of agricultural digestate through STA. Three stages of weight loss were observed [47]. The combustion of the material occurred between 200-560°C, and the solid residue had 15% of the initial mass [47].

Gómez et al. (2004) performed thermal analysis of samples from different sources and at different stages of Anaerobic Digestion, aiming to use this technique to monitor the AD process by evaluating the stability of the digestate [69]. The sample entering the digestor presented two stages at the DTG curve [69]. The first one had a peak at 300°C, and the second one, which was between 450-500°C, had two peaks [69]. As the digestion progressed and the stability of the samples increased, in the first stage there was a decrease in the peak intensity, and in the second stage both peaks were shifted to higher temperatures and the intensity of the first one decreased [69]. At the end of the digestion, the sample only presented one peak in each stage [69]. The authors also concluded that, as the stability increased, there was also an increase in the solid residue remaining after 600°C [69].

Zhang et al. (2018) studied the thermal behavior under combustion of corn stalk digestate and the chars produced from its torrefaction at different temperatures [38]. It was observed that the torrefaction increased the ignition temperature of the material and the temperature at which the weight loss was maximum [38]. Those effects mean that the combustion occurs at higher temperatures which increases its efficiency [38].

Table 2.7: Summary of the main parameters and conclusions of some of the thermal studies performed by other authors on digestate.

Ref	**Raw Material of AD**	**Sample mass (mg)**	**Heating rate (°C/min)**	**Atmosphere, flow (mL/min)**	**Temperature profile (°C)**	**Degradation stages**	**Residue (%)**	**DTG maximum peak (°C)**
[26]	Food waste	35	10 and 60	N_2, 20	RT-1000	2	35	300
[30]	Food waste	30	5	N_2, 20	RT-1000	3	30	300
[67]	Sewage Sludge	20	5, 20, 50 and 100	N_2, 100	50-900	3	51	270
[67]	Food waste	20	5, 20, 50 and 100	N_2, 100	50-900	3	34	459
[67]	Vinasse	20	5, 20, 50 and 100	N_2, 100	50-900	3	34	302
[67]	Cow manure	20	5, 20, 50 and 100	N_2, 100	50-900	3	47	316
[49]	Food waste	5	10	N_2, 100	30-800	3	40	300
[68]	Sewage sludge and Cattail	25	15	N_2, 100	25-800	3	45	303
[53]	BMSW and agricultural waste	6	10	N_2, 50	50-850	3	37	475
[8]	Food and agricultural waste	20	10	Air, 20	RT-980	3	10	-
[69]	OFMSW	-	25	Air, 100	RT-600	3	40	500
[38]	Corn stalk	6	10	N_2, 20	30-800	-	40	325
[38]	Corn stalk	6	10	Air, 20	30-800	2	22	292
[47]	Agricultural waste	-	10	Air, 40	RT-900	3	15	-
[47]	Agricultural waste	-	10	Argon, 40	RT-900	3	40	330

BMSW - Biodegradable Municipal Solid Waste; OFMSW - Organic Fraction of Municipal Solid Waste; RT - Room Temperature.

Chapter 3

Methodology

This chapter will describe the methods used throughout this work to study the valorization of digestate. It is divided into two main parts: i) the study of its potential for agricultural applications (through the analyses performed by the Portuguese ALS Life Sciences lab); ii) the study of its thermochemical valorization (via STA in the IST lab). In both cases, samples were collected from the same plant, responsible for the treatment and recovery of MSW in Portugal.

3.1 Biogas Plant

Efacec is a Portuguese company focused on developing products and systems with high added-value, acting in different important sectors of economic activity. With almost 70 years of brand, and international presence in more than 65 countries, it is currently focused on anticipating Energy, Environment and Transport solutions that improve everyone's day to day life, while contributing to a sustainable world in the new energy era.

In the environment area, Efacec helped implement the MBT plant from which the samples were taken, capable of treating around 43 000 tons of undifferentiated urban waste per year.

This plant has a first reception area, where operators manually remove the bulkier waste destined for landfill. Then, the waste undergoes a dry mechanical pre-treatment where it passes through a sieve with a perforation of 80 mm. This results in two distinct fractions: the coarse fraction, greater than 80 mm, which is rejected, and the fine fraction, with less than 80 mm, which is destined for the production of an organic suspension. The latter passes through a magnetic separator before proceeding to the subsequent treatment.

The next stage corresponds to a hydro-mechanical pre-treatment. This begins with an equipment called pulper that has the following objectives: i) disintegrate the biodegradable waste to optimize digestion; ii) remove heavy non-biodegradable contaminants (stones, bones, glass, etc.); iii) remove light non-biodegradable contaminants (textiles, wood, plastic, etc.). To do this, while the waste is being fed to the pulper, an agitator operates at a low speed that minimizes the disintegration of the non-biodegradable waste and allows the sedimentation of contaminants and their subsequent removal. After the feeding is complete, the agitator speed increases to turn the biodegradable waste into a suspension. After pulping, this suspension, which has an average total solids content of 10%, passes through a sieve where particles larger than 10 mm are retained. Then it goes to a grit removal system, after which it has a total solids content of 7%. Finally, it passes through a thickener, where its volume is reduced, and the solids concentration is increased to ensure the necessary characteristics for digestion.

The suspension fed to the digesters generally has a total solids content of 8% and a volatile solids content of 64%. The digestion process is wet and mesophilic, with temperatures around 35℃. 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 225m^3 of digestate is removed and sent to the next stage of dehydration.

After digestion, a flocculation agent is added to the digestate, which then 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 a content between 30 and 35%. The former goes to a water treatment zone and the latter to the pre-composting zone.

Before composting, a structuring material is added to the digestate. Then, it is sent to an aeration system and a sanitization process, which takes place at temperatures between 60 and 80℃ for at least seven days. After composting, the material is laid out in piles that are aerated for eight weeks. In total, the entire composting process, including pre and post-treatments, takes about 12 weeks. After that, quality control is performed where the compost must have less than 40% of moisture and a level of maturity V in the Rottegrad test.

An overview of the described process can be seen in Figure 3.1.

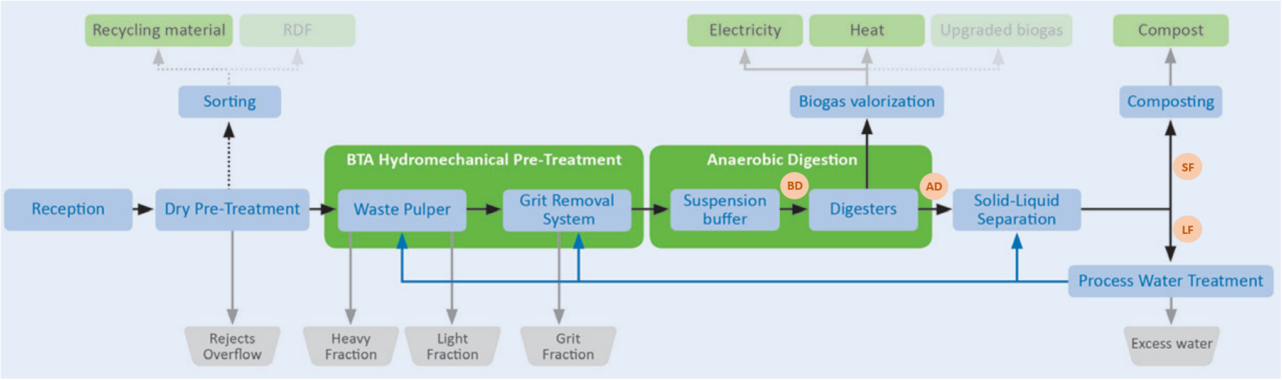

Figure 3.1: Overview of the mechanical and biological treatment performed to the MSW in the Portuguese plant studied in this work.

3.2 Samples

The samples analyzed throughout this work were taken from different phases of the process, represented as orange circles in Figure 3.1, according to the following nomenclature:

- BD - Before Digestion
- AD - After Digestion

- SF - Solid Fraction
- LF - Liquid fraction

At the entrance of the digester (Figure 3.2(a)), the material was mostly water with some visible pieces and a strong odor. After the digestion (Figure 3.2(b)), the digestate was a dark viscous liquid.

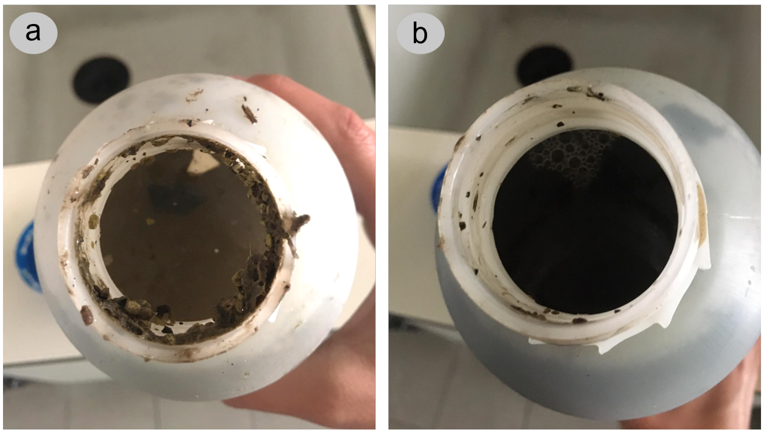

Figure 3.2: Samples taken: a) before the digestion; b) after the digestion.

After the solid-liquid separation, the liquid fraction was an aqueous, yellowish liquid (Figure 3.3(a)), and the solid fraction was a solid, wet, dark material (Figure 3.3(b)).

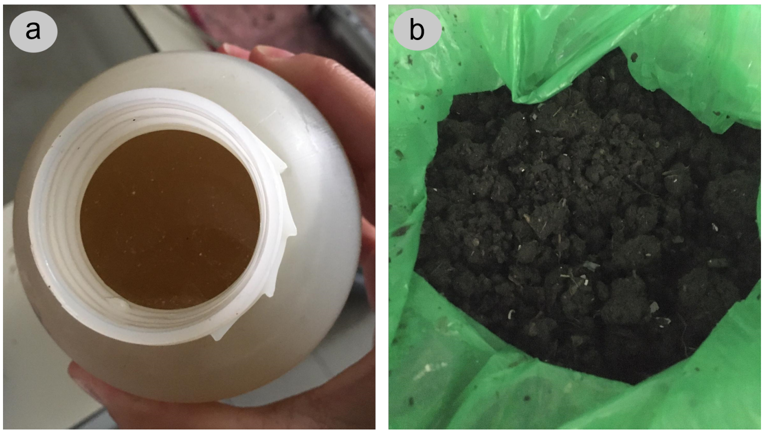

Figure 3.3: Samples taken after the solid-liquid separation: a) liquid fraction; b) solid fraction.

3.3 Analysis of the adequacy as Soil Fertilizer

To assess the agricultural properties of digestate, a set of different analyses were requested to the Portuguese laboratory ALS Life Sciences, based on the requirements of the legislation discussed in Chapter 2. The analyses were performed for all four samples to compare the properties of each.

The requested parameters, as well as the sampling and analysis methods that the laboratory should follow according to the legislation, are shown in Table 3.1. All the analyses were performed in duplicate and the medium value was considered.

Table 3.1: Analyses requested to the ALS Life Sciences lab to assess digestate agricultural potential.

