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Chemical and thermal properties of mixes of extruded refuse derived fuel and pine

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...Un GRAZIE ai miei genitori che con il sudore dei loro
sacrifici mi hanno permesso di raggiungere questo traguardo,
a mio fratello che con la sua caparbietà mi ha insegnato a provarci sempre,
a Giovanni che è l'amore della mia vita, presente in ogni istante,
a mia nonna che non ha mai smesso di vegliare su di me da lassù...

RESUMO

O aumento contínuo do consumo de eletricidade e dos preços dos combustíveis fósseis tradicionais são um forte incentivo para a necessidade da utilização de péletes como combustível para aquecimento e produção energética, tanto para uso doméstico quanto para aplicações industriais.

Este trabalho experimental avalia a possibilidade da mistura de combustível sólido derivado de resíduos (CDR) e pinho (biomassa) para a produção de péletes, com o objetivo de desviar resíduos urbanos dos aterros sobre-utilizados e saturados e reduzir as emissões de gases com efeito de estufa produzindo fontes alternativas de energia.

Em termos experimentais foram estudadas principalmente as propriedades térmicas e químicas de péletes de pinho e CDR, onde estes últimos são obtidos através do tratamento dos rejeitados dos tratamentos mecânicos e biológicos (MBT) realizados no centro municipal de tratamento de resíduos sólidos da Associação de Municípios da Região do Planalto Beirão.

Determinou-se o conteúdo da humidade, das cinzas, da matéria volátil e do carbono fixo presente em cada amostra de péletes preparadas com diferentes misturas de pinho e CDR, nomeadamente: 100% pinho, 5% CDR:95% pinho, 10% CDR:90% pinho e 15% CDR:85% pinho.

Foi também realizada a análise de alguns elementos com características poluentes, como o cloro, enxofre e azoto com o método de combustão na bomba calorimétrica, obtendo-se a sua concentração percentual, para estudar o impacto ambiental ou técnico no processo de combustão das misturas de péletes preparadas.

Do ponto de vista da avaliação térmica destes combustíveis foi avaliado o poder calorífico superior também recorrendo ao calorímetro.

O trabalho experimental foi concluído com uma análise das cinzas decorrentes da combustão das péletes sob avaliação na caldeira doméstica (20 kW) quanto ao seu teor de metais pesados (Pb, Cd, Cu, Ni, Zn, Cr). Desta forma pretendeu-se fazer uma caracterização das cinzas e avaliação da sua toxicidade.

Verificou-se que as características das péletes produzidas com adição de CDR não apresentavam características marcadamente diferentes das preparadas apenas com pinheiro. O teor de cloro, enxofre e azoto, com a adição de 15% de CDR nos péletes, apresentam valores baixos (0,06%, 0,04%, 0,005%) e o poder calorífico superior (PCS) aumentou para 21,02 MJ/kg. A caracterização das cinzas não apresentou diferenças significativas com a adição de CDR e são classificadas como não perigosas.

ABSTRACT

The continuing increase in the prices of electricity and traditional fossil fuels is a strong incentive for pellets to be more in demand for heating fuel and energy production, both for domestic use and in industry.

This paper evaluates the possibility of mixing refuse derived solid fuel (RDF) and pine (biomass) for pellet production, with the aim of diverting waste from saturated landfills and reducing greenhouse gas emissions produced from other energy sources.

This study focuses mainly on the thermal and chemical properties of pellets made of pine and RDF, made using a series of mechanical and biological treatments (MBT) carried out at the municipal solid waste treatment centre of the Associação de Municípios da Região do Planalto Beirão.

The content of humidity, ash, volatile matter and fixed carbon of each sample of pellets was determined. Tests were carried out on different mixes: 100% pine, 5% RDF:95% pine, 10% RDF:90% pine and 15% RDF:85% pine.

Tests were also performed for pollutants such as chlorine, sulphur and nitrogen caused by the combustion method in the calorimetric bomb. Concentrations were recorded as a percentage to study the environmental and technical impact in the combustion process.

For the thermal evaluation of these fuels, the highest heating value was also measured using the calorimeter.

The experimental work was concluded with an analysis of the ash resulting from the combustion of the pellets under evaluation in the domestic boiler (20 kW) for their heavy metal content (Pb, Cd, Cu, Ni, Zn, Cr). In this way, the ash was analysed and its hazardous potential evaluated.

It was found that the pellets produced with RDF addition did not exhibit markedly different characteristics from those made only of pine. The content of chlorine, sulphur and nitrogen, with the addition of 15% of RDF in the pellet, shows low values (0.06%, 0.04%, 0.005%) and the highest heating value (HHV) increased to 21.02 MJ/Kg. There was no significant difference between the ash with or without the addition of RDF and it can be classified as non-hazardous.

ABSTRACT

Il continuo aumento dei consumi di energia elettrica e dei prezzi dei combustibili fossili tradizionali sono un forte incentivo per la necessità di utilizzare pellet come combustibile per il riscaldamento e la produzione di energia, sia per uso domestico e sia per applicazioni industriali.

Questo lavoro sperimentale valuta la possibilità di miscelare combustibile derivato da rifiuti solidi (CDR) e pino (biomassa) per la produzione di pellet, con lo scopo di dirottare i rifiuti urbani dalle discariche ormai sature e ridurre le emissioni di gas a effetto serra prodotte da fonti di energia alternative.

Questo documento si concentra principalmente sulle proprietà termiche e chimiche del pellet di pino e CDR, dove questi ultimi sono il risultato di una serie di trattamenti meccanici-biologici (MBT) eseguiti presso il centro municipale di trattamento dei rifiuti solidi, dalla Associazione dei Comuni della Regione Planalto Beirão.

E’ stato determinato il contenuto di umidità, ceneri, materia volatile e carbonio fisso presente in ciascun campione di pellet preparato con miscele differenti: 100% pino, 5% CDR:95% pino, 10% CDR: 90% pino, 15% CDR:85% pino.

E’ stata inoltre effettuata l'analisi di alcuni elementi con caratteristiche inquinanti quali cloro, azoto e zolfo con il metodo di combustione nella bomba calorimetrica al fine di ottenere la concentrazione percentuale e studiare l'impatto ambientale o tecnico durante il processo di combustione.

Dal punto di vista della valutazione termica di questi combustibili è stato determinato il potere calorifico superiore utilizzando lo stesso calorimetro.

Il lavoro sperimentale è stato completato con un'analisi delle ceneri derivanti dalla combustione di pellets in una caldaia domestica (20 kW) e del suo contenuto di metalli pesanti (Pb, Cd, Cu, Ni, Zn, Cr) con l’intento di caratterizzare le ceneri e valutare la loro tossicità.

Si è constatato che le caratteristiche dei pellets prodotti con l’aggiunta di CDR non presentano notevoli diversità da quelle preparate con solo pino. Il contenuto di cloro, zolfo e azoto, con l'aggiunta del 15% di CDR nel pellet, mostra valori bassi (0,06%, 0,04%, 0,005%) e il valore di riscaldamento più elevato (HHV) è aumentato a 21,02 MJ/kg. La caratterizzazione delle ceneri non ha mostrato differenze significative con o senza l'aggiunta di CDR e sono classificate come non pericolose.

PALAVRAS CHAVE

RU (RESÍDUOS URBANOS)

TMB (TRATAMENTO MECÂNICO-BIOLÓGICO)

CDR (COMBUSTÍVEIS DERIVADOS DE RESÍDUOS)

PINHO

PÉLETE

COMBUSTÃO

ANÁLISE PROXIMA

ANÁLISE ELEMENTAR

CINZAS

METAIS PESADOS

KEY WORDS

MSW (MUNICIPAL SOLID WASTE)

MBT (MECHANICAL-BIOLOGICAL TREATMENT)

RDF (REFUSE DERIVED FUELS)

PINE

PELLET

COMBUSTION

PROXIMATE ANALYSIS

ELEMENTAL ANALYSIS

ASH

HEAVY METALS

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Giovanni, the person who was closest to me, present at every moment, aware of my every concern, anxiety and fear. He is my present and my future, he has walked by my side always for 10 years, in this Erasmus experience and not only. Day after day, he has transmitted to me peace, patience, courage, strength and, above all, love. There are not enough lines to thank him.

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1. INTRODUCTION

Nowadays, the problem of waste disposal is one of the most important challenges that humanity needs to solve, because it is a cause of environmental pollution (the storage of waste can be harmful to the soil and its destruction in incinerators can cause pollutant emissions) and damage to human health.

Waste management can be done in different ways; it can be dumped in landfills, burned in incinerators (because they produce energy from the combustion of waste), treated in compost or recycled for re-use. The order in which the methods of waste management are listed above is exactly the opposite of the order that should be followed in terms of proportion in waste management policy. Solutions aim to engage the public and change behaviour but are often met with public protests that slow down this process. This is the so-called NIMBY syndrome “Not in my back yard”, or public hostility against the presence in their area of public management systems, including recovery plants and waste disposal sites, due to the concern over the negative effects on health and in the area.

Another aspect that cannot be overlooked is undoubtedly the problem of environmental pollution linked to the concentration of urban and industrial waste. It is evident that human and industrial activities contribute to the increase in the quantity of greenhouse gases in the atmosphere and to climatic change.

In order to have sustainable development, it is therefore necessary to use renewable energy sources (solar, geothermal, wind power, etc.) that are inexhaustible and that do not have a significant negative environmental impact. This category of renewable sources for energy production includes fuel derived from solid urban waste (RDF) and biomass, which are the focus of this thesis.

This paper will focus on the preparation and feasibility study of a mix of RDF and pine (biomass), with a maximum of 15% RDF replacing the biomass. Countries like Austria, Sweden, Germany and the Netherlands have experienced high levels of recycling (material recovery of 50-60%), combined with high energy recovery rates (40-50% of energy recovery) in thermoelectric power plants (Del Zotto et al., 2015).

The main objective of this work is to demonstrate that the use of alternative RDF fuels will bring benefits, such as economic and environmental savings due to the reuse of something already existing (waste) and reduction of deposits in landfills.

The main focus of this work is to study the chemical and thermal properties of the different mixtures of RDF and pine, in the form of pellets, using:

- 5% RDF + 95% pine
- 10% RDF + 90% pine
- 15% RDF + 85% pine

The proximate analysis of the pellet sample is performed to obtain the content of humidity, ash, volatile matter and fixed carbon. Knowledge of these parameters is fundamental for the application of the test sample as a fuel in a biomass thermoelectric power plant.

An elemental analysis is also carried out using the calorimetric bomb, which will evaluate the content of chlorine, sulphur and nitrogen, in order to assess the environmental or technical impact of the combustion process. This procedure will also determine the high heating value (HHV) of the mixes.

The work ends with the analysis of the ash from the combustion in the furnace, its characterization and evaluation of hazardous potential in terms of heavy metals.

The work planned and carried out for this thesis is set out in Table 1, and the schedule is shown in Table 2.

Table 1. Work planned and carried out.

Task	Title	Description
T1	Literature review	Collection of information on chemical and thermal properties of mixes of extruded Refuse Derived Fuel (RDF) and Pine.
T2	Determination of calorific properties of the RDF-Pine mixes	Determination of the high heating value (HHV) of chlorine, sulphur and nitrogen using the calorimetric bomb.
T3	Measurement of chemical emissions of the RDF-Pine mixes and analysis of ashes after combustion in the oven	Evaluation of chlorine, sulphur, nitrogen, volatile matter and related environmental impacts. Characterization of combustion ash with the measurement of heavy metals and toxicity.
T4	Results analysis	Data analysis, statistical evaluation and comparison.
T5	Completion of thesis	Organization of thesis and presentation of work.

Table 2. The proposed work schedule is as follows.

Task	March 2019	April 2019	May 2019	June 2019	July 2019
T1	■	■			
T2	■	■			
T3		■	■		
T4			■	■	
T5			■	■	

The organization of this document is in chapters with the following information:

- Literature review
- Presentation of the experimental methodologies followed
- Results analysis and evaluation of their meaning
- Conclusion of the work and presentation of all the bibliography consulted
- Annexes with experimental data used for calculations and analysis of results

2. LITERATURE REVIEW

The disposal of solid urban waste is a problem that is present throughout the world. In the environmental and economic scenarios, waste deriving from industrial activities takes on greater importance, since it is generated by various types of process and involves high economic and environmental costs for industrial managers.

This is one reason why today the aim is to reduce, reuse and recycle waste, as an alternative to using traditional raw materials, thus reducing the costs to industry, as well as preserving the environment.

Rising fossil fuel prices and the requirements of reducing greenhouse gases (GHG) force energy users to use economically advantageous materials with a significant fraction of biomass (Garg et al., 2007).

Although with the global growth in demand for energy more and more renewable energy sources have been developed (biomass energy, hydroelectric energy, geothermal energy, solar energy, wind and marine energy), their application is still limited due to the short duration of the technology and the high construction costs (Chen et al., 2015).

However, one of the most used renewable sources is biomass, which is a good fuel for boilers. It is seen as a residue from agricultural processing and waste from the food industry, an agricultural and forestry product and it is also a biological product, deriving from animal biological activity (Demirbas, 2005).

Biomass, which in this case study is pine, is an economically advantageous material given the rising prices of fossil fuels. It was considered a "zero emission" fraction with no contribution to greenhouse gas emissions (Garg et al., 2007). Biomass is considered a renewable source of energy because the carbon dioxide that it releases during combustion can be reabsorbed by other plants in the growth phase along with sunlight by photosynthesis (Demirbas, 2003). But Directive 2018/2001 enforces the analysis of the overall utilization of biomass taking into account its CO_2 capture and storage moving away from initial context of zero emissions from biomass burning.

Another advantage of using pine as a fuel is its high calorific value, which when compacted into pellets produces a more stable and controlled combustion in terms of emissions (Rosato, 2018). Global pellet production has increased considerably in recent years. Between 2006 and 2012, it grew from 7 to 19 million tonnes, with Europe and North America practically responsible for the entire production and consumption of densified products (Duca et al., 2014). The reasons for this success are many, namely the need to replace fossil fuels, both for questions of price and reduction of GHG, the higher energy density of the pellet compared to raw biomass and therefore the lower transport costs, ease of handling resulting from the ability of pellets to "flow" almost like a liquid fuel and, finally, the very precise particle size, which allows for more stable combustion and better control of emissions (Rosato, 2018). Also, according to the study by some authors (Marsh et al., 2007) pellet fuel is denser than the non-processed material and therefore contains more energy per volume. It allows a regular spacing of the vacuum through which the combustion system helps the passage of gases. Dust and odours are reduced to a minimum since pellet fuels are homogenized and as such the smaller particles are trapped in the material matrix (Marsh et al., 2007).

These products have specific certification, the ENplus (European Standard EN 14961-2, 2011), with high calorific value and low ash content. Table 3 shows the various qualitative types of pellets according to the three quality classes: ENplus-A1, ENplus-A2 and EN-B, based on the technical specifications described by the European Standard EN 14961-2.