Parameter	**Unit**	**Method**
Moisture	%	EN 13040
Density	kg/m^3	-
pH	-	EN 13037
Amoniacal nitrogen	% DM	EN 13652
Kjeldahl nitrogen	% DM	EN 13652
Nitrate/Nitrite	% DM	EN 13652
Total nitrogen	% DM	EN 13654
Granulometry	% FM	Fraction $>$10mm: weighing of 1kg of the original sample, sieving using a 10mm sieve, and weighing the materials separated by sieving. Fraction $<$25 mm: weighing 1kg of the original sample, sieving using a 25mm square mesh sieve, and weighing the materials separated by sieving.
Organic matter	% DM	Drying in an oven at 103$\pm$2°C, followed by ignition at 450$\pm$25°C. Weighing of the mass lost during ignition with an analytical balance with a scale interval of 0.001g.
K_2O	% DM	EN 13650
Cd, Pb, Cu, Cr, Ni, Zn, Hg	mg/kg of DM	EN 13650
P_2O_5	mg/kg of DM	EN 13650
Salmonella spp	-	ISO 6579
Escherichia coli	n° of viable cells/g of FM	ISO 16649-2; ISO/TS 16649-3; ISO 9308-2
Degree of maturity	I to V	Methodology proposed in ”Gutesicherung Kompost RAL -GZ 251 (2006)”. Methodology proposed in ”Methods book for the analysis of compost (1994) Federal Compost Quality Assurance Organization, pp16-19”.
Anthropogenic material and stones	% DM	Methodology proposed in ”Methods book for the analysis of compost (1994) Federal Compost Quality Assurance Organisation, pp. 41-43”. Indication of stones $>$5mm and glasses, metals, and plastics $>$2mm.
Fitotoxicity	% of germination	EN 16086-1; EN 16086-2; ISO 11269-2; ISO 17126; Methodology proposed in ”Zucconi, F. Pera, A., Forte M., and de Bertoldi, M. (1981). Evaluating toxicity of inmature compost. BioCycle, 22, 54-57”.
Weed seeds and propagules	n°/L of sample	CEN/TC BT TF 151; ONORM S2023 in ”Analytic methods and quality control of compost (Austrian Standards Institute, 1996)”.
Phosphonates	wt %	-
Hexavalent chromium (Cr VI)	-	-
Inorganic arsenic	-	-
Biuret ($C_2H_5N_3O$)	-	-
Organic carbon	-	-
PAH_{16}	-	Sum of naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene and benzo[ghi]perylene.
Oxygen uptake rate	mmol O_2/kg organic matter/h	-
Self heating factor	l biogas/g volatile solids	Indication of the gas released during 28 days. Perform three trials and use the average result.

Due to the samples' characteristics, the laboratory could not perform some of the analysis, namely:

- PAH_{16}: the sample at the exit of the digestate presented higher values of total solids and active organic matter, which made the analysis unfeasible;
- Cr VI: the sample at the exit of the digester was not homogeneous, which made the filtration necessary for the analysis impossible to perform.

Efacec already had some analyses performed on these samples, which were also used to compare some of the parameters.

3.4 Simultaneous Thermal Analysis

3.4.1 Materials

The material used in the STA was the solid fraction resulting from the dehydration of the digestate in the presses. It was collected from the plant and then stored in a laboratory fridge at Instituto Superior Técnico for several days. For the experiments, samples with weights between 57 and 122mg were used without any pre-treatment.

The thermal analyses were performed in the simultaneous thermal analyzer (STA 6000, PerkinElmer) shown in Figure 3.4. The samples were placed inside the equipment in an alumina crucible, whose melting point is 2 000°C, significantly above the experimental temperatures, which prevents its melting. Besides that, this material is highly inert, which ensures that it does not react with the samples.

Before each experiment, the samples were placed in the crucible and weighed on an analytical balance with an error of ± 0.1mg. Even though the equipment had its own balance, this was done to ensure that the measurements provided by the device were correct. The analysis equipment is extremely sensitive, so any external interference by the operator could interfere with the results. In addition, there are three main effects inherent to the experiment that can also affect the measurements: 1) viscosity effect - the increase of gas viscosity with temperature leads to small variations in the apparent weight of the sample; 2) impulsion effect - the decrease of gas density with temperature leads to an increase in the apparent weight of the sample; 3) effect of thermal transpiration - due to the temperature difference between the samples and the program, convection currents are generated, affecting the weight of the sample. All these effects are negligible in experiments where there is a significant weight loss, and therefore do not need to be corrected.

During the experiment, the data obtained was recorded in a computer program connected to the equipment. In the end, a refrigeration system ensured that the analyzer returned to its initial temperature.

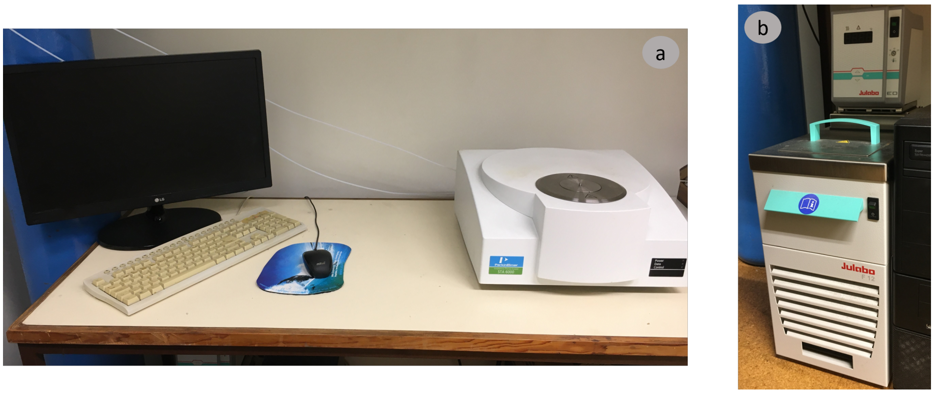

Figure 3.4: Equipment used in the thermal analysis: a) Simultaneous Thermal Analyzer; b) Refrigeration system.

Figure 3.5: Crucible used and furnace where it was placed.

3.4.2 Experimental Procedure

The first two experiments, 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.

The first two tests were performed at dynamic conditions, presenting 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. The first experiment was performed using air to evaluate the sample's behavior under combustion, and the second with nitrogen to assess the behavior under pyrolysis. For both, a gas flow rate of 20ml/min was used. After the pyrolysis test, the remaining solid was subjected to a combustion trial with the same temperature profile.

The pyrolysis experiment followed by combustion allowed the determination of the proximate analysis of the mixture, i.e., the determination of its moisture, volatile matter, fixed carbon, and ash content. Under pyrolysis conditions, the moisture content is calculated from the initial mass loss generally observed up to 110°C and associated with an endothermic peak. The rest of the mass loss observed in pyrolysis corresponds to the release of volatile matter. What remains after this experiment consists of fixed carbon and ash. The combustion test is performed to determine the content of each. The mass loss verified in this test corresponds to the fixed carbon, the combustible fraction of the material. In turn, the residue that remains at the end corresponds to the ash, the inorganic fraction of the sample.

The subsequent tests were performed in isothermal conditions under a nitrogen atmosphere with a 20mL/min flow rate. These aimed 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 described tests are summarized in Table 3.2, along with the nomenclature used for each one throughout Chapter 4.

Table 3.2: Experiments performed in the STA and nomenclature used to refer to them.

E1	Combustion
E2.1/E2.2	Pyrolysis followed by combustion
E3.1/E3.2	Torrefaction at 200°C followed by combustion
E4.1/E4.2	Torrefaction at 250°C followed by combustion
E5.1/E5.2	Torrefaction at 300°C followed by combustion
E6.1/E6.2	Torrefaction at 350°C followed by combustion

3.4.3 Data processing

The data obtained from the program was analyzed on an Excel sheet.

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.

3.5 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). These parameters are extremely useful when designing, for example, a pyrolysis reactor and in the modeling of the reactor for optimization of the operating conditions. Besides that, if well adjusted, the models allow a more comprehensive analysis of the results obtained in the STA and can also be used as a predictive tool.

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, $w_{\text{i,t}}$.

$$w_{\text{t}} = \sum_{i=1}^{n} w_{\text{i,t}} \tag{3.1}$$

This type of model allowed the estimation of the initial fraction of each major component in the sample. This way, a better understanding of the composition of the digestate was possible, serving as a complement of the thermal analysis.

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, $w_{\text{exp,t=0}}$, and assuming the fractions of each component, x_{i}, the first estimate of each component's initial mass was made using Equation 3.2.

$$w_{\text{i,t=0}} = w_{\text{exp,t=0}} \times x_{\text{i}} \tag{3.2}$$

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:

$$\frac{dw_{\text{i,t}}}{dt} = -k_{\text{i}}(T) \times w_{\text{i,t}} \tag{3.3}$$

The kinetic constant of each component, k_{i}, depends on the temperature and can be obtained through the Arrhenius equation:

$$k_{\text{i}}(T) = k_{\text{i}}(T_{\text{ref}}) \times exp\left(-\frac{Ea_{\text{i}}}{R} \times \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}}\right)\right) \tag{3.4}$$

where Ea_{i} corresponds to the activation energy of each component, R to the universal gas constant (8.314J·mol^{-1}·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:

$$R = (w_{\text{exp,t}} - w_{\text{t}})^2 \tag{3.5}$$

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:

$$\frac{\sqrt{\frac{R}{N}}}{\overline{w}_{\text{exp}}} \tag{3.6}$$

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

Chapter 4

Results and Discussion

4.1 Analysis of the adequacy as Soil Fertilizer

A first overview of the legislation applicable to the use of digestate in soils, described in detail in Chapter 2.3, provides the operational requirements of the biogas plants. Since the Portuguese plant under study performs mesophilic digestion, both the national and European regulations require pasteurization or composting of the digestate. The composting process applied to the solid fraction of digestate in the plant under study is performed between 60-80°C for at least seven days. Thus, the compost obtained meets this specific requirement.

The present study intended to analyze the properties of the digestate at the exit of the digester and after the solid-liquid separation, both without any pasteurization or composting. This way, although they did not meet the legislation in this particular aspect, the study aimed to find out if they were in agreement with the remaining quality parameters, which could open the discussion regarding a restructuration in the current legislation.

The results of the analyses performed to the residues at the entrance of the digester are presented in Appendix A for consultation, as they were not relevant for the study of digestate's valorization.

At the same time that the results from the laboratory were received, Efacec was told that the biogas plant was presenting much lower biogas production values than usual. Thus, the first step in the interpretation of results was to compare the values of the digestate at the exit of the digester with typical values found in the literature and with analyses performed previously. The parameters whose values diverge from the expected are shown in Table 4.1.

The comparison showed that both the percentage of volatile solids, phosphate, and the different heavy metals in the digestate were inferior to the expected.

The volatile solids content is extremely relevant in biogas production since the higher its value in the waste at the entrance of the digester, the higher the biogas production.

Regarding the phosphorus content in the residues, it can be inhibitory but only when in excess. Since the phosphorus compounds are not involved in the digestion's reactions, the values observed in the digestate are usually similar to those in the residue before digestion. Strangely, this was not verified

Table 4.1: Parameters whose results diverge from the expected for the digestate samples after digestion. The 'Literature' column corresponds to the typical values found in literature, and the 'Previous' column corresponds to the values obtained in previous analyses performed in different samples exiting digester.

	Results	**Literature**	**Previous**
VS (%)	2.40	3.5-7.0	-
P_2O_5 (% DM)	0.25	1.00-3.00	1.44
Cu (mg Cu/kg DM)	3.50	50-450	300
Zn (mg Zn/kg DM)	14.11	200-450	440
Pb (mg Pb/kg DM)	2.12	70-150	76
Cd (mg Cd/kg DM)	0.02	0.5-1.5	0.74
Ni (mg Ni/kg DM)	0.94	10-80	34
Cr (mg Cr/kg DM)	0.48	10-100	67

for the samples under study. Before digestion, the samples presented an average phosphate content of 595 mg/L, while after digestion the value was only 136 mg/L.