Table 3. Different quality types of pellets according to the European Standard EN 14961-2.

Property	Unit	ENplus-A1	ENplus-A2	EN-B	Test method
Diameter	mm	6 or 8	6 or 8	6 or 8	EN 16127
Length	mm	3.15 ≤ L ≤ 40	3.15 ≤ L ≤ 40	3.15 ≤ L ≤ 40	EN 16127
Water content	w-%	≤ 10	≤ 10	≤ 10	EN 14774-1
Content in ash	w-%	≤ 0.7	≤ 1.5	≤ 3.0	EN 14775 (550 °C)
Mechanical durability	w-%	≥ 97.5	≥ 97.5	≥ 96.5	EN 15210-1
Fine particles (<3.15 mm)	w-%	≤ 1.0	≤ 1.0	≤ 1.0	EN 15210-1
Net calorific value	MJ/kg	16.5 ≤ Q ≤ 19	16.3 ≤ Q ≤ 19	16.0 ≤ Q ≤ 19	EN 14918
Apparent density	kg/m^3	≥ 600	≥ 600	≥ 600	EN 15103
Nitrogen (N)	w-%	≤ 0.3	≤ 0.5	≤ 1.0	EN 15104
Sulphur (S)	w-%	≤ 0.03	≤ 0.03	≤ 0.04	EN 15289
Chlorine (Cl)	w-%	≤ 0.02	≤ 0.02	≤ 0.03	EN 15289
Melting behavior of the ashes	°C	≥ 1200	≥ 1200	≥ 1100	EN 15370

2. LITERATURE REVIEW

The pellet studied in this thesis was prepared with pine (biomass) to which was added the solid fuel derived from wastes: Refuse Derived Fuel - RDF, which has a high calorific value, a low moisture and ash content and the ability to produce energy (Brás et al., 2017).

The RDF also includes a high biomass value derived from the nature of urban waste and its organic content. These characteristics are strongly dependent on human consumption in the regions where it is produced (Brás et al., 2017). It can therefore be assumed that the use of alternative pelletized fuels, such as waste-derived fuel and biomass, produce numerous benefits as well as representing an economic but, above all, ecological way of dealing with and solving various existing problems.

In recent decades the problem of waste production has increased with industrial and economic development, the increase in population and urban areas and, consequently, the increase in consumption. Waste produces negative effects on the environment, on the climate, on human health and on the economy. The quantity and type of waste can generate strong impacts on the environment, especially if they contain dangerous substances, which is why it is important to resort to a good management policy in order to reduce the volume produced and hazardous waste.

Even landfills can create problems if they are not designed correctly, because they can contaminate soils and aquifers with the chemicals in the waste and consequently damage the health of animals and people. Landfills also release methane, a very powerful and polluting GHG that affects the climate. From an economic point of view, when waste is disposed of in landfills, all the raw materials and products are lost that could produce additional value if reused or recycled and reintroduced into the economic cycle (European Commission, 2015).

With the new rules based on the proposals that the European Commission presented in 2015 to promote the circular economy, a reduction in waste production is expected and when this is not possible, an increase in recycling is anticipated. As a result, landfill disposal will be reduced and by 2035 waste will have to be reduced to make up a maximum of 10% of the total urban waste produced.

With regard to the new rules on selective collection, there are plans to expand the existing obligation to separate paper and cardboard, glass, metals and plastics and to collect dangerous waste separately by 2023, as well as organic waste and textiles (European Commission, 2015).

Also, according to the study by Menikpura et al. (2013) the disposal of solid urban waste is still a problem in many countries, including European countries. The increase in the price of raw materials, the lack of space for new landfills and restrictions imposed by European regulations have led to the need to replace fossil fuels with waste-derived fuels. All this generates the need to create a system that aims at good recycling of materials and energy, which reduces the emissions of greenhouse gases and the volumes of waste destined for landfills, which leads to a lower environmental impact, lower consumption of energy resources and lower economic costs.

Another alternative to landfills is waste heat treatments, in particular RDFs, which reduce volume and therefore space for final disposal and through which energy is recovered (Gallardo et al., 2014).

It is also important to make the correct estimate of the possible energy content of the residual fractions of the mechanical and biological waste treatment, and therefore of the RDF, to plan the production of energy through its combustion (Aranda et al., 2012).

2.1 WASTE MANAGEMENT IN EUROPE

According to the official statistics of the European Union, updated in May 2019, a general picture is given of the production of waste and its treatment in the European Union (EU) and in various countries that are not members of the EU (Eurostat Statistics Explained, 2019). It is based exclusively on data in the framework of Regulation (EC) n.2150/2002 of the European Parliament and of the Council concerning waste statistics.

About 2,533 million tonnes of waste were generated in the EU-28 by all economic activities and households in 2016, which was the year with the highest amount recorded for the EU-28 between 2004 and 2016 (Figure 1). This year, each European produced, on average, 4,968 kg of waste, with Finland at the top of waste producers – 22,359 kg, and Italy and Portugal with average production of 2,705 and 1,427 kg/inhabitant, respectively (Eurostat Statistics Explained, 2019).

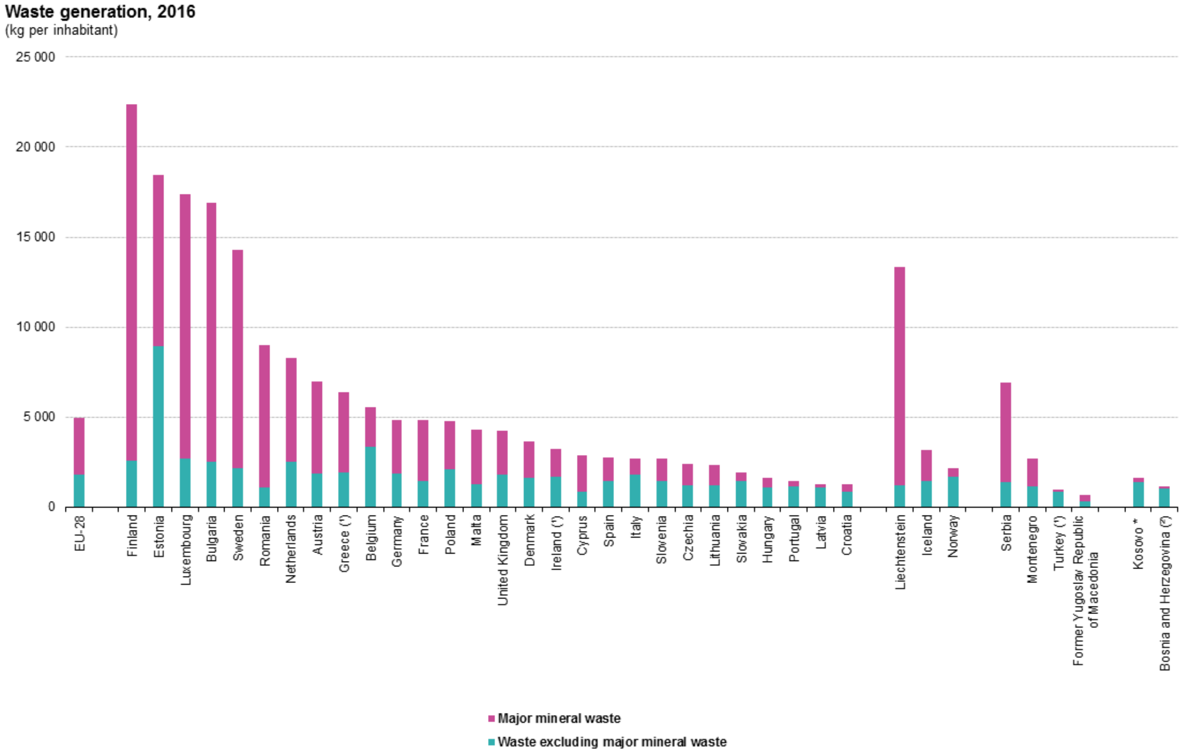


Figure 1. Waste generation (kg per inhabitant), EU-28, 2016 (Eurostat Statistics Explained, 2019).

The share of different economic activities and of households in total waste generation in 2016 is presented in Figure 2. The sectors with the heaviest influence in waste production are construction (36,4 %), followed by mining and quarrying, manufacturing, waste and water services. Households produced about 8,5 % of all the waste produced in the EU. The activities which produced the least waste are other economic activities, mainly services and energy.

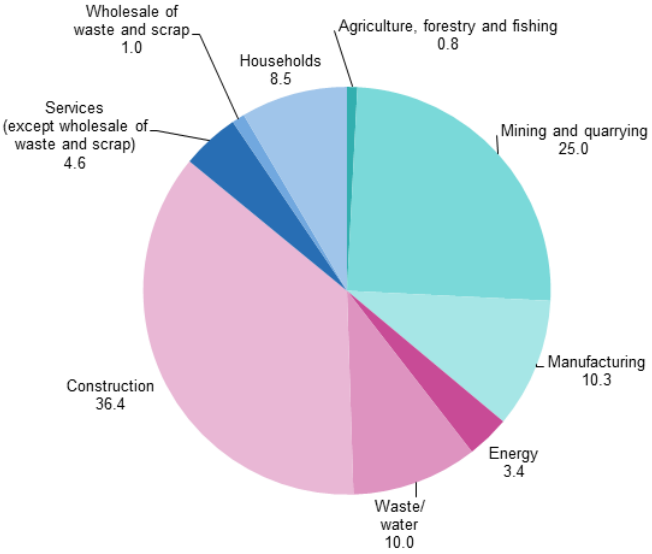
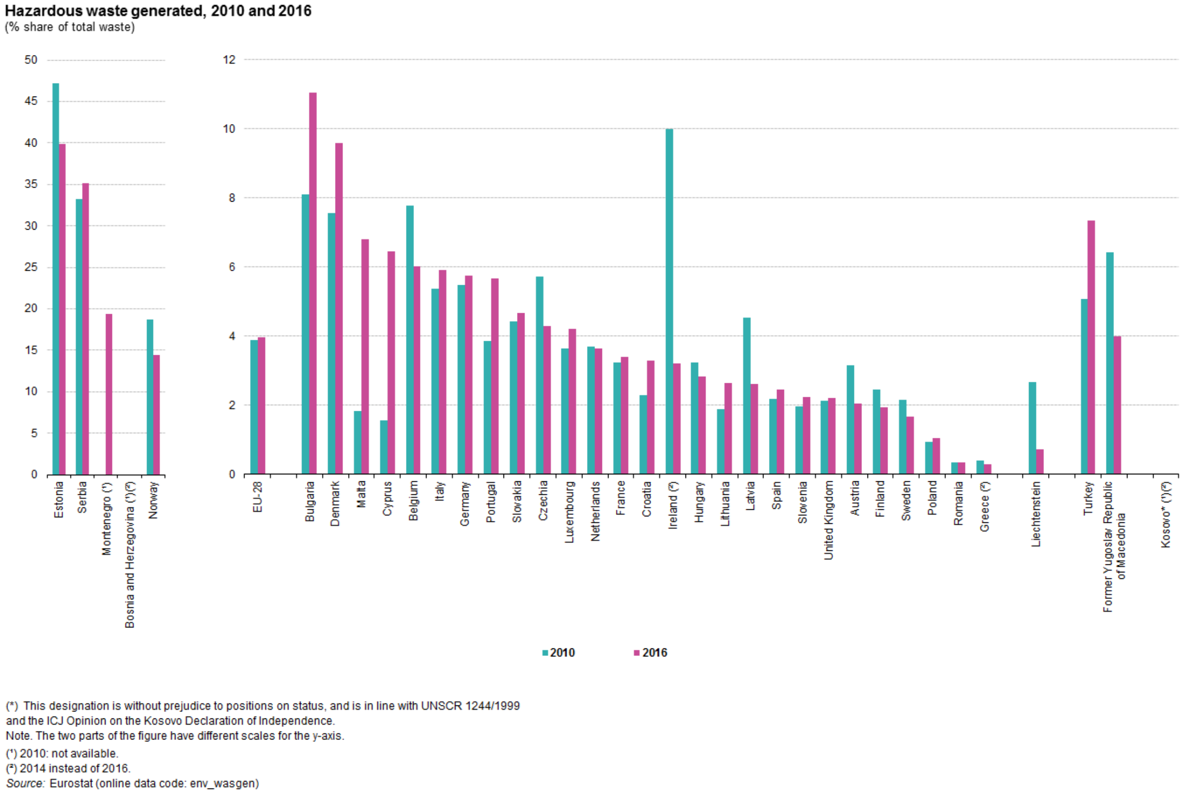


Figure 2. Waste generation by economic activities and households, EU-28, 2016 (Eurostat Statistics Explained, 2019).

Several of the Member States with particularly high levels of waste generated per inhabitant reported very high shares of waste from mining and quarrying, while elsewhere construction and demolition often contributed high shares. These types of waste are generally classified as major mineral wastes and can be related to the different economic structures.

On the other hand, regarding the production of hazardous waste in the EU in 2016, about 100 million tonnes (4.0 % of the total) was classified as hazardous waste (Figure 3). These different materials, although they could include some important resources, have an elevated risk to human health and to the environment if not managed and disposed of safely. The amount of hazardous waste is increasing, at least when compared with the 2010. Some countries have a higher amount of hazardous waste production related to the energy production from oil shale (Eurostat Statistics Explained, 2019).



(*) This designation is without prejudice to positions on status, and is in line with UNSCR 1244/1999 and the ICJ Opinion on the Kosovo Declaration of Independence.
Note. The two parts of the figure have different scales for the y-axis.
(¹) 2010: not available.
(²) 2014 instead of 2016.
Source: Eurostat (online data code: env_wasgen)

Figure 3. Hazardous waste generated, 2010 and 2016, EU-28, 2016 (Eurostat Statistics Explained, 2019).

In the same period, about 2,000 million tonnes of waste were treated in the EU-28, produced internally and imported. Figure 4 shows the development of waste recovery and disposal between 2004 and 2016. The quantity of recovered, or in other words recycled waste, including waste for energy recovery, grew by 28.6 % from 960 million tonnes in 2004 to 1,235 million tonnes in 2016. But even with the definition of environmental restrict policies, the reduction of waste subject to disposal decrease only 10.1 % from 2004 to 2016.