The heavy metals content in the substrate can also affect digestion. Majeed et al. (2019) reported that low concentrations of Cu, Fe, Ni, Cd, and Zn promote biogas production, while high concentrations inhibit the process [70]. The verified contents of heavy metals in the samples before digestion are lower than the beneficial concentrations reported by the authors, which might be related to the lower biogas production [70].

This way, as all these parameters are important to classify digestate as a fertilizer, the interpretation of the results in the light of the legislation was made taking into consideration that the observed values could be different from those under normal conditions.

All the results received are presented in Appendix A, in the units provided by the laboratory.

4.1.1 European commercialization

As explained in Chapter 2.3, when the digestate is intended for European commercialization as a fertilizer, it should meet the requirements of CMC5. Besides operational specifications, the digestate should meet the maximum limits presented in Table 4.2. Unfortunately, the analyses of most of those parameters were not performed due to the samples' characteristics.

Table 4.2: 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.

	Maximum allowed	**AD**	**SF**	**LF**
PAH_{16} (mg/kg DM)	6	-	3.18	0.23
Each macro impurity $>$2mm (g/kg DM)	3	-	-	-
Sum of all macro impurity $>$2mm (g/kg DM)	5	-	3.75	-
Oxygen Uptake Rate (mmolO_2/kg OM/h)	25	-	-	-

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 CM5 requirements, the digestate should also meet the specifications of the PFC for which it is intended. The values demanded for each PFC are shown in Table 4.3, together with the results from the laboratory.

Table 4.3: 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.

	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	$\leq1\,500$	14.11	2 402	5.43
Salmonella (/25g FM)	0		0	0	0	-	-	-
Escherichia (UFC/g FM)	≤1000		$\leq1\,000$	$\leq1\,000$	$\leq1\,000$	22	48 108	30
Phosphonate (wt %)	≤0.5		≤0.5	≤0.5	≤0.5	-	-	-
Dry matter (wt %)	-		≥20	-	-	5.25	26.65	0.82

The samples collected right after digestion can not be classified as PFC1 (organic fertilizer) as they do not meet the minimum nutrients and organic matter content. Also, they can not be used as PFC3 (organic soil improver) as they do not present the minimum organic matter and dry matter content required for this category. All of this could be resolved through a drying process, which would increase these concentrations.

In terms of heavy metals, the samples after digestion presented much lower contents than the maximum allowed for all PFCs. However, as mentioned before, these are not the typical values verified for the digestate in this plant. Despite that, previous analyses, which revealed much higher heavy metal contents, also agreed with the limits for all PFCs. The only exception was the copper limit for PFC4.

Unfortunately, the content in Cr VI, biuret, and phosphonates were not tested, which did not allow a complete investigation.

Finally, regarding pathogens, the samples after digestion met the limit for Escherichia coli. However, previous analyses revealed values superior to the limit allowed. Thus, further tests would be necessary for a precise conclusion. Concerning Salmonella, it is absent in 1L, which corresponds to approximately 1 020g of sample. However, this result does not guarantee that it is absent in 25g of sample, as the legislation requires.

In conclusion, the raw digestate has the potential to be classified as PFC4 (growing medium) or PFC6 (non-microbial plant biostimulant). If it is dried, it could also meet the requirements of the other PFCs. However, further studies should be conducted with a higher number of samples and at different periods since the raw material is often changing.

The results for the liquid fraction led to similar conclusions to those of the raw digestate. However, in this case, the dry matter content and the concentrations of nutrients and organic matter are too low to consider drying. Thus, the liquid fraction only has the potential to be classified as PFC4 or PFC6.

On the contrary, the solid fraction revealed a sufficient concentration of nitrogen and dry matter. However, it does not satisfy the minimum content of the remaining nutrients and the maximum limit for most heavy metals. Besides that, it revealed a much higher content in pathogens than the allowed. This way, the solid fraction could never be commercialized as a European fertilizer without further treatment such as composting or pyrolysis.

4.1.2 National commercialization

On a national level, the digestate might be classified as an organic fertilizer (group 2) or organic corrective (group 5).

Group 2 requires at least 85% of the sample to pass through a sieve with a mesh opening of 10mm, which was not tested. Besides that, it establishes minimum contents in nutrients and organic matter according to different fertilizer classifications. Those values, together with the results obtained from the laboratory, are presented in Table 4.4.

Table 4.4: 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.

	Minimum allowed				**Results**		
	N-fertilizer	**NPK-fertilizer**	**NP-fertilizer**	**NK-fertilizer**	**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

From the results, it is possible to conclude that both the raw digestate after digestion and the liquid fraction do not meet the minimum contents in macronutrients to be classified as organic fertilizers. Once again, this could be achieved through a drying process. However, since the concentrations are extremely low, a large amount of water would need to be removed, requiring intensive heat consumption.

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.

The classification as group 5 presents considerably more requirements than group 2. First, 99% of the material should pass through a 25 mm square mesh sieve, which was not analyzed. Then, it should meet the specifications of Table 4.5.

Table 4.5: Requirements to be classified as an organic corrective 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.

	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	-

For the samples after digestion, it was not possible to analyze the fitotoxicity, organic matter content, Salmonella, weed seeds and propagules, and physical impurities. The pH was also not analyzed, but previous analyses revealed an average value of 7.4, in accordance with the requirements. As with the European legislation, it does not meet the maximum moisture value allowed. In terms of pathogens, it meets the requirements for Escherichia coli.

Lastly, regarding the heavy metals content, the results obey all the maximum limits. However, they do not represent the typical values. Previous analyses revealed that the raw digestate: I) meets the limits of all categories for Pb, Cr, and Ni; II) is in the limit of class I for Cd and Hg, agreeing with all the other limits; III) does not meet the requirements of classes I and II for Cu; IV) does not meet the requirements of class I for Zn.

In conclusion, 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.

The solid fraction meets the requirements for fitotoxicity, physical impurities, and pH. However, it does not obey the maximum moisture content and limits of pathogens. Besides that, the results for Cu and Zn are superior to the maximum allowed for all categories, and for most of the other heavy metals, it only meets the requirements of classes IIA and III. Thus, the solid fraction does not seem promising for national commercialization as a fertilizer.

The liquid fraction meets the limits for pH, Escherichia coli, and heavy metals, except class I for Hg. However, it is far from the maximum limit of dry matter.

4.2 Simultaneous Thermal Analysis

This section presents and discusses the results obtained from the different tests performed on the simultaneous thermal analyzer.

The values of the TG curve correspond to the quotient between the mass at a certain moment and the initial mass in the form of %.

For the dynamic trials, both the mass variations and the heat exchanges were represented as a function of temperature since there is a direct correlation between temperature and time. For the torrefaction trials, in turn, these variations were plotted as a function of time since those are isothermal processes. The curves as a function of temperature for these tests can be seen in Appendix B.

All the curves do not show the results of the last step of the trial (cooling down to room temperature), as it is not relevant for the study.

4.2.1 Blank trials

The expected results for the blank trials were a horizontal straight line on the DSC curve since no heat exchanges were occurring. Under perfect conditions, this line should present a zero ordinate. However, it was known that the device used in this study presented a deviated endothermic baseline, which interfered with the results.

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 did not present a horizontal straight line, showing, instead, an increasing endothermic behavior from 500ºC. Thus, the results obtained from each trial would be much more exothermic when corrected.

This behavior was repeated for the three blank trials performed, showing a quite similar pattern (Appendix B), 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.

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.

4.2.2 Combustion (E1)

By observing the TG/DTG curves represented in Figure 4.1, 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 since the sample was not previously dried. It could also be related to the release of some lighter volatiles. The maximum weight loss rate occurs during this stage, at around 116°C. The DSC curve, represented in Figure 4.2, shows that this interval is associated with the only endothermic peak of the process, with a consumption of approximately 1 026kJ/kg of fresh sample, corresponding to the energy required for drying.

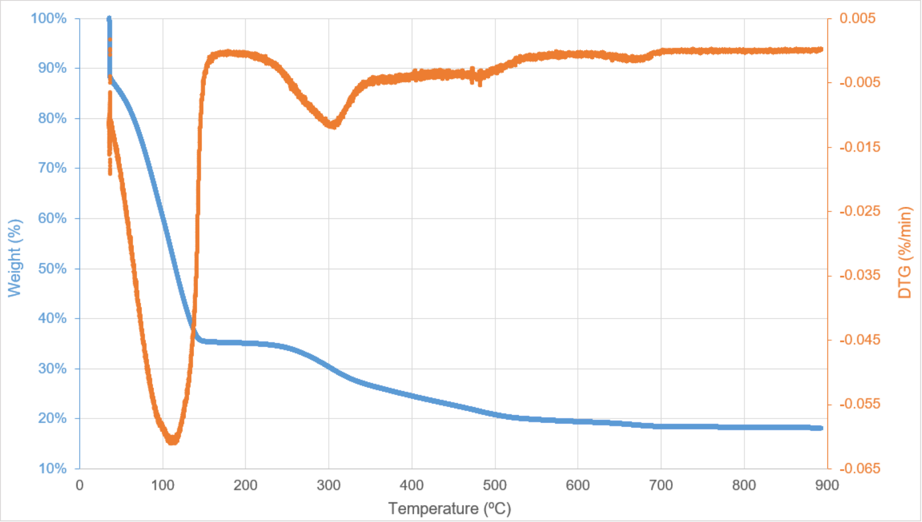

Figure 4.1: Experimental TG and DTG curves for the first combustion trial (E1).

Excluding the drying, the second stage has the highest weight loss rate, showing a DTG peak at around 309°C. This step occurs between 224-345°C, presenting a weight loss of about 5%. It corresponds to cellulose and hemicellulose degradation, coinciding with the findings of Monlau et al. (2016), who reported a peak at around 277°C for these components [8].

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 an associated weight loss of around 7% and a slight peak in the DTG curve at 484°C. Monlau et al. (2916) reported peaks for different samples of digestate at these same temperatures, corresponding to the lignin degradation [8].

At around 672°C, a small peak can be observed in the DTG curve, corresponding to a weight loss of 2%. According to Liu et al. (2020), who reported a small peak between 630-680°C, it might be related to the decomposition of calcium carbonate formed during the decomposition of calcium-containing organic compounds [49].

From 680°C, there is no longer a significant mass decrease, obtaining a solid residue of 18%, which should correspond to the ash content, similar to the values found in the literature. The thermal degradation steps that occur after drying can be seen in more detail in Figure B.4 of Appendix B.

The DSC curve shows that the most significant heat release due to the combustion occurs between 168-540°C, similar to the values found in the literature, with two major peaks around 325 and 474°C [47]. This corresponds to a total heat release of 1 346kJ/kg of fresh sample, superior to the heat required for drying and thus resulting in a positive energy balance of 320kJ/kg, making it potentially favorable for its use as a solid fuel.

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

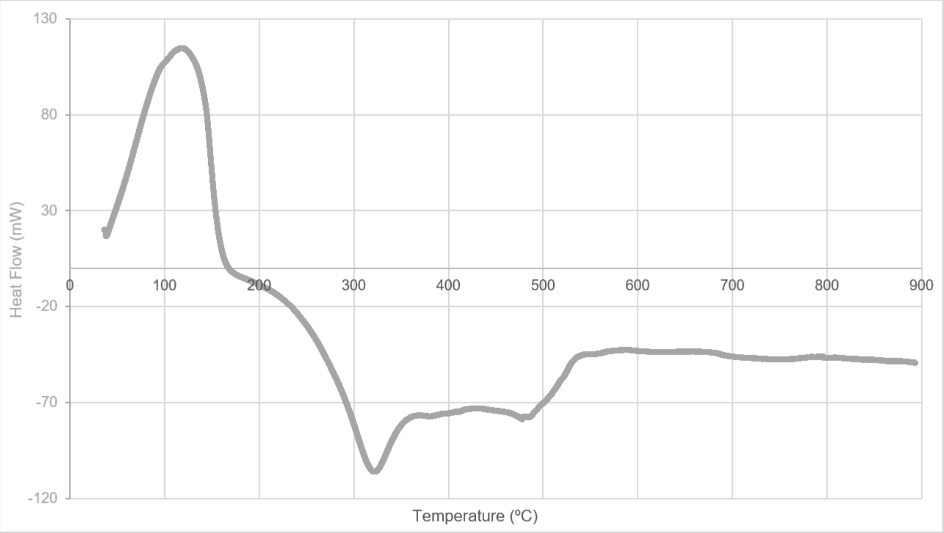

Figure 4.2: Experimental DSC curve for the first combustion trial (E1).