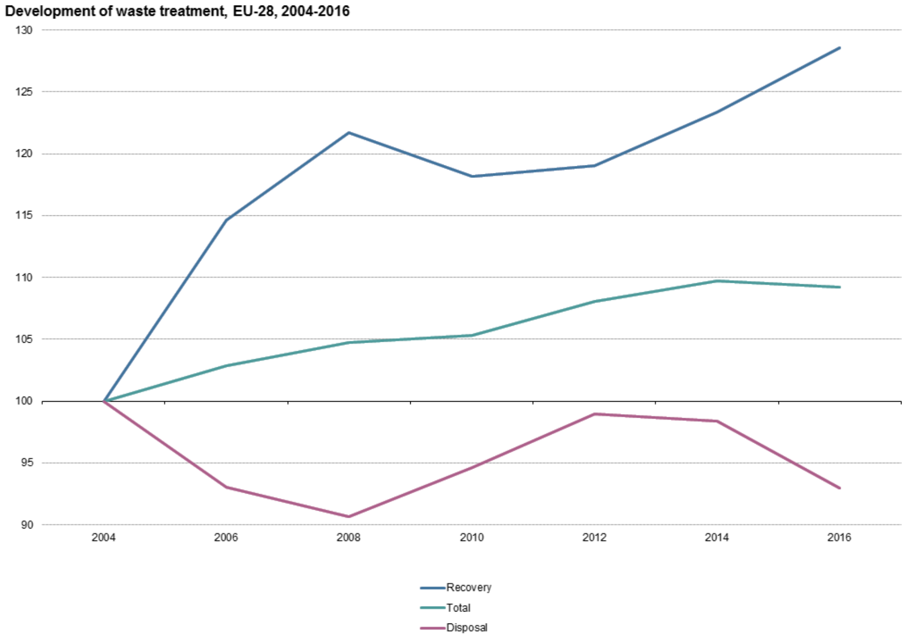
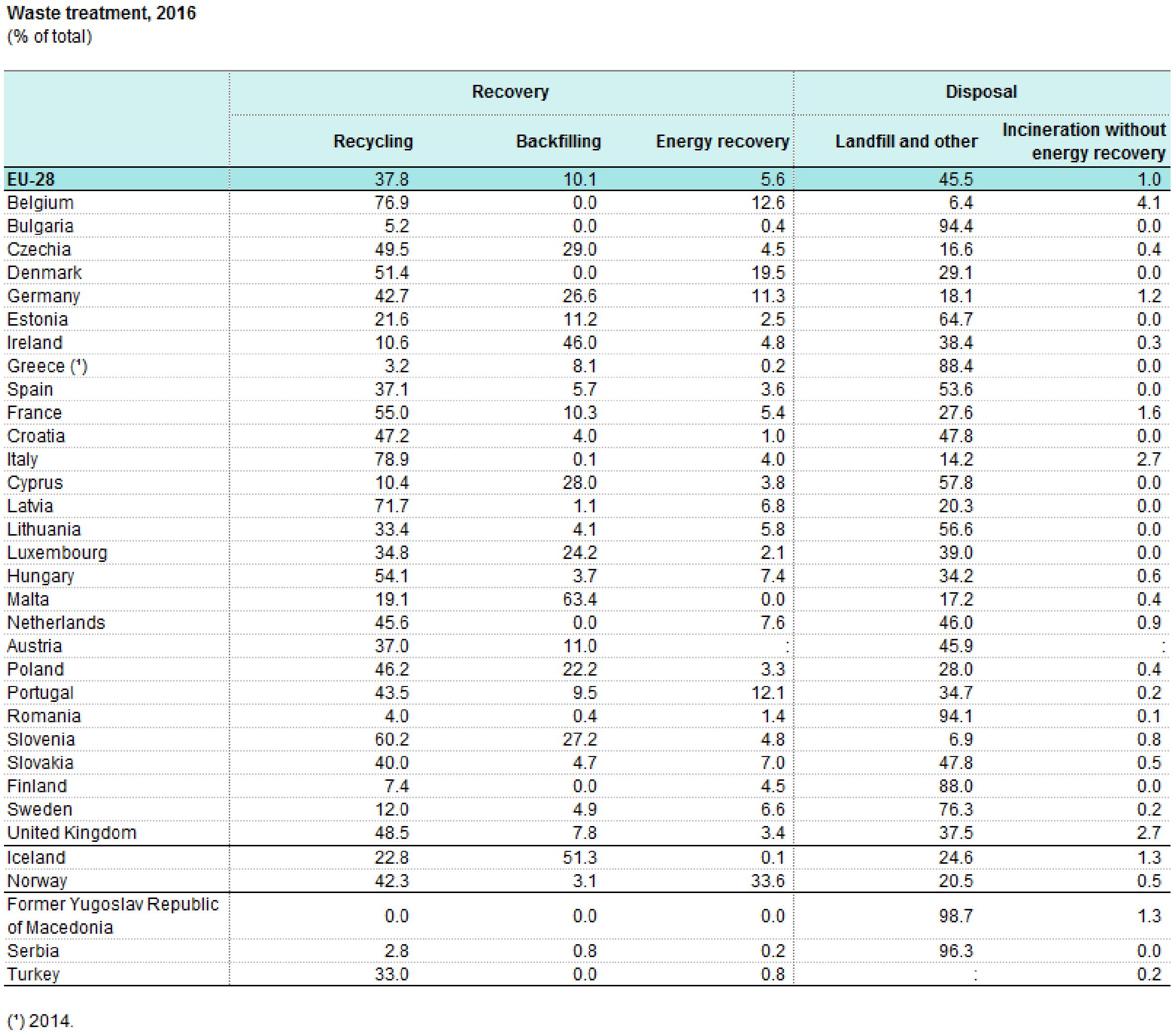


Figure 4. Development of waste treatment, EU-28, 2004-2016 (Index 2004 = 100) (Eurostat Statistics Explained, 2019).

The strategies followed by the EU Member States for waste treatment are shown in Table 4. Some Member States had very high recycling rates (Italy and Belgium), while others in 2016 still have landfill as the single process of waste treatment, namely Bulgaria, Romania, Sweden and Finland.

Table 4. Waste treatment, 2016.



Waste treatment, 2016
(% of total)

	Recovery			Disposal	
	Recycling	Backfilling	Energy recovery	Landfill and other	Incineration without energy recovery
EU-28	37.8	10.1	5.6	45.5	1.0
Belgium	76.9	0.0	12.6	6.4	4.1
Bulgaria	5.2	0.0	0.4	94.4	0.0
Czechia	49.5	29.0	4.5	16.6	0.4
Denmark	51.4	0.0	19.5	29.1	0.0
Germany	42.7	26.6	11.3	18.1	1.2
Estonia	21.6	11.2	2.5	64.7	0.0
Ireland	10.6	46.0	4.8	38.4	0.3
Greece (¹)	3.2	8.1	0.2	88.4	0.0
Spain	37.1	5.7	3.6	53.6	0.0
France	55.0	10.3	5.4	27.6	1.6
Croatia	47.2	4.0	1.0	47.8	0.0
Italy	78.9	0.1	4.0	14.2	2.7
Cyprus	10.4	28.0	3.8	57.8	0.0
Latvia	71.7	1.1	6.8	20.3	0.0
Lithuania	33.4	4.1	5.8	56.6	0.0
Luxembourg	34.8	24.2	2.1	39.0	0.0
Hungary	54.1	3.7	7.4	34.2	0.6
Malta	19.1	63.4	0.0	17.2	0.4
Netherlands	45.6	0.0	7.6	46.0	0.9
Austria	37.0	11.0	:	45.9	:
Poland	46.2	22.2	3.3	28.0	0.4
Portugal	43.5	9.5	12.1	34.7	0.2
Romania	4.0	0.4	1.4	94.1	0.1
Slovenia	60.2	27.2	4.8	6.9	0.8
Slovakia	40.0	4.7	7.0	47.8	0.5
Finland	7.4	0.0	4.5	88.0	0.0
Sweden	12.0	4.9	6.6	76.3	0.2
United Kingdom	48.5	7.8	3.4	37.5	2.7
Iceland	22.8	51.3	0.1	24.6	1.3
Norway	42.3	3.1	33.6	20.5	0.5
Former Yugoslav Republic of Macedonia	0.0	0.0	0.0	98.7	1.3
Serbia	2.8	0.8	0.2	96.3	0.0
Turkey	33.0	0.0	0.8	:	0.2

(¹) 2014.

In conclusion it can be stated that, among existing treatments, energy recovery is one of the most widespread treatments It is a technology that plays an extremely important role in the integrated waste management system, both because it allows a considerable reduction in the weight and volume of the waste and because it allows a significant recovery of energy. But, like any combustion process, it has an impact on the environment due mainly to the emission of hazardous substances into the atmosphere. There is no doubt, therefore, that the burning of waste involves the dispersion of a quantity of pollutants into the environment. Incinerators operating with an inaccurate selection of the waste to be treated, with inadequate combustion techniques or inadequate management, can emit a variety of inorganic micro-pollutants (heavy metals) and organic micro-pollutants that are harmful to human health and to the environment.

Today, according to the latest provisions of the European Directive 851/2018/EC, the share of urban waste that can be disposed of in landfills will be limited to a maximum of 10% by 2035. Waste management needs to be improved and transformed into sustainable material management to protect and improve the quality of the environment, protect human health, to promote a circular economy, to intensify the use of renewable energies and to increase energy efficiency (European Directive 851/2018/EC).

2.2 MATERIALS, TREATMENTS AND EMISSIONS

2.2.1 Refuse Derived Fuels (RDF)

Municipal solid waste (MSW) is a heterogeneous mix of different materials (plastic, paper, wood, organic, food, textiles, etc.), present in varying quantities depending on the habits of the local population and the place where they are produced. Through a series of mechanical-biological treatments, several rejected fraction are produced (Figure 5), and may be used as the raw material for solid RDF, which should have low moisture content and high calorific value that leads to the production of energy. The preparation of RDF is needed in order to eliminate precious or non-combustible materials, reduce their dimensions to use them as an alternative fuel, in order to achieve sustainable management, and produce clean, green energy (Brás et al., 2017).

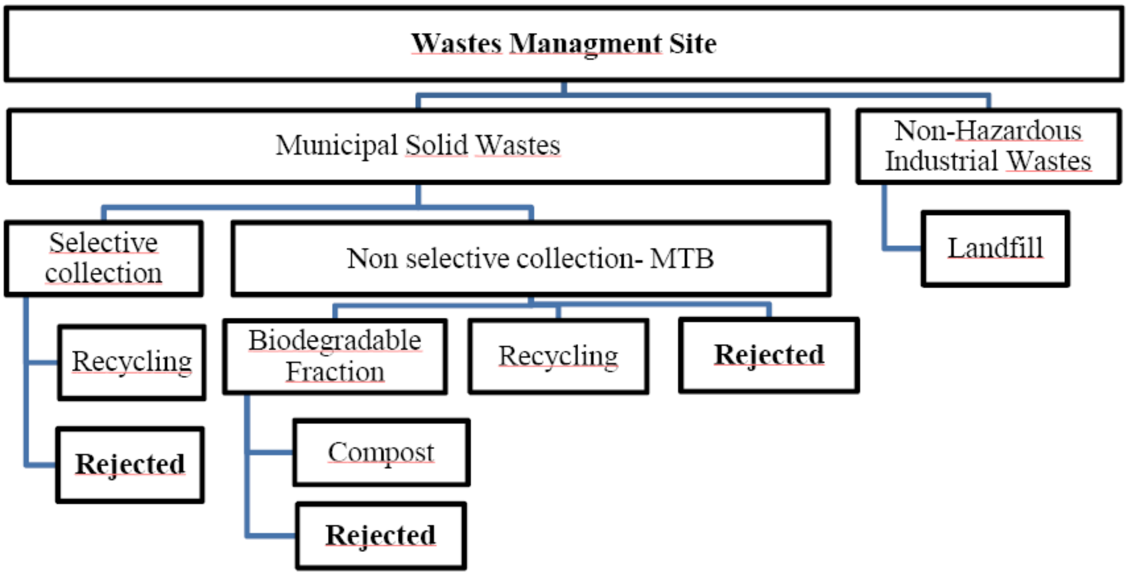


Figure 5. Chart showing the processes in the waste management system (Brás et al., 2017).

The starting point of the RDF production process is the waste management site from which urban solid waste and non-hazardous industrial waste are separated. Non-hazardous industrial waste is sent to landfills, while solid urban waste is divided into selective collection and non-selective collection, passing through a mechanical and biological treatment (MBT). In the selective collection, waste can be placed in various specialized containers (recycling) and of all the materials that can be recycled, plastic best lends itself to complete recycling.

All materials that cannot be recycled and that must be selected and processed by ad hoc systems must directly end up in the undifferentiated collection. For example, glasses, cups and ceramic plates should not be thrown into the glass but into the undifferentiated collection as they are materials that cannot be recycled and that undergo mechanical-biological treatments. The mechanical phase takes place using mechanical systems that separate and classify the various types of waste. The biological phase, on the other hand, consists of the anaerobic digestion and composting of the wet biodegradable parts from the first mechanical phase in the MBT that, with specific unit operations and equipment, separates the biodegradable wet fraction from other differentiated dry fractions (paper, plastic, glass, aggregates, etc.). Part of the last faction of waste can be recycled or sent to landfill but the goal is to use them for the production of RDF fuel.

In this way the use of alternative fuels can solve the problem of lack of space. It also means that new treatment industries can be created and it reduces the use of non-renewable resources, thus improving overall environmental performance.

The ideal structure of RDF consists of a high content of plastic, paper or cardboard, wood or other organic materials. The high heating value is given by paper/cardboard, wood, textiles and plastic. Another important advantage of RDF is its low production cost. It is often used in the cement industry to replace non-renewable fossil fuels by reducing environmental impacts and especially greenhouse gas emissions. The drawback associated with these fuels is their heterogeneity, humidity and ash, chlorine or sulphur content associated with energy density, ignition, combustion and corrosion problems in boilers (Brás et al., 2017).

RDF production may undergo all or some of the following operations:

- source separation;
- mechanical selection or separation;
- volume reduction (breaking up, cutting, grinding);
- separation and selection;
- mixing;
- drying and pelletizing;
- packaging and storage.

The complexity of the RDF production system depends on the characteristics of the raw materials that may be used in their production and the final utilization. Figure 6 shows a fluff type RDF prepared from municipal solid wastes.

Figure 6. RDF composition (plastic, paper, wood, organic, textiles, etc).

2.2.2 Mechanical-biological treatment (MBT)

There are two processes that may be used to treat urban waste: mechanical treatment and biological treatment. These together constitute the so-called mechanical biological treatment, known by the acronym MBT.

MBT selects and separates organic matter from non-organic matter in undifferentiated urban solid waste, with the intention of recovering it for anaerobic digestion. It also aims to recover the fraction of undifferentiated recoverable components, reducing the fraction of urban waste that will be deposited in landfills (Tomé, 2018).

The waste that arrives in a plant is the undifferentiated waste, which is then treated. The first mechanical phase allows the separation and classification of the various components of the waste using automated mechanical systems such as industrial magnets, screens and separators of various types. An electronic optical system sets aside bulky waste and recyclable plastic materials. Subsequently, magnets identify ferrous waste and other metallic materials. Glass and organic materials are subjected to screening. Recyclable components such as paper, metals, plastic and glass and other waste destined for recycling plants are removed from the mass of waste.