4.2.3 Pyrolysis (E2)

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.

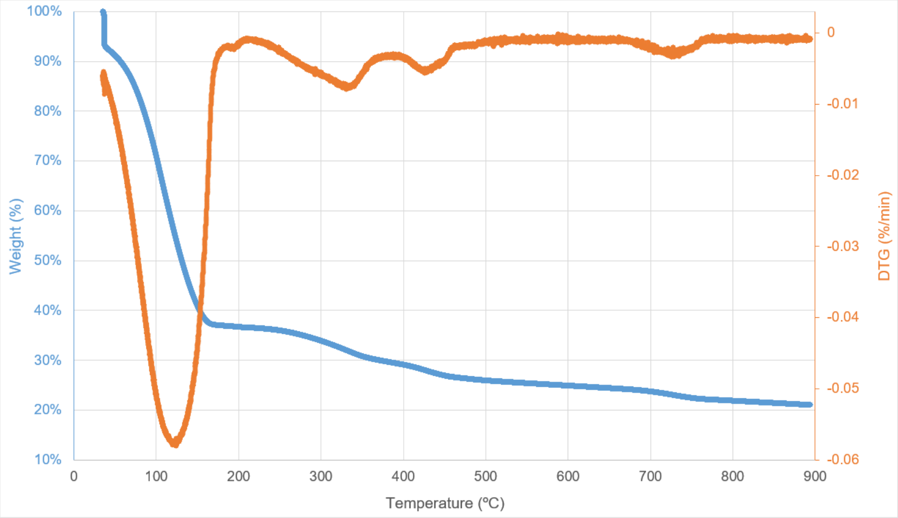

Figure 4.3: Experimental TG and DTG curves for the pyrolysis trial (E2.1).

The first step, as in combustion, corresponds to the loss of moisture which in this trial was about 66%, very similar to the value obtained in the first test. The drying process started at the beginning of the experience and ended at around 204°C. The maximum weight loss rate was observed in this interval, at around 124°C. The drying stage was also visible in the DSC curve as an endothermic peak with a consumption of 1 097kJ/kg, once again concordant with the value obtained in the first trial.

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. All these values are in agreement with the literature. Zaman et al. (2017) reported the following intervals for the decomposition of these components during pyrolysis: 200-280°C for hemicellulose, 240-350°C for cellulose, and 280-500°C for lignin [71].

All the described steps that occurred after drying can be seen in more detail in Figure B.5 of Appendix B.

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

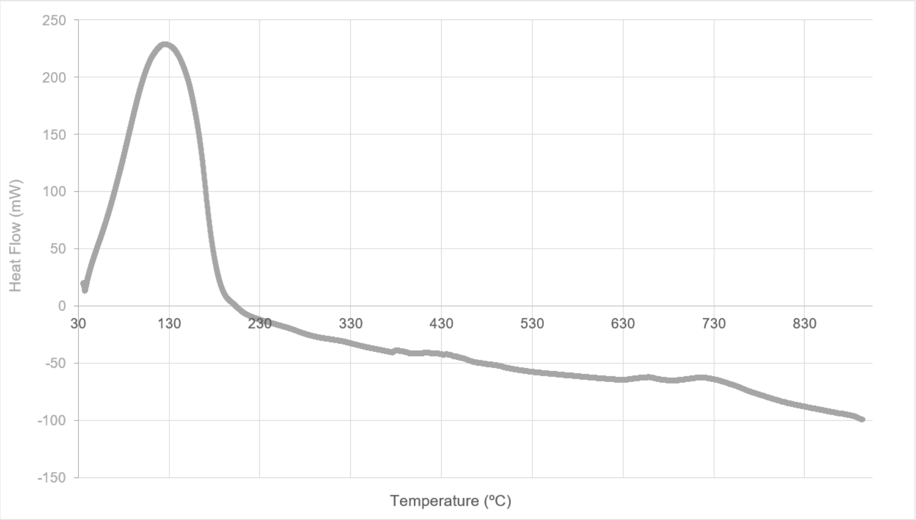

Figure 4.4: Experimental DSC curve for the pyrolysis trial (E2.1).

The behavior observed in the DSC curve (Figure 4.4) is quite different from the first experiment since, as explained before, pyrolysis is generally not a self-sustained process. This way, 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.

The solid residue from pyrolysis was burned in an oxidative atmosphere, and the results can be seen in Figures 4.5 and 4.6. The main objectives of this trial were to conclude the proximate analysis of the digestate and assess if its burning could also be interesting from an energetic point of view.

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.

During the combustion, the pyrolysis residue released about 992kJ/kg, corresponding to only 186kJ/kg of fresh digestate sample, an insignificant result. 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.

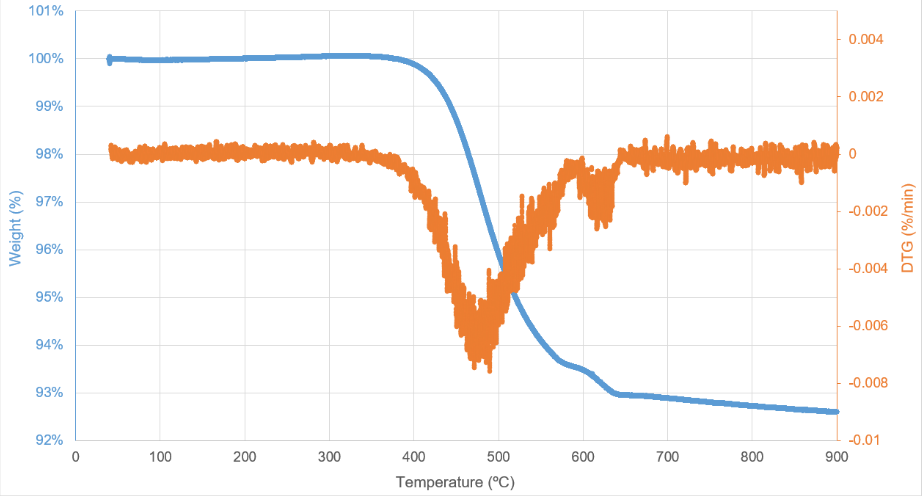

Figure 4.5: Experimental TG and DTG curves for the combustion of the pyrolysis residue (E2.2).

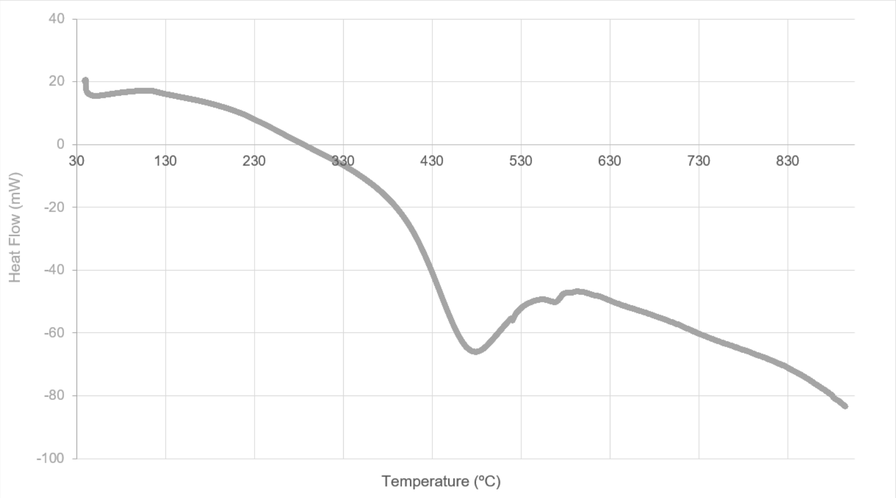

Figure 4.6: Experimental DSC curve for the combustion of the pyrolysis residue (E2.2).

With the results of these trials (E2.1/E2.2), it was then possible to obtain the proximate analysis of the material, following the procedure described in Chapter 3.4.2. The results can be seen in Table 4.6.

Table 4.6: Proximate analysis of the solid fraction of digestate used in STA, presented as percentage of fresh matter (FM)

Moisture (wt % FM)	**Volatile Matter (wt % FM)**	**Fixed Carbon (wt % FM)**	**Ashes (wt % FM)**
66	15	1	18

The moisture content obtained is in accordance with the expected for the solid fraction of the digestate, which 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 values obtained can be compared with the findings of Opatokun et al. (2015), who reported, on a dry basis, 61.8% of volatile matter, 25.6% of ashes, and 12.6% of fixed carbon [26]. The values obtained in the present work on a dry basis were: 52% of ashes, 45% of volatile matter, and 3% of fixed carbon.

The high ash content 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 a total of 16% of the raw material, being the interesting fraction from the thermochemical valorization point of view.

The fixed carbon content is considerably low but easily increased through a torrefaction process. This process, described in Chapter 2.4, consists of a slow pyrolysis where the organic matter is graphitized instead of volatilized. This can be done when the goal is to obtain vegetable coal to be commercialized or used in the biogas plant.

Regarding the volatile matter, although this analysis does not allows 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.

4.2.4 Torrefactions

The combustion trial (E1) concluded that the energetic balance of the process is positive, which means that its burning could be used in the plant to increase overall energy production. However, regarding the commercialization of digestate, its marketing value is relatively low. This happens due to its high moisture content, which decreases its energetic density and increases the storage and transport costs. It is also related to the fact that digestate still presents some pathogens.

The torrefaction process can resolve these issues, producing vegetable coal with a higher marketing value.

Thus, four torrefaction experiments were performed at different temperatures. After each, the torrefied material underwent a combustion trial to assess its combustible properties and compare them with the raw digestate.

The results obtained in all the torrefaction experiments were quite similar, as shown in Figure 4.7.

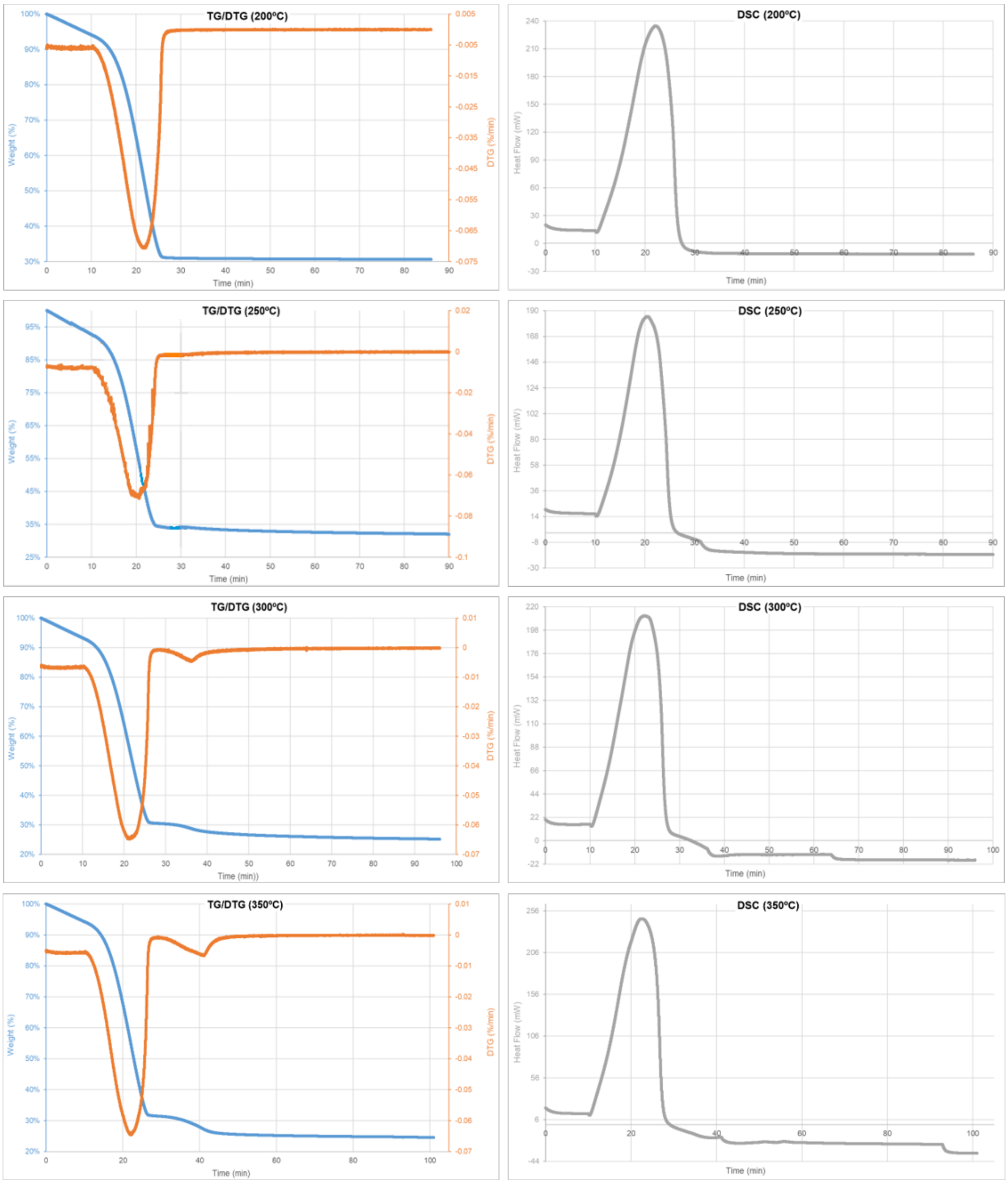

Figure 4.7: TG, DTG, and DSC curves obtained in the four torrefaction experiments represented as a function of time.

Through the TG and DTG curves, it is possible to conclude that all the torrefactions present a significant peak of weight loss at around 115°C. This corresponds to the loss of moisture content, representing an average of 69% of the samples' masses. Alongside, the DSC curve shows the corresponding endothermic peak, which starts at the beginning of the experience until approximately 200°C. The heat consumption for the drying of the samples was, on average, 1 377kJ/kg of fresh sample, which is a little higher than the energy required for drying in the first combustion experiment (E1).

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. Zhang et al. (2018) had reported a mass yield of 85% on a torrefaction at 200°C and Optokun et al. (2016) a value of 61% and 300°C [38][30].

The most relevant results of each trial are presented in Table 4.7, following the nomenclature from Chapter 3.4.2.

Table 4.7: Summary of the results obtained in each torrefaction experiment.

	E3.1 (200)	**E4.1 (250)**	**E5.1 (300)**	**E6.1 (350)**
DTG_{peak} (°C)	116	109	116	119
Weight loss (%)	69	67	70	69
Heat consumption (kJ/kg FM)	1 442	1 323	1 347	1 396
Mass yield (wt% DB)	98.5	94.7	83.3	79.1

FM - fresh matter; DB - dry basis.

The combustion behaviors of the torrefied materials can be seen in Figure 4.8.

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 peak 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 for all materials due to cellulose, hemicellulose, and lignin degradation. The highest ignition temperature, i.e., the temperature at which the material starts to burn, is observed for the torrefied produced at 300°C. The higher this temperature, the higher the temperature at which combustion occurs, which allows for more efficient heat extraction.

At the end of each experiment, the remaining solid residue, which corresponds to the material's ash content, is more than 50%, similar to the value obtained for the dried digestate. 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. The mentioned values and some details of the peaks observed in the DTG curve can be seen in more detail in Table 4.8.

From the DSC curves, it is possible to conclude that the most significant heat releases occur between 190-605°C for all the materials. After those temperatures, there is an apparent considerable heat release from the curves even though there are no additional mass changes.

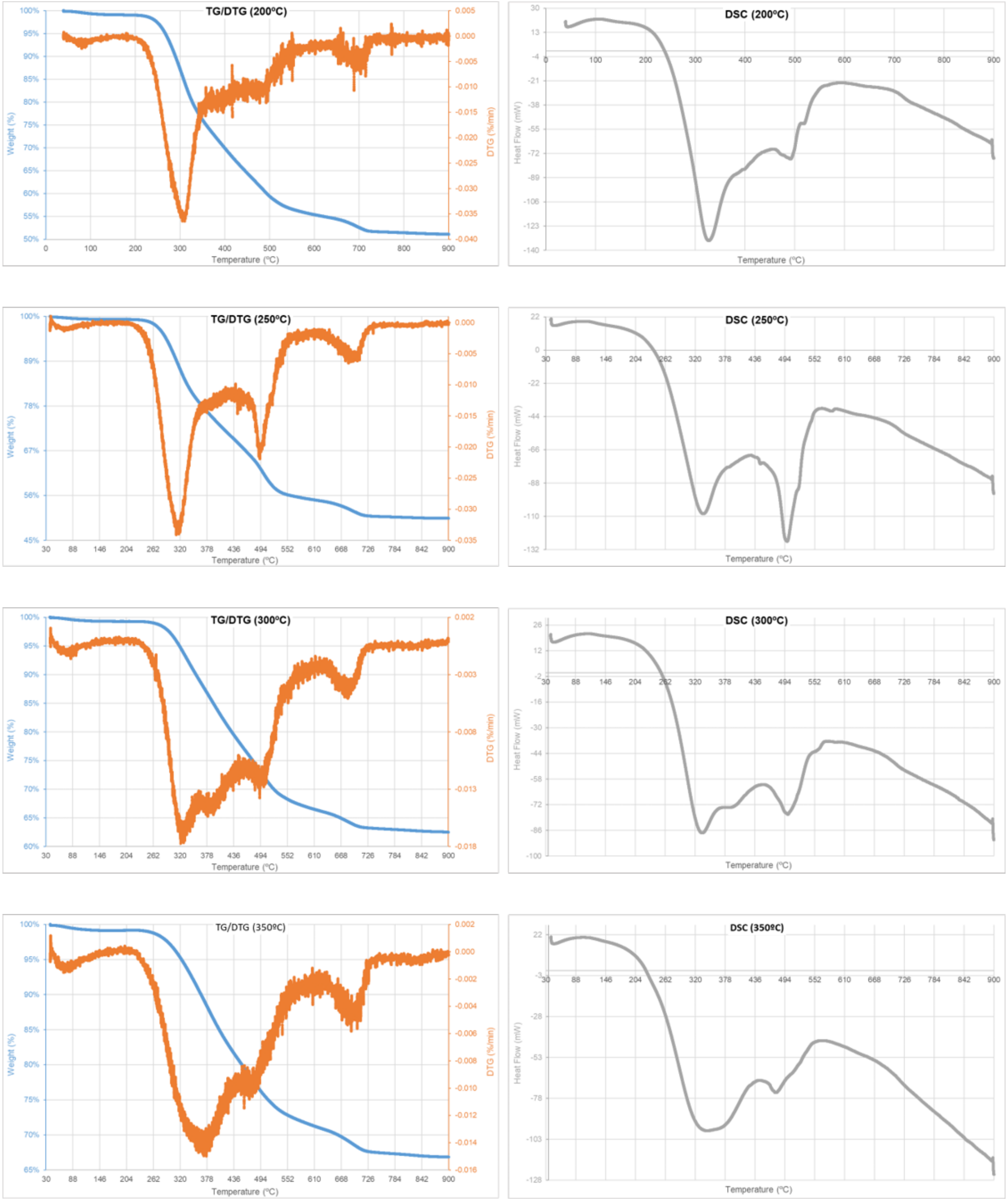

Figure 4.8: TG, DTG, and DSC curves obtained in the combustion of the torrefieds.

Table 4.8: Summary of the data obtained from the TG and DTG curves of the combustion trials performed on the raw digestate and on the torrefied materials obtained from it.

	1^{st} peak		2^{nd} peak		3^{rd} peak		Ti	Solid
	T(°C)	**Rate (%/min)**	**T(°C)**	**Rate (%/min)**	**T(°C)**	**Rate (%/min)**	**(°C)**	**residue (%)**
E1	303	0.012	484	0.005	672	0.002	239	52
E3.2 (200)	309	0.036	490	0.011	698	0.006	226	51
E4.2 (250)	316	0.034	495	0.021	702	0.006	247	50
E5.2 (300)	328/384	0.018/0.015	504	0.013	682	0.005	257	62
E6.2 (350)	375	0.015	475	0.011	698	0.005	244	67

Ti - ignition temperature.

Table 4.9 presents the temperature and heat release rate corresponding to the maximum DSC peak and the final heat release temperature of each trial. The maximum heat release rates occur for the torrefied materials obtained at 200 and 250 °C, suggesting that these have better combustible properties.

Table 4.9: Summary of the data related to the heat release of the raw digestate and its torrefied materials, obtained directly from the DSC curves of each trial.

	T_{max} (°C)	Maximum rate (mW)	T_{final} (°C)
E1	320	105.7	540
E3.2 (200)	329	132.9	585
E4.2 (250)	498	126.5	603
E5.2 (300)	334	87.4	605
E6.2 (350)	339	97.7	591

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 4.10 for all the trials, except the pyrolysis (E2.1) since, as mentioned before, the interest in this process is more related to the products formed, which were not analyzed in these trials.

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.

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

Table 4.10: Main conclusions regarding the combustible properties of the raw digestate and its torrefied materials.

	E1	E3.2 (200)	E4.2 (250)	E5.2 (300)	E6.2 (350)
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.

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 [72][73]. 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. As mentioned in Chapter 2.4.1, 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.

4.3 Kinetic models

As mention in Chapter 3.5, the kinetic models developed to describe the weight loss of digestate during the processes allow for a better understanding of the samples' composition and the determination of the kinetic parameters.

4.3.1 Modelling of combustion (E1)

The model developed to describe digestate's behavior under combustion is shown in Figure 4.9, together with the experimental data of the respective trial.

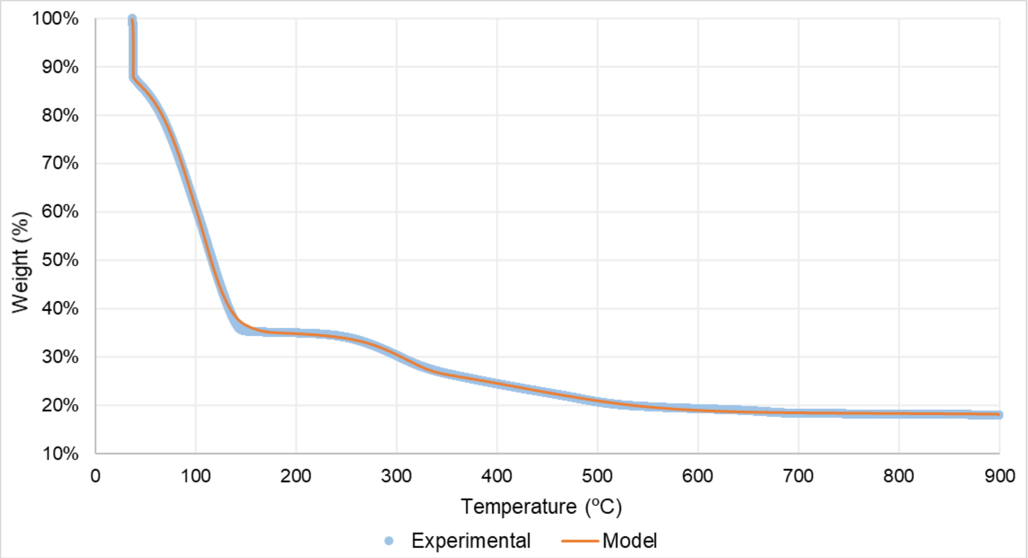

Figure 4.9: Model fitting of the combustion trial of raw digestate (E1).