Generally organic waste goes towards digestion and composting in a biological treatment, involving the anaerobic digestion and the composting processes of the wet part coming from the first mechanical phase. In the absence of air, anaerobic digestion processes the biodegradable wastes in specific conditions in which biogas is produced. This energetic fuel may be used to produce electricity and heat. What remains after the digestion is subjected to composting, which takes place in a jet of air that leads to the formation of aerobic microorganisms, decomposing the remaining organic matter and stabilizing the final material that can be used as soil amendment. Furthermore, by exploiting the anaerobic digestion or composting of the biodegradable matter, the treatment of waste with TMB makes it possible to reduce greenhouse gas emissions. Figures 7 and 8 show the Planalto Beirão - Ecobeirão mechanical-biological treatment plant.

Figure 7. Selection and separation lines of the MBT.

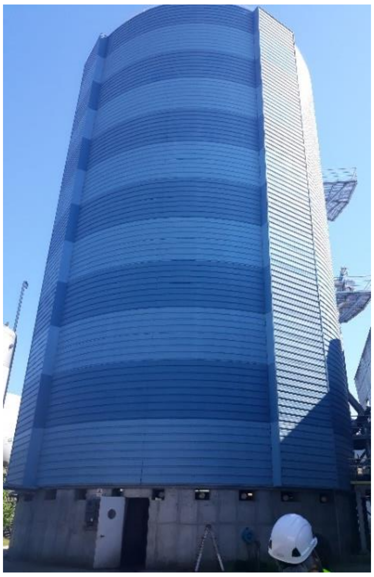


Figure 8. Anaerobic digester for biodegradable wastes.

From all the processes described, part of the non-hazardous waste ends up as waste after being treated, and is usually called rejected fractions. It can possibly become secondary solid fuel - the RDF. These fractions are prepared to obtain a fuel that consists of smaller fragments and that contains a higher energetic value.

2.2.3 Secondary solid fuels (SRF) and related European Legislation

It is important to promote the use of waste-derived fuels, paying particular attention to recovered solid fuels, which have more stable physico-chemical properties than waste and are cheaper raw material than primary fuels (Del Zotto et al., 2015).

A small difference between SRF and RDF is that the former is made only of high calorific waste, while the RDF is made of any type of waste, with the previous removal of inert and hazardous materials (Garg et al., 2007). The former are better than RDFs in terms of quality and heating. They are produced using mostly non-recyclable waste (such as paper fragments, packaging or “dry” non-differentiated fractions), appropriately selected and processed by ad hoc systems. An effective separate collection cycle is therefore a necessary prerequisite for producing quality SRF which can be efficiently exploited as energy. The potential of SRF is particularly great in cement plants, replacing traditional fossil fuels. Due to the capacity of high residence times at high temperatures, these allow the total destruction of polluting organic substances, in addition to the reduction of urban solid waste management costs.

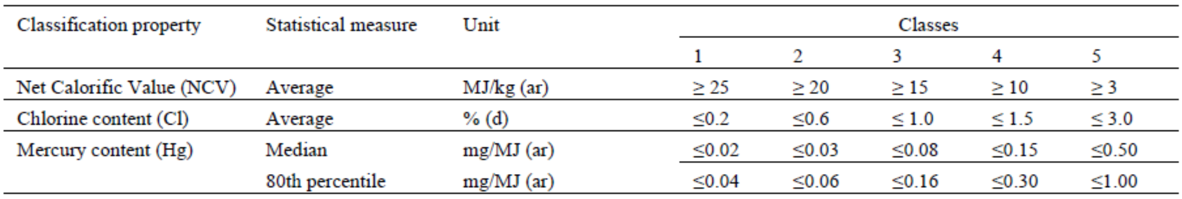
Environmentally, the use of SRFs is an improvement because it makes it possible to replace fossil fuels in industrial plants and reduces emissions of pollutants (such as CO_2, NO_X, metals, etc.). Secondary solid fuels meet specific standards related to fuel parameters (net calorific value, chlorine content and mercury concentration) and quality assurance during the production process. This standardization process improves the marketability of particular fuel flows and the development of quality assurance mechanisms (Del Zotto et al., 2015).

According to the European regulatory framework regarding Solid Recovered Fuels (SFR), it is important to take into account the following standards:

- SRF sampling procedures in accordance with UNI (Italian National Institution of Unification) EN 15442 (sampling methods) and UNI EN 15443 (sample preparation);
- sampling methods by type of plant;
- the calculation of the values of the median of the parameters for the purposes of classification and specification of the SRF in accordance with the UNI EN 15359;
- the SRF quality management system and the requirements for its application in compliance with UNI EN 15358;
- an example of a quality manual and related application model, in the production and marketing of SRF from collection to delivery, in accordance with UNI EN 15358.

In particular, according to UNI CEN/TS 15359 “Solid Recovered Fuels-Classification and Specification” there are 125 classes of SRF, based on the limits for the three properties of the fuel (average value for net calorific value, average value of the chlorine content on a dry basis, average value of the mercury content). Table 5 shows each property divided into five classes by limit value and each one is assigned a number from 1 to 5.

Table 5. SRF classification (UNI CEN/TS 15359).



Classification property	Statistical measure	Unit	Classes				
			1	2	3	4	5
Net Calorific Value (NCV)	Average	MJ/kg (ar)	≥ 25	≥ 20	≥ 15	≥ 10	≥ 3
Chlorine content (Cl)	Average	% (d)	≤0.2	≤0.6	≤ 1.0	≤ 1.5	≤ 3.0
Mercury content (Hg)	Median	mg/MJ (ar)	≤0.02	≤0.03	≤0.08	≤0.15	≤0.50
	80th percentile	mg/MJ (ar)	≤0.04	≤0.06	≤0.16	≤0.30	≤1.00

((d) in a dry state); ((ar) as received).

In Italy the current regulation on SRF has been modified with the issue of Legislative Decree n.205 of December 3, 2010. It establishes sampling methods, definitions and characteristics, parameters of interest and analytical methods, paying attention to the same three main parameters mentioned above: NCV (economic parameter), chlorine content (technological parameter) and mercury (environmental parameter).

2.3 PROCESSES OF ENERGETIC VALORIZATION OF RDF - CHARACTERISTICS, ADVANTAGES AND DISADVANTAGES

Waste management, which is the reality of our daily lives, has been ignored for many years. Population growth, technological developments and industrialization are increasingly producing large amounts of solid waste, which has a negative impact on the environment and public health.

Nowadays, municipal solid waste (MSW) treatments have a serious problem in countries where the population density is very high and the space for landfill is limited. The disposal of waste in specific ground spaces could be a simple and inexpensive method for the disposal of non-recyclable solids but nevertheless causes many serious problems, such as groundwater pollution, due to the leaching of toxic components and emission of odours and contaminants. On the other hand, MSW incineration has many advantages, including a significant reduction in volume (around 70-90%), energy recovery and complete disinfection (Mustafa et al., 2009).

According to Ma and co-workers (2010), incineration is an alternative technology in future waste management, which has the advantage of energy recovery and volume reduction (90%).
The non-combustible materials are removed and processed giving rise to the RDF derived fuel, having a more uniform particle size distribution and a higher heating value than untreated municipal solid waste (Ma et al., 2010).

There are many advantages of RDF and many studies have confirmed this. The benefits of energy recovery from MSW are largely unquestionable, both for the energy benefit itself and for the positive environmental implications, mainly related to the saving of primary energy derived from fossil fuels (Thorneloe et al., 2005). The energy benefits certainly include a reduction in the consumption of natural resources, a sustainable re-use of biomass and greater security of supply. The environmental benefits can be the reduction in the amount of waste destined for landfill, a greater recovery of recyclable materials in previous recycling operations and reduction of greenhouse gas emissions (eg CO_2, CH_4 etc.), fine dust and reduction of NOx and SOx (Del Zotto et al., 2015).

As already defined in the previous paragraphs, RDF is a sort of alternative solid fuel, deriving from urban or industrial solid waste, such as plastics or materials that are difficult to recycle after decomposition, often used in clinker production industries as a secondary fuel, recovering energy and reducing emissions. Considering the scale of global cement production, even a slight decrease in global average emissions per ton can lead to CO_2 reduction and contribute substantially to decrease climate change. Global warming is one of the most critical environmental problems of the humanity. The increase in greenhouse gases leads to global warming and one of the main greenhouse gases produced by human activities is carbon dioxide (Mustafa et al., 2009).

However, the use of RDF in cement kilns also has disadvantages, such as the problem deriving from the chlorine content. When the chlorine content is high, the concrete is weakened in terms of compressive strength of 2, 7 and 28 days (Mustafa et al., 2009). Chlorine compounds and alkali-silica reactions create salts. These salts generate microfractures and the compressive strength decreases (European Committee for Standardization [ECS], 2002). Furthermore, chlorine also creates iron oxidation in the concrete (Mustafa et al., 2009).

Another drawback associated with these fuels is their heterogeneity, humidity and ash or sulphur content associated with energy density, ignition, combustion and corrosion problems in boilers (Brás et al., 2017).

2.4 ENERGY PRODUCTION

The production of energy from carbonaceous wastes in biochemical, thermochemical and mechanical processes (Figure 9).

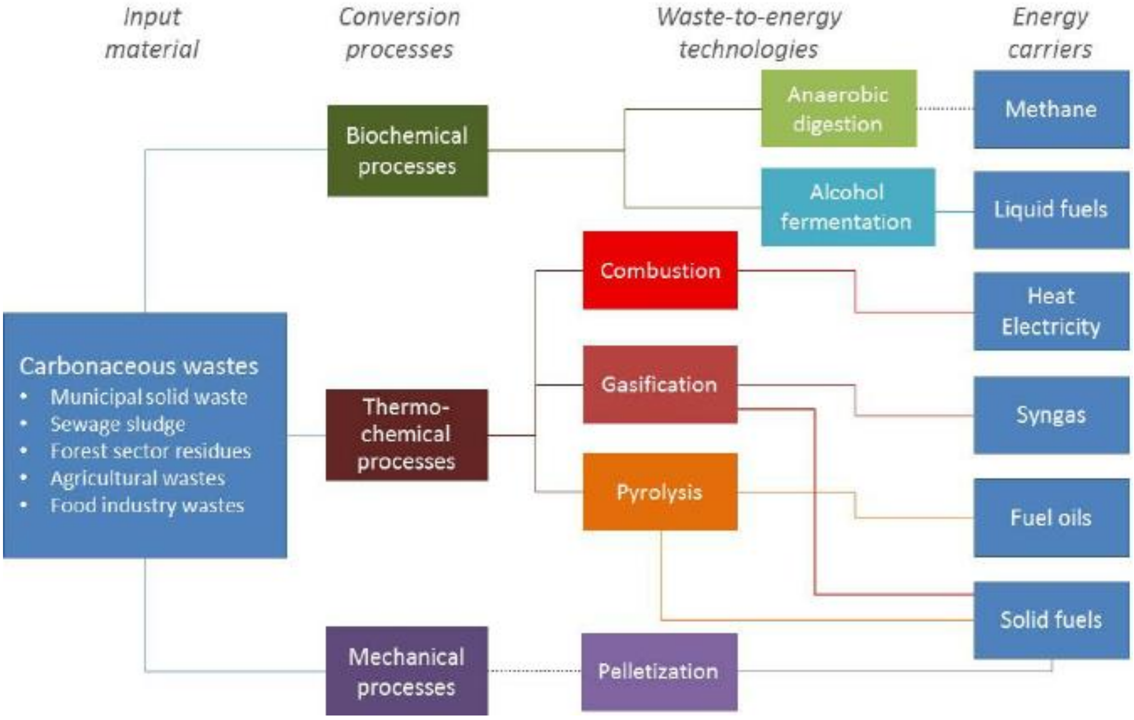


Figure 9. Processes of energy recovery from fuels (Calò and Pongracz, 2013).

Pelletisation in the mechanical process to increase the density of the material by compression, allowing better conservation and transport. The compaction in the form of pellets gives properties of resistance to the solid product, in addition to the reduction of odours and loss of dust.

Anaerobic digestion and alcoholic fermentation are part of the biochemical processes. They allow energy to be obtained through chemical reactions combined with the contribution of enzymes, fungi and microorganisms that are generated in biomass, waste and agricultural and animal by-products (Cocchi, 2014). Anaerobic digestion is an excellent technology for producing energy from waste even on a very small scale. It is commercial and is suitable for the production of energy from organic waste, sludge and waste from the food industry. The biogas produced can be used as a fuel for transport or combined heat and power (CHP) (Calò and Pongracz, 2013).

Alcoholic fermentation allows to produce bioethanol which is an alcohol, to be produced starting from the sugars and carbohydrates contained in different agricultural products (Cocchi, 2014).

The thermochemical processes, on the other hand, mainly include combustion, pyrolysis and gasification and are based on the action of heat that allows the transformation of matter into energy through chemical reactions. Combustion is the most direct and most commonly used process in converting biomass into energy. However, this conversion involves high complexity due to the physical and chemical aspects involved (Quaak et al., 1999; Van Loo and Koppejan, 2008). Combustion is an ancient and very common technology for cogeneration and is suitable for energy recovery from a wide range of mixed solid waste.

Today, around 90% of the energy used in transport and the production of electricity and thermal energy comes from the combustion of the various fuels available. Despite the forecast of a decrease in this percentage, it is estimated that combustion will remain the most commonly used energy conversion process in the coming decades (Coelho and Costa, 2007). The temperatures reached in combustion are very high, of the order of 2000 °C, and therefore the heat generated can be used for the generation of steam for thermoelectric purposes or for other industrial uses (Galloni and Guazzoni, 2010).

Once the ignition of the biomass combustion takes place, it is followed by a sequence of different phases. Heat is produced which allows the material to dry and this depends on the initial moisture content. When the biomass loses moisture, its temperature increases and subsequently the volatilization phase takes place, in which the volatile species contained in the fuel are released, namely volatile substances. After this process coal combustion begins, leaving the inorganic part of the biomass, the ashes (Dias, 2002). Normally combustion starts when there is an external heat source and the small parts of a mixture of combustible and oxidizing agent are present and once the conditions of temperature and pressure are reached (Pinho, 2005a).

According to the study by Werther et al. (2000), if biomass has a high moisture content, it can cause poor ignition, reducing the combustion temperature, which makes it difficult to burn the reaction products and, in turn, affects the quality of combustion. The direct combustion of the RDF produces electricity, as with other traditional fuels, using the heat produced by the reaction to heat the water and produce vapour, which is then sent to the turbines. This process gives rise to a series of unwanted products such as ash and unusable solid deposits, as well as an enormous amount of carbon dioxide. By definition, combustion is a redox chemical reaction, which requires a fuel and an oxidant (typically the oxygen contained in the air) as reactants. The products are usually carbon dioxide, water and heat.

Pyrolysis, however, is seen as a more commercial technology, is used on a large scale, and the product is pyrolysis oil (Calò and Pongracz, 2013). Pyrolysis is very important for energy recovery from biomass, since biomass has a high volatile content that can fluctuate on average between 80 and 85% (Nussbaumer, 2003). The quantity and type of products released during pyrolysis depend, among other factors, on the type of fuel, temperature, pressure, heating rate and reaction time (Van Loo and Koppejan, 2008). The products released are mainly H_2O, CO_2, CO, light hydrocarbons (mainly CH_4) and H_2 (Coelho and Costa, 2007).

According to the study by Galloni et al. (2010), pyrolysis begins once the drying phase is over, followed by an increase in temperature, after which the solid begins to decompose releasing volatile substances. By definition, pyrolysis is a process of thermochemical decomposition of organic materials, obtained by applying heat and in the complete absence of an oxidizing agent. The nature of the substances that are obtained depends on the temperature and the starting solid, in general they are:

- TAR (Topping Atmospheric Residue): high molecular weight hydrocarbon compounds found in the gas phase only due to the high temperature;
- Gas: low molecular weight hydrocarbons (methane, ethane, in condensable, etc.)
- Char: residual solid matrix that is obtained at the end of the volatilization, has a very high carbon content and a morphological structure similar to coal, as well as a high porosity.

The TAR and the gas then undergo a gas phase gasification process which leads to the formation of CH_4, H_2 and CO. The char instead undergoes a heterogeneous reduction / oxidation process with the production of CO, CO_2, H_2 and CH_4 (Galloni and Guazzoni, 2010).

The last thermochemical technology is the gasification, where a gas is formed from the solid combustible. Gasification gives rise to gases that can be used as transport fuels in special vehicles, chemical products or further transformed into liquid fuels. Syngas (or synthesis gas) refers to a gas mixture, essentially consisting of carbon monoxide (CO) and hydrogen (H_2), with the presence in varying quantities of methane (CH_4) and carbon dioxide (CO_2). The transformation takes place at very high temperatures (around 1000 °C) in a special thermal degradation that leads to the creation of the gaseous synthesis mixture. This is then used inside a cogenerator to produce thermal and electrical energy, which, deriving from the synthesis of pre-existing organic materials, is considered renewable energy. Generally, the gasification process consists of several phases. In the first phase, called drying, any presence of water is eliminated from the biomass; then follows the pyrolysis process, by which, in the absence of oxygen, high temperatures lead to the release of gaseous compounds such as hydrogen and methane, but also of coal (char) and tar (tar). Once the volatile products and the fuel coal react with the oxygen then the combustion process takes place, which brings the necessary heat to the final phase, the actual gasification. In this last endothermic process, also called reduction, the fuel reacts with carbon dioxide and water vapor leading to the creation of the Syngas.

The syngas which has not combusted maintains the energy properties of the solid fuel. Currently, synthesis gas is mainly produced from natural gas, coal or by-products of refineries.

There are many benefits deriving from the production of syngas to apply gas engines, namely (Clarke Energy, ?):

- Generation of renewable energy
- Conversion of problematic waste into useful fuels
- Economical on-site energy production and reduced transmission losses
- Reduction of carbon emissions

According to several studies, the installation of a gasifier is of fundamental importance, because it brings numerous advantages such as the production of renewable energy from biomass and the non-increase in the amount of CO_2 released into the atmosphere after combustion, since the same stored amount of CO_2 is released during photosynthesis (this is the reason because biomass is defined as a renewable energy source with zero emissions) (Filosofia Ambientale, 2016).

2.5 ENVIRONMENTAL IMPACT OF RDF UTILIZATION

Currently there is a growing focus on environmental issues such as global warming or the uncontrolled presence of waste and its lack of proper management. Biomass fuels or those derived from municipal solid waste are sustainable alternatives to fossil fuels and a source of neutral CO_2 energy. They can address concerns about climate change, reduce the environmental impacts of fossil fuels use and potentially improve energy security. However, despite the advantages, RDF combustion can be a source of atmospheric pollution because it might produce volatile organic compounds (VOC), PA (polycyclic aromatic), metals and PM (particulate matter). In particular, significant emissions of toxic heavy metals including cadmium, lead and chromium must be controlled (Zhang et al., 2014).

As mentioned previously, biomass can be used for the production of electricity, heating and fuel for transport and has important environmental benefits due to the elimination of waste and the reduction of CO_2 emissions. However, the energy production process of biomass combustion also has the disadvantage of generating large quantities of ash that influence the efficiency of the conversion process (Agrela et al., 2019).

2.5.1 Gas emissions

Despite the positive effects of biomass combustion for the environment, there are also negative effects of pollutant emissions. The most common emission gases are unburned hydrocarbons (HC), carbon monoxide (CO), sulphur oxides (SO_2 and SO_3), nitrogen oxides (NO, NO_2 and N_2O), carbon dioxide (CO_2) and particles (soot and cenospheres) (Coelho and Costa, 2007).

According to the study by Werther et al. (2000) and Khan et al. (2009), emissions from biomass combustion can be sorted into two groups, unburned pollutants, which are mainly caused by the process and combustion equipment, and pollutants of each type of fuel, which are dependent on their properties. Carbon monoxide is the most common of the unburned pollutants. This gas has the ability to react with the haemoglobin in the blood to form carboxyhemoglobin. As a result, haemoglobin is no longer able to capture and transform oxygen and this can cause death (Coelho and Costa, 2007).

According to Nussbaumer (2003), to keep unburned emissions to a minimum, the combustion temperature should be above 850°C and the residence time greater than 0.5 s. The production of carbon monoxide occurs both in the poor mixing regions and in the rich mixing regions. When there is an excess of air, this causes a decrease in the combustion temperature and causes the formation of carbon monoxide. And when the level of air is too low, the mix between the fuel and the oxidizer is difficult and there is not enough oxygen for the complete oxidation of the fuel, which leads to the production of unburned fuels (Van Loo and Koppejan, 2008; Roy et al., 2013).

As for the NO emission, according to the study by Coelho and Costa (2007), during a combustion process, it is formed from two different sources: the oxidation of molecular nitrogen present in the combustion air and the oxidation of the nitrogen present in the fuel. When the fuel has no nitrogen in its composition, the formation of NO will exist only because of the oxidation of the molecular nitrogen in the combustion air. Volatile organic compounds (VOCs), such as hydrocarbons (aliphatic and aromatic), alcohols, ketones, organic acids, etc., also cause environmental problems and inorganic compounds, such as hydrogen sulphide (H_2S), mercaptans, ammonia (NH_3), etc.

These pollutants, once released into the atmosphere, can cause a pollution problem on a local scale, such as odours and even on a regional/word scale, such as acid rain or photochemical ozone production (Schirmer, 2004).

Along with the VOCs there are also polycyclic hydrocarbons (PAH) and dioxins, which are all classes of organic molecules of non-natural origin produced by human activity.

They are toxic, carcinogenic and polluting (Li et al., 2014). Therefore, from an environmental point of view, it is necessary to limit and control gas emissions because they influence climate change, the growth and decay of plants and the health of humans and animals (Schirmer, 2004). In addition to these pollutants, often in waste-to-energy plants, after waste incineration, solid residues or bottom ash are deposited on the bottom of the combustion chambers and fly ash is produced and transported by combustion gases.

2.5.2 Solid emissions - bottom and fly ash

By definition, the ashes are the inorganic part of biomass and RDF, containing mainly mineral matter, which depends on the type of fuel used (Hansen et al., 2009). The ash formed during the combustion of the biomass can be subdivided into heavy or bottom ash and fly ash. The bottom ash is the fraction produced on the oven grid, during primary combustion, and consists of inorganic components and the unburned biomass fraction. Fly ash, on the other hand, is a finely divided residue that derives from the fuel combustion and is transported by the exhaust gases (Agrela et al., 2019).

Biomass is known, in many cases, to contain dangerous concentrations of trace elements, which will simultaneously produce more potentially dangerous ash. This is why this problem will have to be managed by more stringent waste policies and an evolution of society towards a circular economy (Voshell et al., 2018). In many cases, to allow the recycling of biomass, it is necessary to remove the trace elements for the protection of health and the environment and to implement total ash treatments. According to the study by Vassilev et al. (2013), the annual production of ash produced by the combustion of biomass generated worldwide will continue to increase in the future as biomass will be increasingly used for energy, as it is seen as a zero-emission fuel that will bring benefits for the environment. Policies such as the EU's low-carbon economy roadmap suggest that by 2050 the EU should reduce its GHG emissions by 80% from its 1990 level (European Commission, 2011). In fact, the use of biomass will help reduce greenhouse gas emissions.

According to Vassilev et al. (2013), the ashes entrained in the exhaust gas form coarse ash particles, are rich in elements such as Ca, Mg, Si, K, Al and some unburned organic materials. Within the exhaust gas, the condensation of K, Na, S, Cl and trace elements occurs on these entrained ash particles. But some trace elements contained in the biomass ash are regulated or potentially toxic. In fact, in Europe, the determination of the disposal of ashes in the soil (inert, non-hazardous or dangerous) is subject to the control of leaching amounts of As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se and Zn (Vassilev et al., 2013; VanLoo et al., 2008).

Most metals remain in bottom ash rather than in the fly ash because of they are heavier and particles are larger (Garg et al., 2007). Once burned, biomass ash can contain highly complex chemical substances (metals), which contribute to the difficulties of recycling.

Ash is also produced in the combustion of RDF. High ash levels are prevalent when the RDF sample consists mainly of paper (Grammelis et al., 2010), while in general all plastics contain low quantities of metals (Chiemchaisri et al., 2010), because when they burn they mostly produce pollutants such as dioxins and PAH.

3. EXPERIMENTAL METHODOLOGIES

The experimental methodology is divided into three sections: collection of the RDF and pine sample, physical characterization of the sample and chemical characterization of the sample.

Before compacting the pine (supplied already milled by the Portuguese company PelletsPower) and RDF (supplied by the Planalto Beirão - Ecobeirão waste treatment plant) in pellets, using the pelletizing machine, the RDF milling phase and its mixing with pine wood was performed.

Proximate analysis and elemental analysis and heating value were evaluated, paying the utmost attention to the chemical properties of the sample (RDF and pine mix).

The mixes that studied were:

- Pellets only with pine (100%)
- Pellets with 5% RDF and 95% pine
- Pellets with 10% RDF and 90% pine
- Pellets with 15% RDF and 85% pine.

All the assays were done, at least, in triplicate.

3.1 PROXIMATE ANALYSIS

Proximate analysis includes determining the following characteristics: humidity, volatile matter, ash and fixed carbon. The method used is gravimetric corresponding to the mass difference between the samples subjected to different temperatures. The exposure of the sample at 105 °C favours the evaporation of water from the sample while the exposure at 550 °C in the muffle, subsequently cooled, according to the European standard EN 15403:2011, determines the ash content. At 900 °C the sample in the muffle leads to the oxidation of the organic substance which is considered all volatile matter and the fixed carbon content is obtained by subtraction from the total mass of all the other contributions.

The experimental results are in Annex A.

3.1.1 Determination of humidity

The reference method for RDF was used to calculate the moisture in the pellet sample (EN 15414-3:2011). In parallel, the masses of the capsules used in the dryer for each individual sample were quantified.

Subsequently each sample was dried at 105 °C in an oven under atmospheric pressure, up to constant weight, for about 24 hours (Figures 10 and 11). Moisture quantification derives from the mass loss of the sample and is evaluated from Equation 1.

$$\mathrm{Humidity}(\%) = \frac{100 * (\mathrm{m}_{\text{initial of pellet}} - \mathrm{m}_{\text{after drying of pellet}})}{\mathrm{m}_{\text{initial of pellet}}} \qquad \text{Equation 1}$$

Figure 10. Oven at 105 °C with capsules.

Figure 11. Temperature stabilization in controlled environment (dryer).

3.1.2 Determination of ash content

The ash content includes all the mineral components of the sample. These include compounds of aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), silicon oxide (SiO_2), etc. For the determination of the recovered solid fuel ash, according to the EN 15403:2011 standard, each sample was placed at 550 °C in the muffle, for at least 60 minutes, so that the residue after combustion is only the mineral material. Then it was left to cool in a desiccator and then the capsule was weighed with the sample inside (Figures 12 and 13). For the registration of the ash mass, the application of Equation 2.

$$\text{Ashes (\%)} = \left(\frac{\mathrm{m}_{\text{after calcination of pellet}}}{\mathrm{m}_{\text{initial of pellet}}}\right) * 100 \qquad \text{Equation 2}$$

where:

$\mathrm{m}_{\text{after calcination of pellet}}$ is the difference between the mass of the pellet after combustion at 550 °C and the initial mass of the capsule;

$\mathrm{m}_{\text{after drying of pellet (105°C)}}$ is the difference between the mass of the pellet and the capsule after combustion at 105 °C and the initial mass of the capsule.

Figure 12. Muffle for mass determination.

Figure 13. The samples obtained from the muffle at 550 °C.

3.1.3 Determination of volatile solids

The quantification of the content of volatile solids in the samples of pellets under examination, follows the procedure described by the European standard EN 15402 of 2011. The method specified in the European standard is based on the EN 15148:2010 and the ISO 562:2010.

Volatile matter is determined as the mass loss minus that due to moisture, when the recovered solid fuel is heated by contact with limited air under standardized conditions. Each sample is placed in a silica crucible, weighed, and then heated in a muffle at a temperature of 900 °C, for about 7 minutes (Figure 14 and 15). The percentage of volatile matter is calculated from the loss of mass of the test portion after deducting the loss of mass due to humidity. The volatile matter, expressed as a percentage mass fraction, is given by the equation 3.

$$\text{Volatile solids}(\%) = \frac{100*(\mathrm{m}_{(\text{capsule+pellet})\text{before drying}} - \mathrm{m}_{(\text{capsule+pellet})\text{after drying (900°C)}})}{(\mathrm{m}_{(\text{capsule+pellet})\text{before drying}} - \mathrm{mcapsule})} - \text{humidity}(\%) \qquad \text{Equation 3}$$

where:

$m_{capsule}$ is the mass of the empty capsule, in grams;

$\mathrm{m}_{(\text{capsule+pellet})\text{before drying}}$ is the mass of the capsule added to the mass of the sample before heating, in grams;

$\mathrm{m}_{(\text{capsule+pellet})\text{after drying (900°C)}}$ is the mass of the capsule added to the sample mass after heating at 900 °C, in grams;

humidity (%) is the mass fraction of moisture in the sample in percent**.**

Figure 14. Muffle at 900 °C.

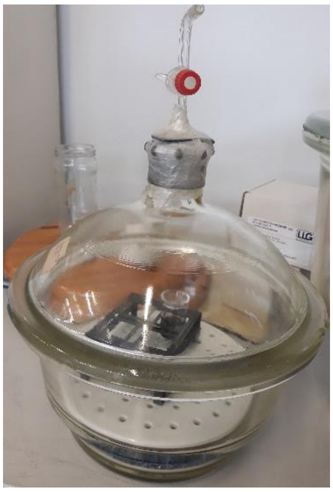


Figure 15. Sample after combustion cools in the dryer.