The fitting observed was obtained by considering 4 pseudo-components. Through the figure, it can be seen that the adjustment was quite successful, which means that the model developed correctly describes the degradation. Furthermore, the error associated with the model was calculated, according to the method presented in Chapter 3.5, and a value of 0.55% was obtained. Thus, it is possible to consider that the kinetic parameters obtained, presented in Table 4.11, are very close to the real ones.

Table 4.11: Kinetic parameters of the combustion of raw digestate (E1), 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	

The first pseudo-component, with a theoretical initial fraction of 65%, corresponds to the water and some lighter volatiles, whose average experimental fraction is 68%. This component presents a high kinetic constant, consistent with the high speed of the drying process. Furthermore, an activation energy of approximately 39.3kJ/mol was obtained for this step, quite similar to water's enthalpy of vaporization, 40.7kJ/mol.

The second pseudo-component, whose degradation occurs until approximately 344°C, probably represents cellulose and hemicellulose. The calculated activation energy was 109.5kJ/mol. Mehrabian et al. (2014) reported activation energies of 193.0 and 147.0kJ/mol for cellulose and hemicellulose, respectively [74]. Gasparovic et al. (2012) stated those values as 175.6 and 132.9kJ/mol [74]. The mass fraction of these components corresponds to only 5% of the initial mass of digestate, as the majority were already degraded during digestion.

The third pseudo-component, with an even smaller kinetic constant, is most likely representing the degradation of lignin and some carbonates formed.

Lastly, the fourth component corresponds to the inorganic fraction of the digestate, with a theoretical fraction of 19%, close to the experimental value obtained for the ashes, 17%. The kinetic constant associated with these compounds is very close to zero as expected since although some of the inorganic compounds, such as carbonates, degrade, this happens very slowly.

4.3.2 Modelling of pyrolysis (E2.1/E2.2)

The model developed to describe the pyrolysis of the raw digestate under dynamic conditions can be seen in Figure 4.12. Similar to the combustion, the adjustment was achieved by considering four pseudo-components.

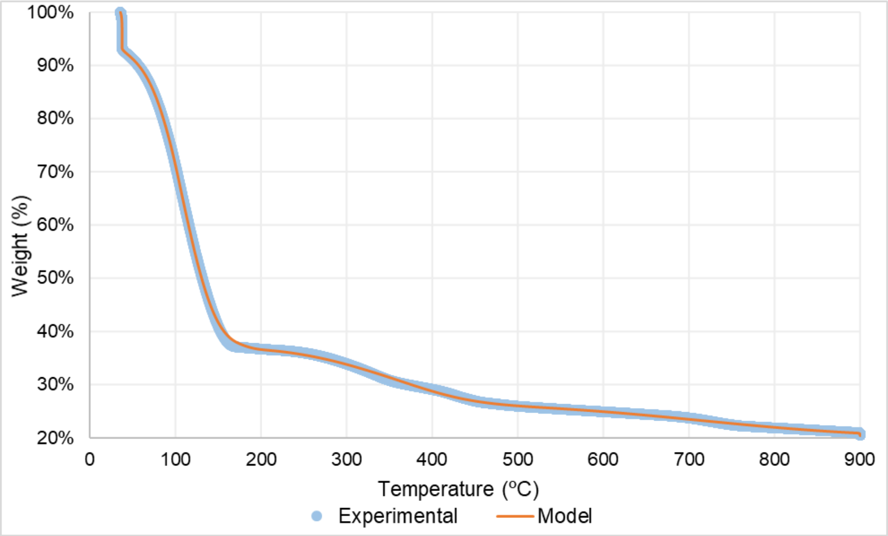

Figure 4.10: Model fitting of the pyrolysis trial of raw digestate (E2.1).

Table 4.12: Kinetic parameters of the pyrolysis of raw digestate (E2.1), 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	

Once again, a good fitting was achieved, with a deviation of only 0.43%.

The theoretical fraction obtained for water was 63%, very close to the experimental value, 66%. The activation energy was, once again, similar to the enthalpy of vaporization of water. The kinetic constant was smaller than the verified under an oxidant atmosphere, which suggests that the process occurs more slowly.

The second and third compounds should represent cellulose, hemicellulose, and lignin. However, the activation energies are quite smaller than the ones verified in the literature [75].

The fourth component, with a theoretical fraction of 20%, corresponds to the inorganic fraction of digestate, whose experimental value was 18%.

The model used to describe the combustion of the pyrolysis residue is shown in Figure 4.11. Based on the graph, it can be seen that the fitting between 450-650°C was not the most suitable. However, overall, the deviation was only 0.07%, which is quite satisfactory.

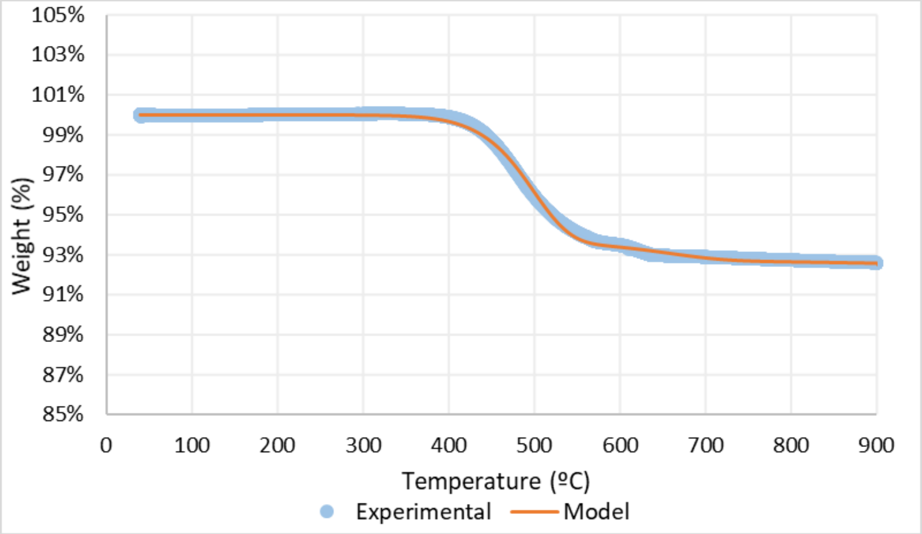

Figure 4.11: Model fitting of the combustion trial of the pyrolysis' residue (E2.2).

Table 4.13: Kinetic parameters of the combustion of the pyrolysis' residue (E2.2), according to the developed model.

	1	**2**	**3**	**Deviation (%)**
x_i	0.06	0.01	0.93	0.07
$k_{250^\circ C}$ (s^{-1})	6.13E-05	2.35E-06	5.80E-06	
Ea (J/mol)	111 154	110 200	20 640	

4.3.3 Modelling of torrefactions (E3/E4/E5/E6)

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 4.12, the model described the weight loss during the torrefactions with the following deviations: 4.43% for 200°C, 11.46% for 250°C, 5.40% for °C, and 4.77% for 350°C.

These quite elevated errors can be justified for two reasons. First, the samples studied throughout this work have a huge variability, so the fractions corresponding to each component can be quite different from sample to sample. Secondly, the models are purely mathematical and based on the degradation of each component. As seen in Chapter 4.2.4, in the DTG's of the torrefactions performed at 200 and 250°C there is only one peak, (corresponding to water loss), and in the torrefactions at 300 and 350°C, there are only two peaks. Thus, the components whose degradations occur above the temperature range of the torrefactions are not detected during the model's calculations, 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 adjustments obtained are presented in the following figures and the values of the fractions and deviations obtained can be seen in Table 4.14.

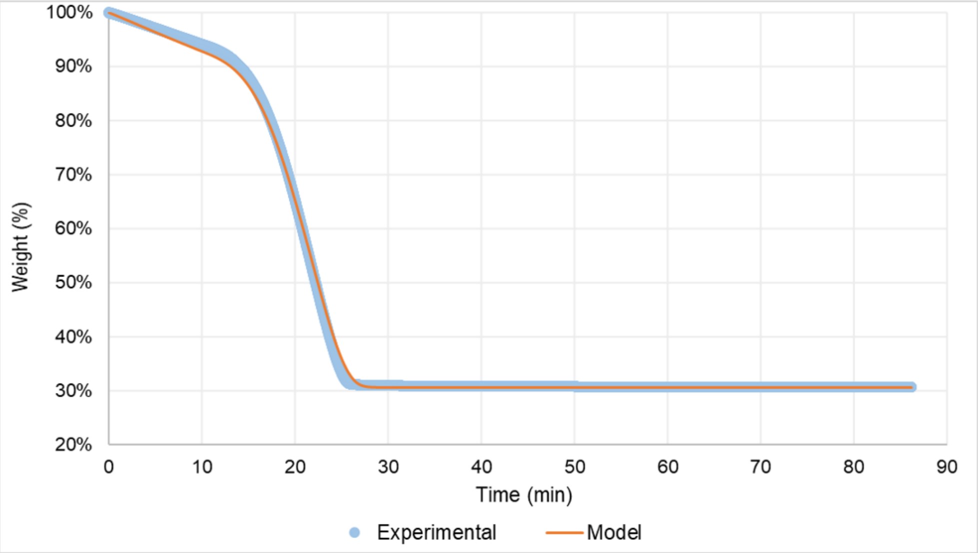

Figure 4.12: Model fitting of the torrefaction of digestate at 200°C (E3.1).

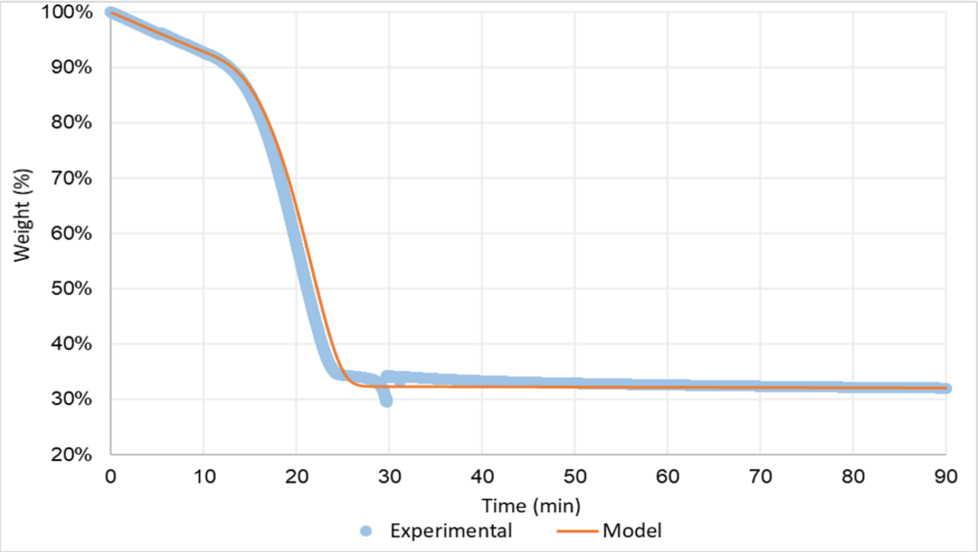

Figure 4.13: Model fitting of the torrefaction of digestate at 250°C (E4.1).