3.1.4 Determination of fixed carbon

Fixed carbon is the residual fuel obtained by the difference between the value 100 and the sum of the average percentages of humidity, volatile matter and ash, previously determined, according to Equation 4.

$$\text{Fixed carbon}(\%) = 100 - (\text{Avg. volatilesolids}\% + \text{Avg. ashes}\% + \text{Avg. humidity}\%) \qquad \text{Equation 4}$$

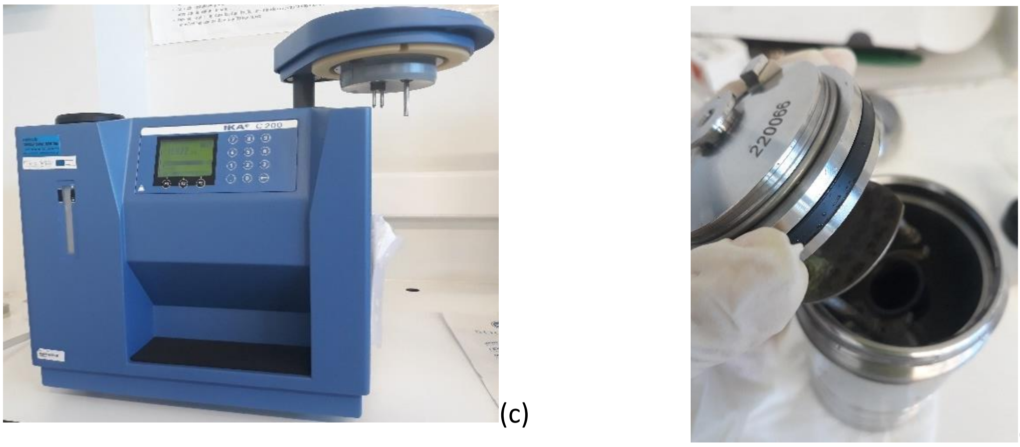
3.1.5 Higher heating value (HHV)

For the determination of the high heating value (HHV) of the samples, the procedure described by the European standard EN 15400:2011 was followed.

An IKA C200 calorimeter (Figure 16) containing pellet samples of different mixture composition (pine and RDF mix) was used, which at the end of the combustion process determines the actual value of HHV, expressed in J/g.


(a)


(b)



(c) (d)

Figure 16. Process of HHV determination:
(a) Pellet mass determination; (b) Oxygen filling; (c) calorimeter; (d) calorimetric bomb.

3.2 ELEMENTAL ANALYSIS

This type of analysis makes it possible to determine the main chemical elements by exploiting their combustion. The quantity of the single elements is usually expressed in percentage form and in the present study the content of chlorine, sulphur and nitrogen was evaluated through a combustion process that took place in the IKA C200 calorimeter.

3.2.1 Determination of chlorine

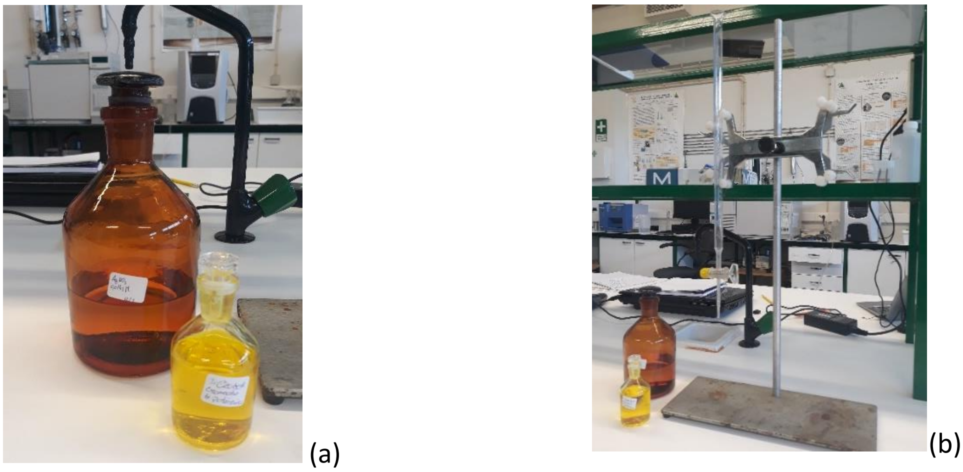
For the determination of the chlorine content in the samples, the IKA C200 calorimeter was used as a combustion instrument. High combustion temperatures (1000°C-1500°C) and oxygen pressure (30 bar) allow the determination of halides released by the combustion gases, absorbed in an aqueous solution. To calculate the total chlorine content, a similar procedure to HHV determination was followed, with addition of 10 mL of potassium hydroxide 0.2 M in the calorimetric bomb to absorb the combustions gases. This solution afterwards was titrated for chlorine determination (Figure 17).
The titration was done with silver nitrate ($AgNO_3$, 0.0141 M), using potassium chromate (K_2CrO_4) as an indicator to obtain a persistent red colour (Figure 17).

The total chlorine was determined according to equation 5.

$$\%\mathrm{Cl} = \frac{(\mathrm{VAgNO3sample} - \mathrm{VAgNO3white})\mathrm{mL} * 0{,}001 * \mathrm{CNaCl} * \mathrm{MMCl}}{\mathrm{msample(g)}} * 100 \qquad \text{Equation 5}$$

where:

- $V_{AgNO3\ sample}$ (mL): volume of $AgNO_3$ spent up to the reddish in the sample
- $V_{AgNO3\ white}$ (mL): volume of $AgNO_3$ spent up to the reddish in the blank test
- C_{NaCl} (M): is the molar concentration of sodium chloride equal to 0.0141 M
- MMCl (g/mol): molar mass of chlorine equal to 35.45
- m_{sample} (g): mass of the sample (pellet)



(a) (b)

Figure 17. Titration of chlorine:
(a) Reagents for titration; (b) Titration system

3.2.2 Determination of nitrogen

Using the IKA C200 calorimeter, as a combustion tool, and the UV/VIS Lambda 25 spectrophotometer was possible to quantitate the nitrate content based on its absorption spectrum, keeping in mind that all the nitrogen in the sample is oxidised to nitrated during combustion.

To achieve this, various procedures were performed in the laboratory similar to the previous described but with the addition of 10 mL of deionized water to the calorimetric bomb previous to the combustion process (Figure 18). This absorbing solution was collected to a 50 mL volumetric flask, and analysed in order to evaluate of nitrate content according with 4500-NO_3^-B: Nitrogen (Nitrate) (APHA, 1998).

To calculate the % of N the equation 6 is used:

$$N\,(\%) = \frac{0{,}0226 * C_{NO_3^-} * V * f}{m_p} \qquad \text{Equation 6}$$

where:

$C_{NO_3^-}$ is the concentration of nitrate in the sample obtained from the calibration line (mg/L) that follows Beer's law up to 11 mg/L;

V the sample volume used in the experimental procedure (L);

f the dilution factor;

m_p the mass of the pellet used in the test (g);

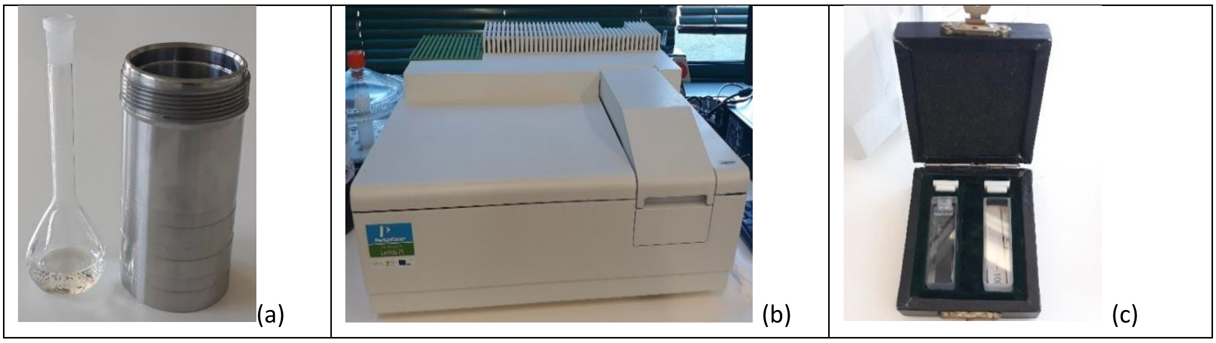


Figure 18. Procedure for nitrogen determination:
(a) absorbing solution; (b) spectrophotometer; (c) quartz cuvettes.

3.2.3 Determination of sulphur

The sulphur determination was carried out by the turbidimetric analysis method of sulphate ions (SO_4^{-2}) precipitated in an acetic acid medium with barium chloride ($BaCl_2$) in the form of uniform crystals of barium sulphate ($BaSO_4$) of the absorbing solution from the calorimetric bomb (4500-SO_4^{2-} E:Sulfate). The absorption of light by the barium sulphate suspension is measured with a spectrophotometer and the concentration of (SO_4^{-2}) is determined by comparison with a standard curve (APHA, 1998). The procedure involves the recovery of the solution, deriving from the pellet combustion process in the calorimetric bomb, to which is added 10 ml of buffer solution and a magnet, followed by stirring using a magnetic stirrer (Labinco L32). During stirring, a dose of barium chloride crystals is added. The spectrophotometric analysis at 420 ηm is performed after transferring the solution into a cuvette, using a Perkin Elmer Lambda 25 spectrophotometer. The reading must be carried out after a rest of the 5 minutes solution (Figure 19). For quantification, the preparation of a calibration curve is necessary, comparing the absorbance reading of the sample with the calibration curve.

The equation 7 was used for the quantification of sulphur (S).

$$S\,(\%) = \frac{0{,}0333 * C_{SO_4{}^{2-}} * V * f}{m_p} \qquad \text{Equation 7}$$

where:

$C_{SO_4{}^{2-}}$ is the concentration of sulfate in the sample obtained from the calibration line (mg/L) according turbidimetric method, APHA 1998;

V the sample volume used in the experimental procedure (L);

f the dilution factor;

m_p the mass of the pellet used in the test (g);

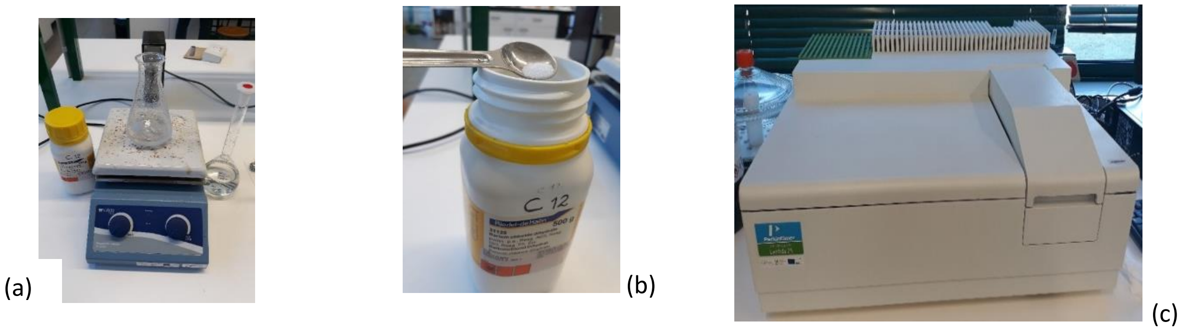

(a) (b) (c)

Figure 19. Procedure for sulphur determination:
(a) absorbing solution agitation; (b) Barium Chloride reagent; (c) spectrophotometer.

3.3 CHARACTERIZATION OF COMBUSTION ASHES

The present work also focuses on the analysis of ash, deriving from combustion in the domestic boiler (with a thermal power of 20 kW), of the mix of pine and RDF (Figure 20).

The heavy metals were analysed according to the European standard EN 15411:2011 and their leaching characteristics according to European standard EN 12457:2004.

Approximately 4 to 5 kg of pellets were burned in a domestic boiler for several replications for each composition of the pine and RDF mix, and in the end of each assay the ashes were recovered.

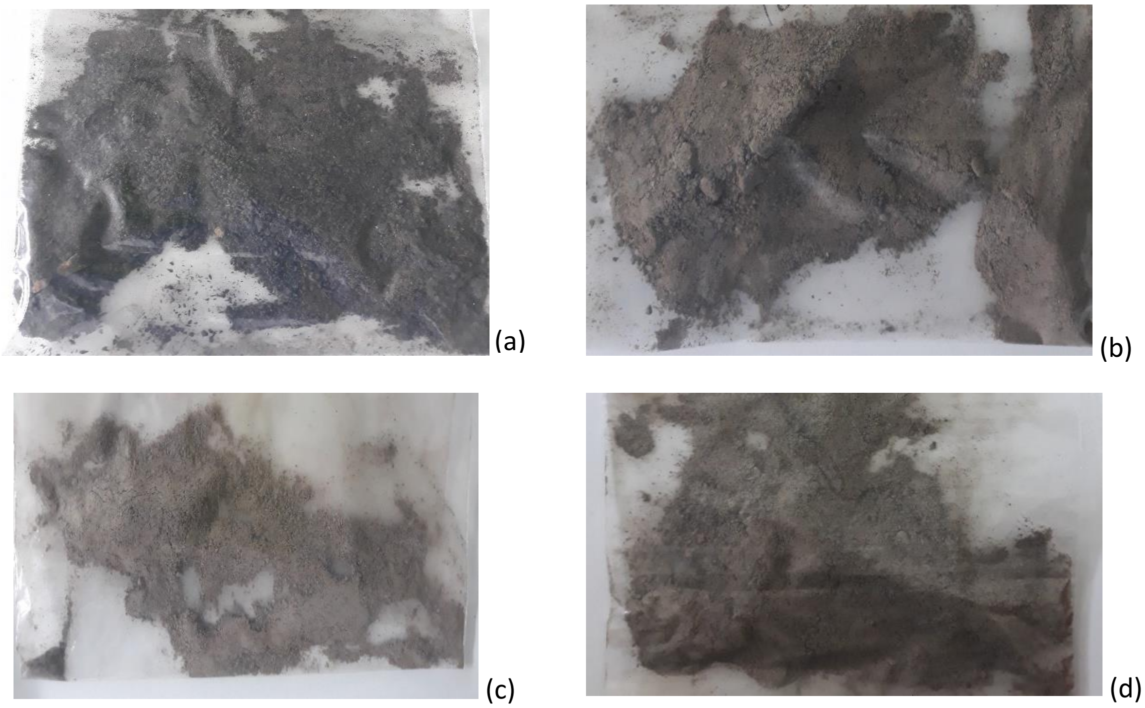


Figure 20. Ashes recovered from the burning processes in the domestic boiler:
(a) pine (100%); (b) 5% RDF and 95% pine; (c) 10% RDF and 90% pine and (d) 15% RDF and 85% pine.

3.3.1 Determination of the heavy metals content

According to the European standard EN 15411:2011 method C, the characterization of heavy metals (Pb, Cd, Ni, Cu, Zn, Cr) contained in the ash samples was carried out. These elements were evaluated according with previous knowledge of pine and RDF composition. The determination consists of a series of procedures (Figure 21):

- weigh 0.5 g of ash for each pellet composition;
- take a glass tube for each sample and add to the weighed ash, 10 ml of an acid mixture prepared by mixing 95 ml of nitric acid and 5 ml of perchloric acid;
- let each tube rest in a digester at 190 °C for at least 10 hours;
- after cooling, the solutions obtained from the digester are transferred to 50 ml containers using a filter.

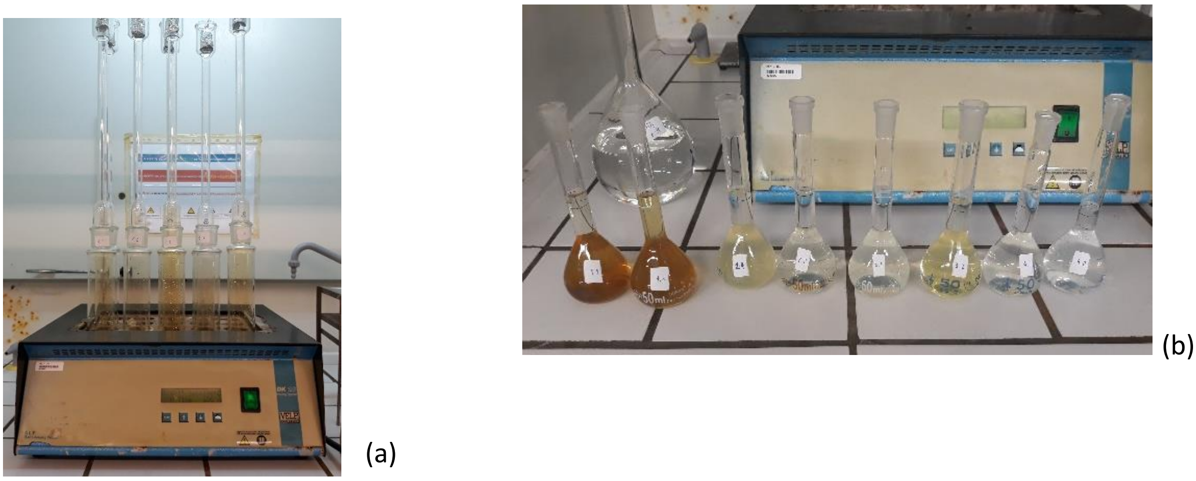


Figure 21. Determination of heavy metals in the ashes:
(a) tubes in a digester and (b) solutions obtained from the digester for elemental determination by atomic absorption spectrophotometry.

3.3.2 Leaching procedure - Hazard classification

According to the European standard 12457-4, after the application of the leaching test we proceed with the characterization of the eluates. The following procedure was performed:

- weigh approximately ± 5 g of ash sample;
- take a vessel for each sample, add the weighed ash and 50.0 mL of deionized water;
- place each vessel on the thermostatic bath at 20ºC and shake for about 24 hours;
- let the vessels rest for about 15 minutes and then filter with filter paper with an vacuum system;
- measure the volume of the eluate, the conductivity (in mS/cm), the temperature (in °C) and the pH of the eluate (and optionally the redox potential Eh in mV)

For a more detailed view of the procedure, the relative photos are in figure 22.

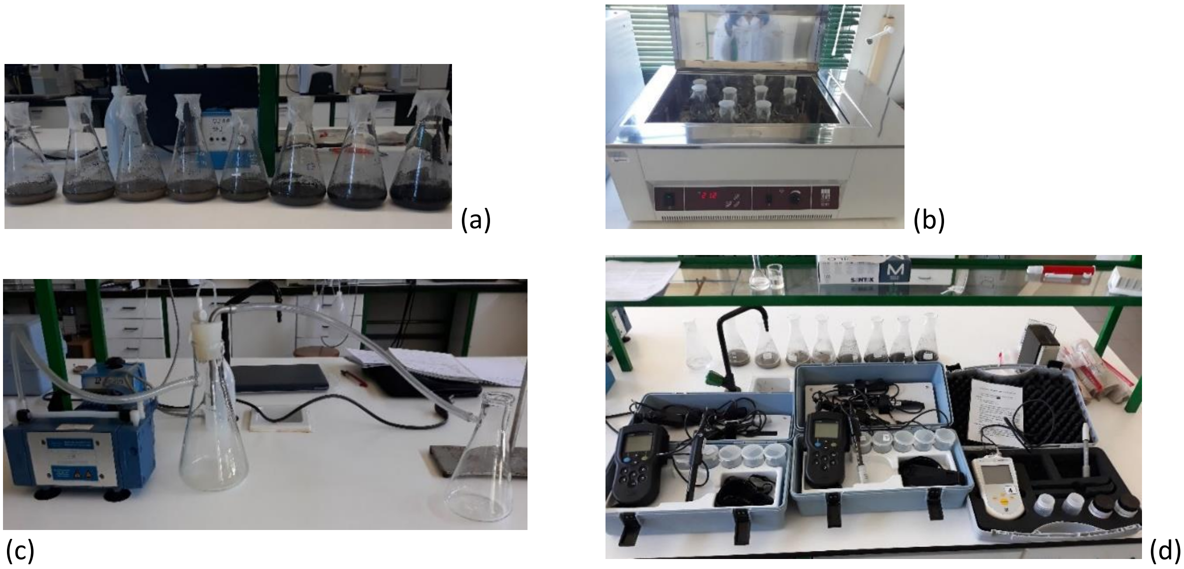

(a) (b) (c) (d)

Figure 22. Leaching test:
(a) Vessels with ash and deionized water; (b) Agitator with samples; (c) filtration vacuum system and (d) electrodes for measuring conductivity, temperature, redox potential, pH.

Trace metals content was evaluated according with EN 15411:2011 standards using a Perkin Elmer Atomic Absorption Spectrometer. All the calibration curves are shown in Annex B.

4. RESULTS AND DISCUSSION

In this chapter the experimental results obtained in the laboratory will be shown and analysed, carrying out the determination of the calorific potential, the proximate and some elemental analysis of the mixes and of the heavy metals contained in the ashes, of the different mixtures of pine and RDF. In particular we will discuss the higher heating value, humidity, ash, volatile matter, fixed carbon, chlorine, nitrogen, sulphur for the raw materials and the heavy metals (Cu, Cr, Cd, Pb, Zn, Ni) for the ashes.

4.1 CHARACTERIZATION OF PELLETS - PROXIMATE ANALYSIS

The proximate analysis is a thermogravimetric analysis technique, during which the progressive weight loss of the sample is measured. Through this analysis it is possible to determine the moisture content, volatile matter, ash and fixed carbon (Galloni and Guazzoni, 2010). Proximate analysis is essential because it provides fuel performance through analytical methodologies. In figure 23 the results are shown.

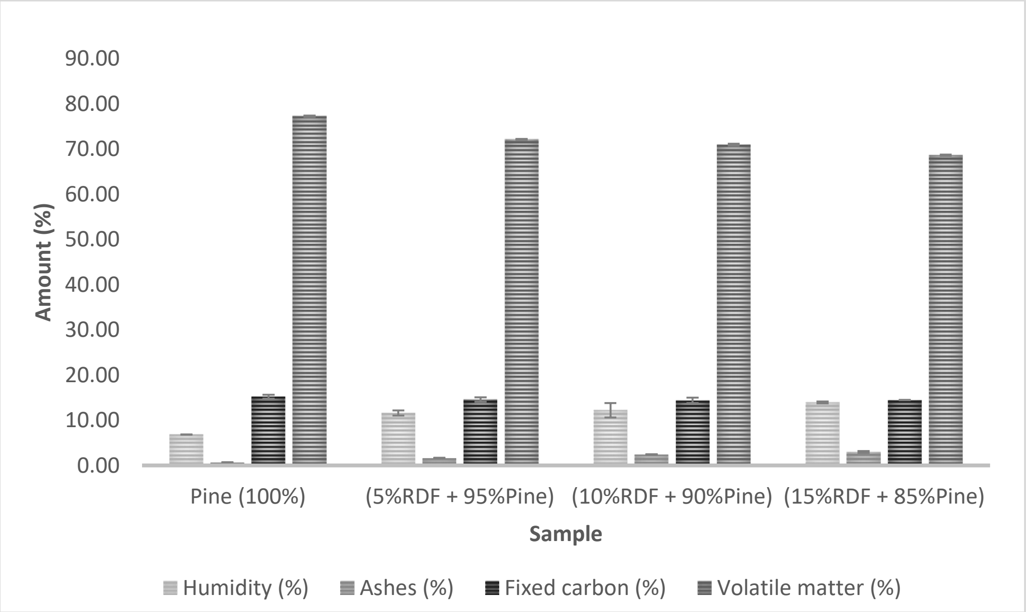


Figure 23. Proximate analysis of the pellets prepared with different mixes of pine and RDF.

4. RESULTS AND DISCUSSION

The percentage of humidity in the samples of pellets studied (pine100%, 95% pine + 5% RDF, 90% pine + 10% RDF, 85% pine + 15% RDF) generally should be higher for pellets of pine alone (6.84%), instead the humidity in the pellet is higher in the presence of RDF. Only pine showed humidity of 6.84%, while for the mix 95% of pine and 5% of RDF the percentage of humidity is 11.64%, with 10% of RDF is 12.22% and with 15% of RDF is 13.93%. These results arise from the pellets production phase where it was verified that the raw material in the presence of RDF was not compacted to the point of obtaining pellets, so it was necessary to increase the addition of water, what outcome in an increase in the percentage of humidity. Is also possible to see that the ashes increase with the addition of RDF (and at the same time as the percentage of pine decreases) because the composition of the RDF is varied and where the sample consists mainly of paper, after its combustion a greater percentage of ash is found. Volatile matter and fixed carbon decrease with the addition of RDF. Urban waste generally consists of different product categories (paper and cardboard, textiles and wood, plastic materials, metallic materials, inert materials and organic fraction) and subjected to a mechanical biological treatment in landfills, giving rise to solid fuel derived (RDF) become drier as the organic fraction present in it decreases.

This explains why the decrease in pine in the analysed pellet sample (pine and RDF mix) and in parallel with the increase in RDF, the content of volatile matter (defined as organic matter) decreases as well as the % of fixed carbon, seen as residual mass after the release of the birds. In fact, for the volatile material we go from a value of about 72.12% (in the case of 5% RDF) to one of 68.66% (with 15% RDF), the same trend for fixed carbon or from 14.60% (with 5% RDF) reaches 14.45% (with 15% RDF).

The humidity influences both the quality of the gas produced and the thermochemical conversion of the energy; its high value leads to a reduction in the superior calorific value and a low thermal input (Brás et al., 2017). Also, according to Khan et al. (2009) and Vounatsos et al. (2015), humidity is an important property with great influence on the calorific value of the fuel, as well as on the combustion process. The higher the moisture content, the lower the calorific value, since more energy will be required for the evaporation of the water present in the fuel. Biomass that has a high moisture content needs more time to dry, which causes a delay in ignition. In turn, there is also a delay in pyrolysis and coal combustion, reducing the combustion temperature and leading to a decrease in volatile combustion (Grammelis et al., 2009).

The ashes are the inorganic part of the biomass that is not used, they mainly contain mineral matter and its content depends on the type of biomass (Hansen et al., 2009). This property of biomass negatively affects the costs of managing and processing energy conversion technologies (McKendry, 2002). Also, according to Beckmann and Ncube (2007) the higher ash content in RDF can influence both handling and processing costs and energy conversion costs. From the analyses of Grammelis (et al., 2009) the ash comes mainly from the paper included in the RDF samples, since as can be concluded from Chiemchaisri (et al., 2010) plastic bags, and in general other plastics include low quantities of ashes. In fact, the percentage of ash can be reduced by decreasing the content of the paper and, respectively, increasing the plastic content. In agreement with what has been studied by Zajac et al. (2019), the high ash content results in a significant reduction in energy efficiency because it implies combustion at low temperatures

Volatiles are a series of organic substances, mostly combustible gases, which are estimated as weight loss in the second heating phase under inert atmosphere (Galloni and Guazzoni, 2010). According to McKendry the volatile content is the organic part of the biomass that is released as a gas (including water) in the first 7 minutes, when it is heated to a temperature of 950 °C (McKendry, 2002). Typically, biomass has a high content of volatile substances (Obernberger and Thek, 2004). Fixed carbon, on the other hand, is the residual mass after the release of the birds, excluding the ash (McKendry, 2002).

In the figures 24 and 25 is possible to do a parallel between the results achieved in the present work and some data presented by other authors.

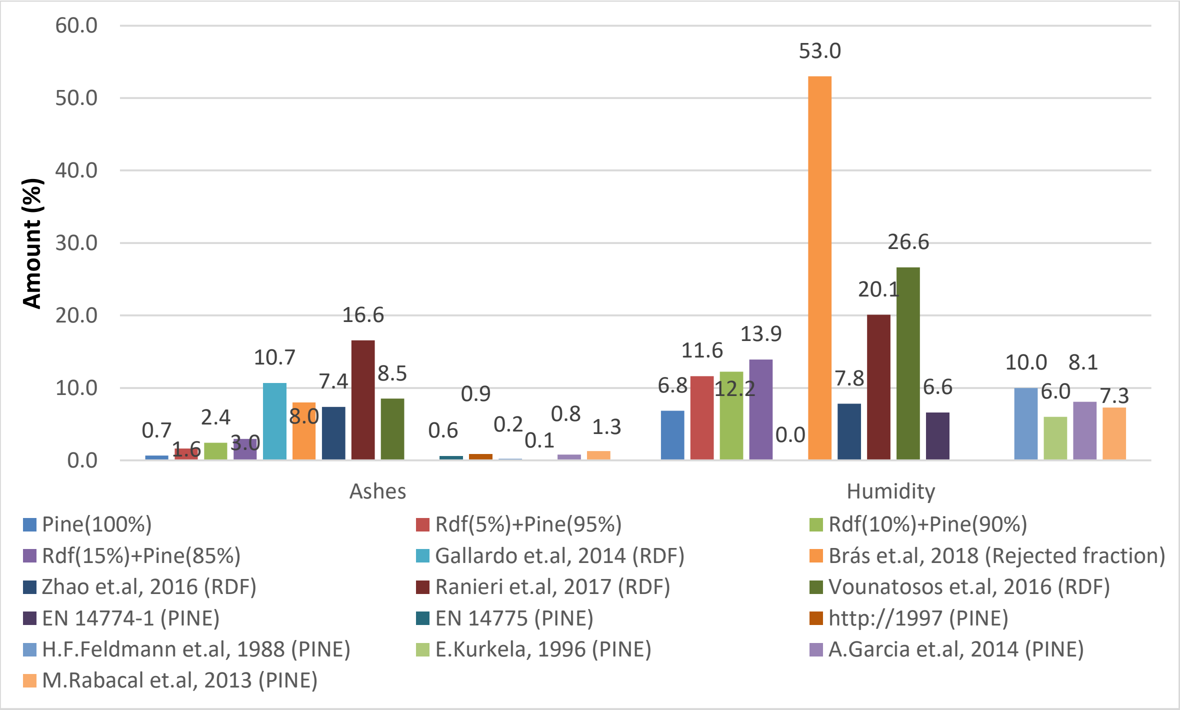


Figure 24. Screening of literature results for humidity and ash content of fuels.