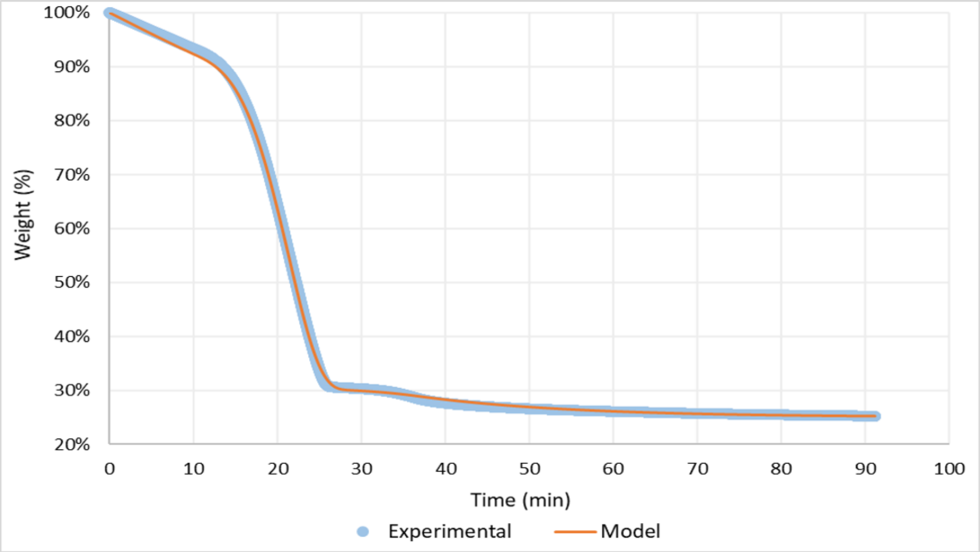

Figure 4.14: Model fitting of the torrefaction of digestate at 300°C (E5.1).

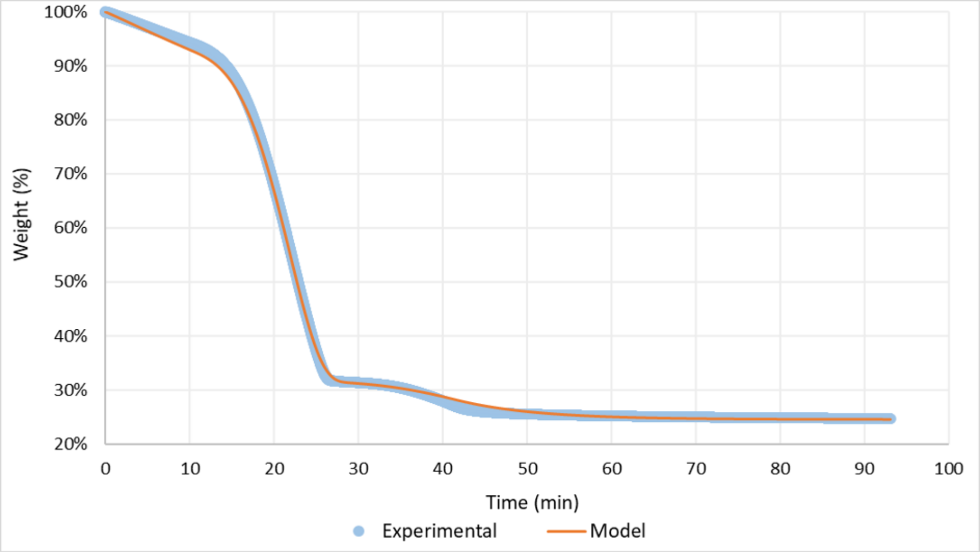

Figure 4.15: Model fitting of the torrefaction of digestate at 350°C (E6.1).

Table 4.14: 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

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.

Chapter 5

Conclusions and Future Work

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 Municipal Solid Waste in Portugal. The study was based on the characteristics of digestate's samples taken at different stages of the process: one right after digestion, and two others corresponding to the fractions obtained in the solid-liquid separation of digestate.

The work was divided into two main parts. The first one intended to analyze the agronomic characteristics of the digestate in the light of national and European legislation, to assess its integration in the fertilizer market. The second one aimed to study the thermal properties of the samples, through Simultaneous Thermal Analysis, to evaluate the potential of thermochemical valorization.

Regarding the first point, when the chemical analyses were received, the biogas plant was presenting abnormal levels of production. It was also verified that the values were not within the expected for the heavy metals, phosphorus, and volatile solids contents. That was a huge limitation since the conclusions taken were not necessarily the same under normal conditions.

Furthermore, unfortunately, it was not possible to analyze all parameters required by legislation, and only two samples from each zone of the process were taken. Thus, to ensure more accurate conclusions it is recommended to analyse in future works all parameters using a larger number of samples, preferably taken at different times, since the composition of the waste used in the digestion is quite variable.

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

Regarding the fresh digestate, it 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. Nevertheless, for both the raw digestate and the liquid fraction, an economic feasibility study should be carried out to assess whether the drying of those materials was justified.

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.

From the chemical analyses it was possible to verify that both the raw digestate and the liquid fraction presented more than 90% of moisture. Because that was a value too high for thermochemical applications, the thermal analyses were only performed to the solid fraction. Unfortunately, the results of those experiments were also biased due to the impossibility of constructing 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.

Thus, different torrefactions trials were performed to the samples in an attempt to increase its 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. Therefore, it is recommended for future work to conduct experimental pyrolysis trials with an analysis of the energetic content of the obtained products. Those trials would also be important to assess whether the high ash content of the digestate could cause problems. Furthermore, since the solid fraction of the digestate cannot be used as fertilizer due to pathogens, it is recommended to perform chemical analyses of the pyrochar produced at different temperatures to study its agricultural properties and inclusion in the fertilizer market.

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, with errors of 0.55 and 0.43%, respectively. The kinetic parameters of the pyrolysis model also described correctly all the torrefactions, with the worst-case being the torrefaction at 250ºC, showing a deviation of only 2.07%.

In conclusion, the work performed allowed a better understanding of the composition of the digestate produced in Portugal. This way, despite lacking some information and time that hindered the drawing of more definitive conclusions, the work allowed the rejection of some routes and indicated future interesting directions.

Finally, it should be noted that in Portugal, from 2025, the selective collection of MSW will be mandatory, so the digestate produced in Portugal will have different characteristics from the one studied in this thesis. Thus, it is recommended a future study similar to this thesis with the new digestate.

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Appendix A

Agriculture Analyses

Table A.1: Results of the chemical analyses performed to the samples of the residues before digestion.

	Sample 1	Sample 2	Average
C_{org} (%DW)	28.7	-	28.7
C_{org} (mg/L)	-	8 290	8 290
BOD_5 (mg O2/L)	26 300	25 300	25 800
DM (%)	9.27	—	9.27
VS (mg/L)	55 000	56 000	55 500
TS (mg/L)	88 000	90 000	89 000
Density (g/mL)	1.03	1.04	1.035
K (mg K/L)	1 470	1 500	1 485
K_2O (mg K_2O/L)	1 780	1 800	1 790
P (mg P/L)	252	265	259
P_2O5 (mg P_2O5/L)	580	610	595
Cu (mg Cu/L)	0.104	0.133	0.119
Zn (m Zn/L)	0.50	1.25	0.88
Pb (mg Pb/L)	0.073	0.137	0.105
Hg (mg Hg/L)	$<$0.01	$<$0.01	$<$0.01
Cd (mg Cd/L)	0.00071	0.00120	0.00096
Ni (mg Ni/L)	0.057	0.065	0.061
Cr (mg Cr/L)	0.0215	0.0331	0.0273
As (mg As/L)	0.040	0.036	0.038
E.coli (NMP/100mL)	$>$24 196	$>$24 196	$>$24 196
Salmonella spp (1L)	0	0	0

Table A.2: Results of the chemical analyses performed to the samples of digestate after digestion.

	Sample 1	**Sample 2**	**Average**
E.coli (NMP/100mL)	1 904	2 613	2 259
Salmonella spp (1L)	0	0	0
C_{org} (mg/L)	538	647	593
CBO_5 (mg O_2/L)	2 690	2 690	2 690
VS (mg/L)	24 300	24 400	24 350
Density (g/mL)	1.02	1.02	1.02
TS (mg/L)	53 000	54 000	53 500
N_{amon} (mg NH_4/L)	2 190	2 130	2 160
N_{total} (mg N/L)	2 790	2 930	2 860
$N_{Kjeldahl}$ (mg N/L)	2 790	2 930	2 860
Nitrite (mg NO_2/L)	<1	<1	<1
Nitrate (mg NO_3/L)	<250	<250	<250
K (mg K/L)	1 390	1 440	1 415
K_2O (mg K_2O/L)	1 670	1 730	1 700
P (mg P/L)	52	67	60
P_2O_5 (mg P2O5/L)	119	153	136
Cu (mg Cu/L)	0.184	0.191	0.188
Zn (mg Zn/L)	0.77	0.74	0.76
Pb (mg Pb/L)	0.116	0.111	0.114
Hg (mg Hg/L)	<0.01	<0.01	<0.01
Cd (mg Cd/L)	0.00092	0.00091	0.00092
Ni (mg Ni/L)	0.05	0.051	0.051
Cr (mg Cr/L)	0.0269	0.0249	0.0259
As (mg As/L)	0.080	0.083	0.082

Table A.3: Results of the chemical analyses performed to the samples of digestate's liquid fraction.

	Sample 1	**Sample 2**	**Average**
N_{amon} (mg NH_4/L)	2 030	1 980	2 005
N_{tot} (mg N/L)	1 490	1 660	1 575
$N_{Kjeldahl}$ (mg N/L)	1 490	1 660	1 575
Nitrate (mg NO_3/L)	<250	<250	<250
Nitrite (mg NO_2/L)	<1	<1	<1
K (mg K/L)	1 300	1 360	1 330
K_2O (mg K2O/L)	1 570	1 640	1 605
P (mg P/L)	20.8	20.9	20.85
P_2O_5 (mg P_2O_5/L)	47.5	47.8	47.65
TS (mg/L)	8 100	8 300	8 200
Salmonella spp (1L)	0	0	0
E.coli (NMP/100mL)	3 441	2 613	3 027
Cd (mg Cd/L)	<0.0005	<0.0005	<0.0005
Pb (mg Pb/L)	0.0058	0.0077	0.00675
Cu (mg Cu/L)	0.0204	0.0202	0.0203
Cr (mg Cr/L)	0.0082	0.0085	0.00835
Hg (mg Hg/L)	<0.01	<0.01	<0.01
Ni (mg Ni/L)	0.0277	0.0235	0.0256
Zn (mg Zn/L)	0.043	0.046	0.0445
Cr VI (microg/L)	<40	<40	<40
Corg (mg/L)	404	394	399
PAH_{16} (microg/L)	1.99	1.75	1.87
CBO5 (mg O2/L)	750	690	720
VS (mg/L)	1910	1890	1900
Density (g/mL)	1.01	1	1.005
pH	7.74	7.72	7.73
As (mg As/L)	0.076	0.073	0.0745
CQO (mg O2/L)	2 080	2 330	2 205

Table A.4: Results of the chemical analyses performed to the samples of digestate's solid fraction.

	Sample 1	**Sample 2**	**Average**
N_{amon} (%)	$<$0.01	$<$0.01	$<$0.01
Nitrite (mg NO_2/kg)	306	24	165
Nitrate (mg NO_3/kg)	286	281	284
N_{total} (%)	2.04	2.16	2.10
OM (%)	47.7	49.9	48.8
P (%)	0.0285	0.044	0.0363
P_2O_5 (%)	0.072	0.101	0.087
K (%)	0.74	0.70	0.72
K_2O (%)	0.89	0.84	0.87
pH	8.43	8.28	8.36
Moisture (%)	73.7	73.0	73.3
Salmonella spp. (/50g)	0	0	0
E.coli (CFU/g)	96 000	215	48 108
Cd (mg Cd/kg)	0.56	0.55	0.56
Pb (mg Pb/kg)	103	82	93
Cu (mg Cu/kg)	292	257	275
Cr (mg Cr/kg)	79	66	73
Hg (mg/kg DM)	0.34	0.34	0.34
Ni (mg Ni/kg)	35.1	31.1	33.1
Zn (mg Zn/kg)	640	640	640
Relative seed G germination (%)	11.1	10	10.6
Root Growth Inhibition (%)	100	100	100
IG	0	0	0
Inert $>$2 mm (%)	$<$0.1	$<$0.1	$<$0.1
Inert $>$5 mm (%)	$<$0.1	$<$0.1	$<$0.1
PAH_{16} (mg/kg DM)	2.95	3.40	3.18
C_{org} (%DW)	23.1	22.5	22.8
Cr VI (mg/kg DM)	$<$0.06	$<$0.06	$<$0.06
As (mg As/kg)	7.2	6.7	6.95
Inert $>$10 mm (%)	$<$0.1	$<$0.1	$<$0.1
Inert $>$20 mm (%)	$<$0.1	$<$0.1	$<$0.1
Maturation	V (mature)	V (mature)	V (mature)
C_{total} (%DW)	23.6	23.8	23.7
C_{inorg} (%DW)	0.47	1.31	0.89
DM (%)	28.7	28.6	28.7
Ignition residue (550°C) (%DW)	57.7	55.8	56.8
CQO (mg/kg)	353 000	640 000	496 500

Appendix B

STA

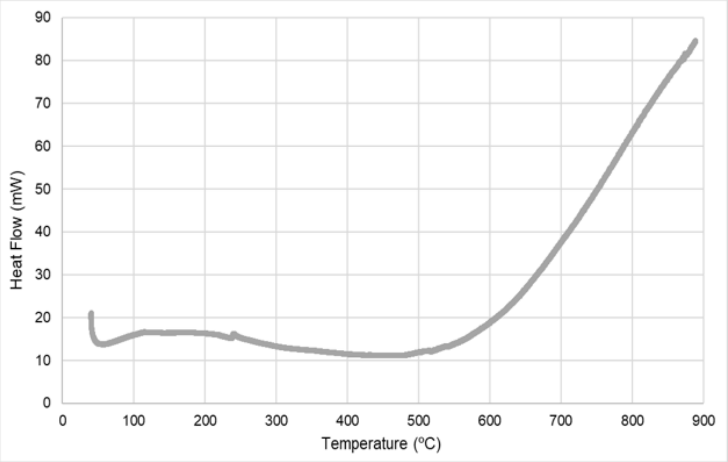

Figure B.1: First blank trial performed under air atmosphere.

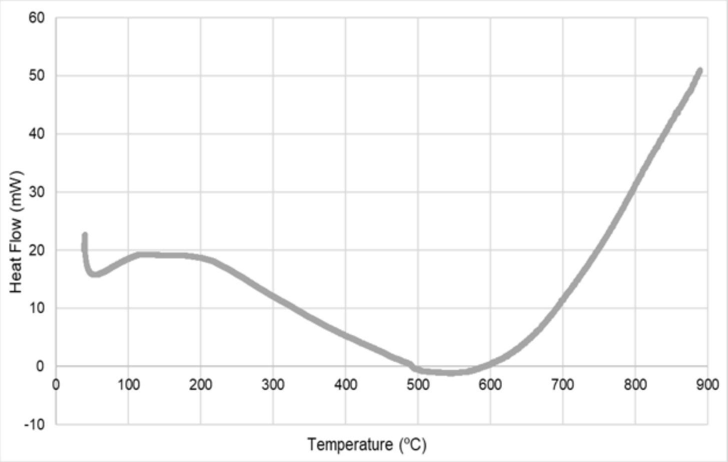

Figure B.2: Second blank trial performed under air atmosphere.

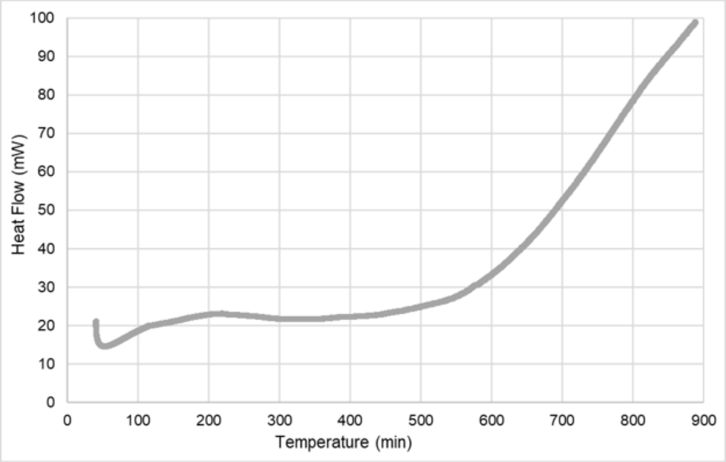

Figure B.3: Blank trial performed under nitrogen atmosphere.

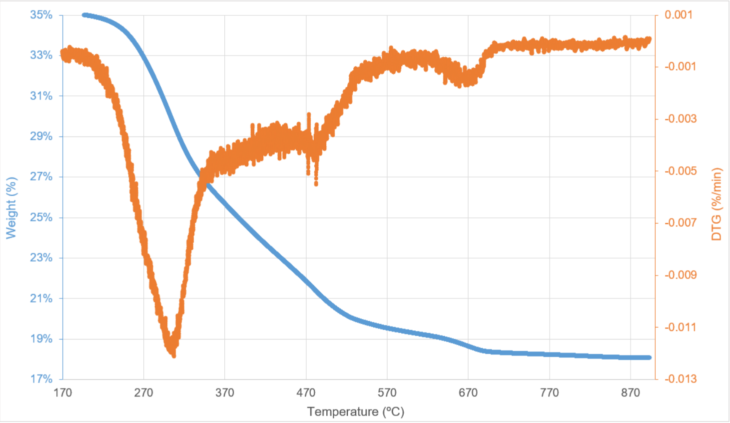

Figure B.4: Experimental TG/DTG curve for the first combustion trial (E1) for the stages between 170 and 900°C.

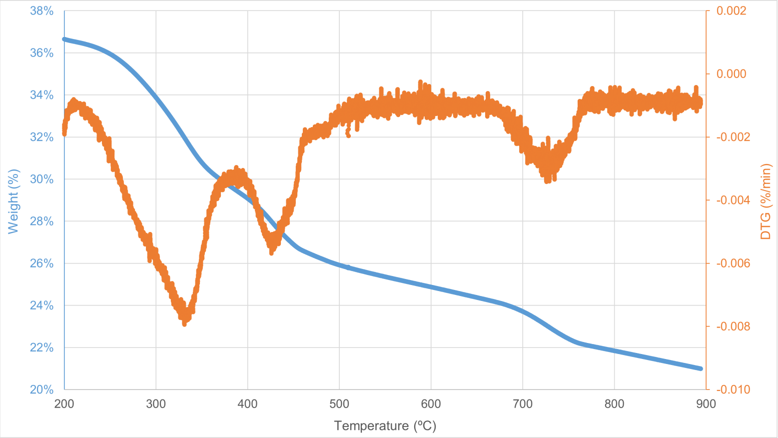

Figure B.5: Experimental TG/DTG curve for the pyrolysis trial (E2.1) for the stages between 200 and 900°C.

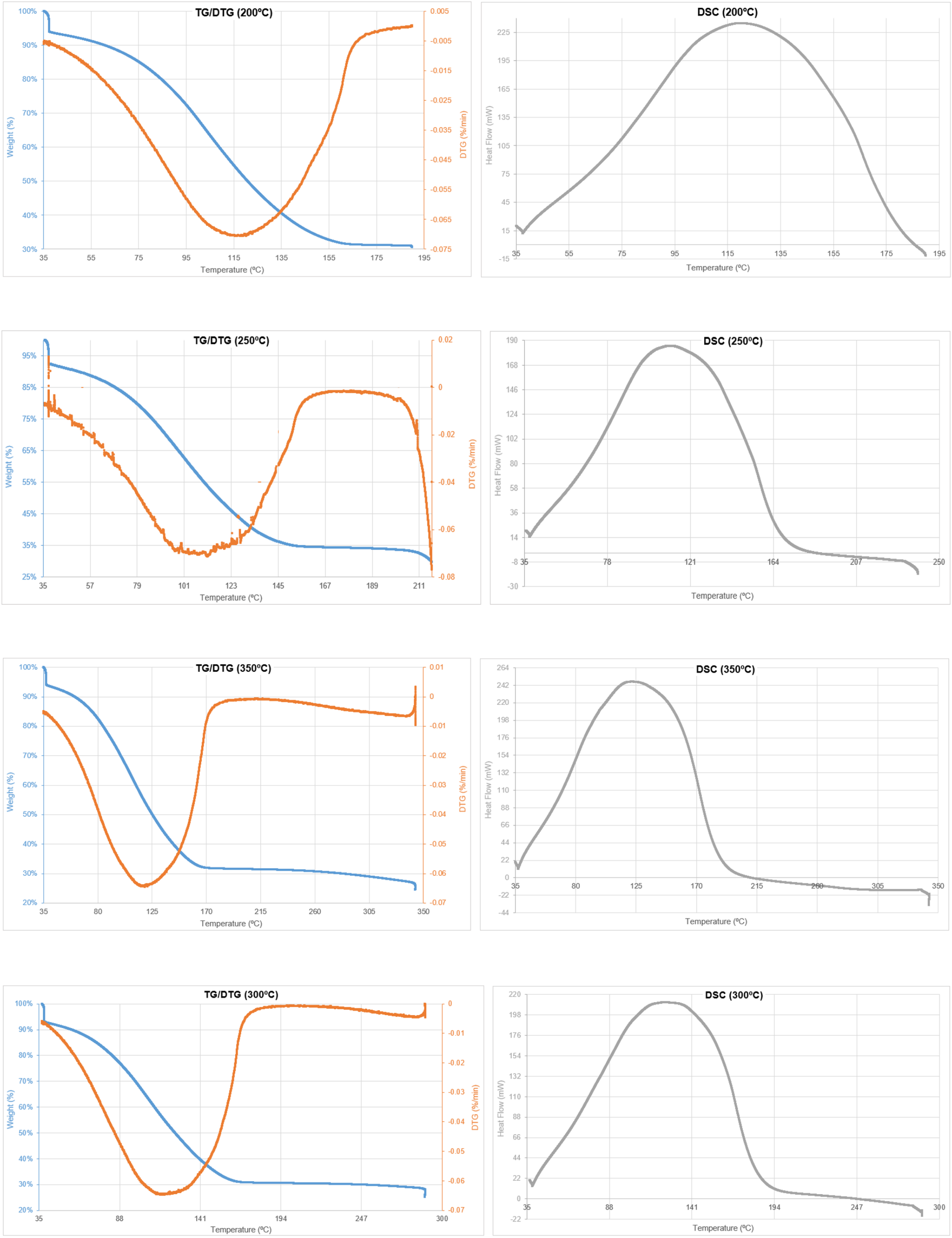

Figure B.6: TG, DTG, and DSC curves obtained in the four torrefaction experiments represented as a function of temperature.