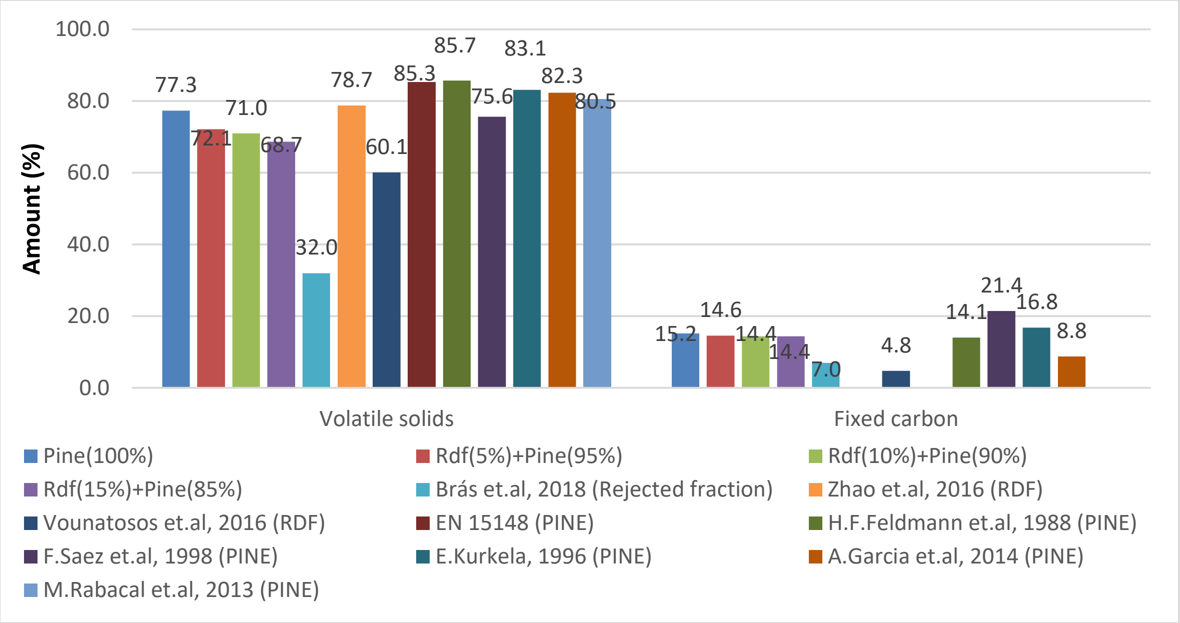


Figure 25. Screening of literature results for volatile matter and fixed carbon content of fuels.

The figures show the values of the humidity, ash, volatile solids and fixed carbon analysis of the present work, compared with those of the pine-only pellet and of only RDF of other authors. Comparing the humidity values presented by Zhao et al. (2016), Ranieri et al. (2017) and Vounatosos et al. (2016) with those from the present work it is noticed a big difference in the results, mainly because the later was done with compact pellets and the remaining figures presented were obtained with low density/fluff RDFs. Also is important to notice that the samples of RDF and RDF + pine are heterogeneous, consisting of a multiplicity of materials (paper, plastic, wood, organic, textiles, etc.) and this leads to an oscillation of these parameters.

There is a high deviation of the percentage of humidity with the sample presented by Brás (et al., 2018) that studied the rejected fractions from MBT and selective collection treatment from a waste management site, so these results are from “RDF” samples not treated. As consequence, the volatile matter and fixed carbon are low (all the results are represented in wet basis).

Regarding to the values of the ash content in pine alone (100%) they are almost similar (see Garcia et al., Feldmann et al., EN 14775, Kurkela), the same for RDF alone (Vounatosos et al., Zhao et al., Gallardo et al.). As mentioned before, the increasing of RDF grows leads to a decrease of volatile matter content fixed carbon, therefore higher percentages of volatile matter are noted in the case of pine-only pellets (see Feldmann et al., Saez et al., Kurkela, Garcia et al., Rabacal et al.).

4.2 CHARACTERIZATION OF PELLETS – ELEMENTAL ANALYSIS

In the laboratory, after the proximate analysis an elemental analysis was carried out with the method of combustion in the calorimetric bomb, evaluating the content of chlorine, sulphur, nitrogen and high heating value.

4.2.1 Chlorine, Nitrogen, Sulphur, Higher heating value

The heating value is the key parameter in a fuel. As the purpose of using the RDF is to assess the possibility of traditional fuel replacement, then it is necessary to evaluate their respective value of HHV. The calorific values of the different mixes under study are shown in Figure 26. The results were very similar to all the mixes showing no decrease in the fuel behaviour with the introduction of RDF. While pine presents values around 19714 J/g, the mixes have HHV of, in average, 20252 J/g, 20683 J/g and 21023 J/g for 95:5, 90:10 and 85:15 (pine:RDF) mixes. Considering the data reported for the characterization of pine and RDF, namely the 6.9% of hydrogen in pine of and 6.29% in RDF (Boletim de ensaios nº 516/12, 2012; Tomé, 2018) and the orientation in EN 15400:2011 that provides the formula for calculating the lower heating value (LHV) expressed in MJ/kg (Equation 8), is possible to evaluate this parameter.

$$\mathrm{LHV} = \mathrm{HHV} - (206 * (\%)\mathrm{Hydrogen}) \qquad \text{Equation 8}$$

Where HHV is the higher heating value in MJ/kg and $(\%)\ \mathrm{Hydrogen}$ is the percentage of hydrogen contained in the material, in %. The experimental results are expressed in Table 6, as well as the estimated values for H and LHV.

Table 6. Calorific potential of the prepared mixes and estimation of their hydrogen content.

Sample	HHV (J/g)	H (%)	LHV (J/g)
Pine (100%)	19714 ± 696	6,90	18292
(5%RDF + 95%Pine)	20252 ± 24	6,87	18837
(10%RDF + 90%Pine)	20683 ± 41	6,84	19274
(15%RDF + 85%Pine)	21023 ± 400	6,81	19620

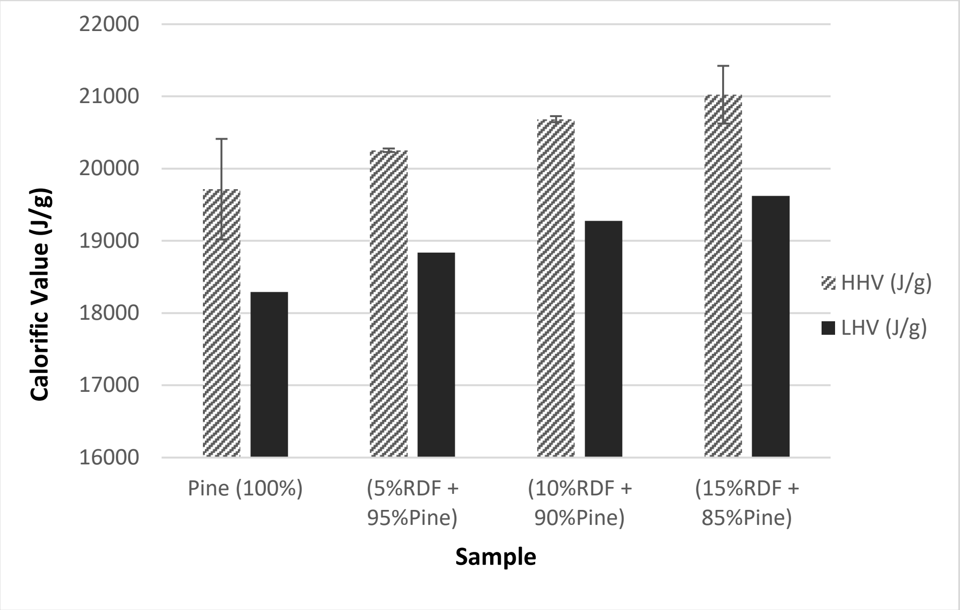


Figure 26. Higher and lower heating values for the different mixes under study.

Since the objective of using RDF is to assess the possibility of fuel substitution, it is important to evaluate its value of LHV. Based on the results obtained, the LHV of the samples are compared with the ones of the most commonly used fossil fuels and that are described in Order No. 17313/2008. In this legal document is referred that biomass pellets have LHV around 16.8 MJ/kg, and coal 29.8 MJ/kg or wood wastes may have LHV between 13.8 and 15.6 MJ/kg. For the mixes produces in this work, values of LHV above 18 MJ/kg were achieved for biomass and higher for the mixes with RDF, what represent a good result and a good perspective for these materials utilization.

The Figure 27 shows the elemental composition of the mixes of pine with different percentage of RDF. The percentage of chlorine obtained from the experimental work turns out to be variable according to the different samples of pellets and is greater in the composition with 10% of RDF (0.08%). Although some results are not expected because adding higher amounts of RDF should represent a proportional increase or decrease of the elemental composition, is possible to conclude that no significant differences were attained. The heterogeneity of the RDF may be the main reason of this variability. Is possible to see that sulphur content is very low with, as expected, the concentration of nitrogen a little higher. These elements are very important once are related with gaseous emissions from the material combustion and consequently pollutant effects, namely in the rain acidification.

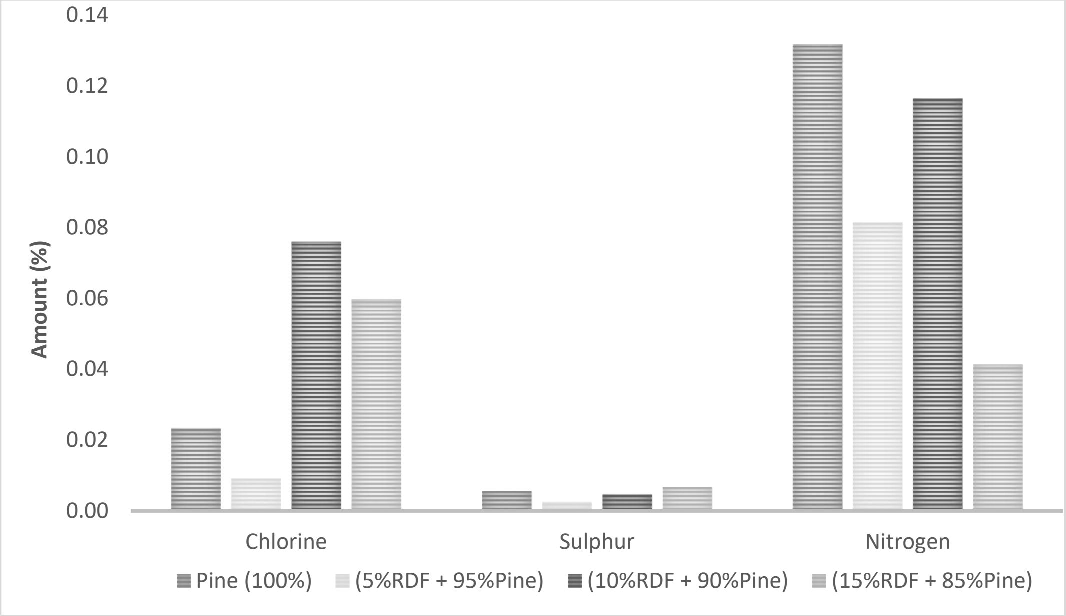


Figure 27. Composition of different mixes under study.

According to the study by Ma et al. (2010), the high chlorine content in MSWs and high-temperature RDFs causes an important mechanism of corrosion and low efficiency in waste-to-energy plants. During combustion the high concentration of chlorine leads to the formation of eutectics in fire ash with a relatively low melting point. These particles condense on the superheaters and over 450 °C the superheater tubes are sensitive to chlorine-induced corrosion.

To reduce the costly problems arising from the presence of chlorine it is important to know its concentration in the waste (Ma et al., 2010). Furthermore, chlorine is a factor that can influence the availability of the boiler in the long term because of its extremely corrosive behaviour, therefore its concentration must be constantly monitored when biogenic fuels are used (Vounatsos et al., 2016).

According to the analysis of Grammelis (et al., 2009) and Wagland (et al., 2011), it is believed that the chlorine content comes mainly from the PVC content, which is a part of the MSW in small percentages, although according with the legal requirements these kind of polymers are not allowed to be present in the RDF.

As far as sulphur is concerned, it is a very widespread chemical element, especially near thermal and volcanic areas. According to the study by Joseph Lewis et al. (2016), the extract-sulphur S, which is a component of liquid and solid fuels, is considered as an important pollutant during combustion and therefore it is important to determine the concentration of sulphur in the fuel using a fast and accurate method. During the combustion of fuels, such as coal and diesel, sulphur is emitted in the form of sulphur dioxide in the atmosphere leading to adverse environmental effects.

4. RESULTS AND DISCUSSION

The large quantities of coal burned by the industry and by the power plants release into the atmosphere sulphur dioxide which reacts with oxygen and water vapor in the air to form sulfuric acid H_2SO_4. This being a strong acid it falls to the ground with rainfall giving rise to the famous acid rains that acidify the soils and water resources. Therefore, various industries rely on both quantitative and qualitative chemical analysis to determine elemental concentrations and compounds in the fuel (Lewis et al., 2016).

Particular attention is also paid to nitrogen. According to a research Jokela and Rintala, (2003) the production and use of synthetic nitrogen fertilizers fixed in food production and biomass growth have more than doubled the flow of nitrogen material, excessive in the community and therefore in the waste disposal system. This nitrogen imbalance in the global cycle has led to uncontrolled release of nitrogen into the atmosphere and water systems.

The anaerobic digestion of MSWs putrescibles could solubilize about 50% of the nitrogen, which is why anaerobic digestion can become an important method to increase the rate of nitrogen recycling towards the ecosystem. The small percentage of global nitrogen (0.02%) that is biologically available is an essential element of life and is classified as the most important element after carbon, hydrogen and oxygen (Jokela and Rintala, 2003).

Atmospheric gas N_2 is the most stable form of nitrogen and high amounts of energy are needed to break the triple bond of N_2. Thus, only a relatively small number of organisms are able to use N_2 in the nitrogen fixation process (Brock and Madigan, 1991). According to the study by Nelson (and Cox, 2000) most of the nitrogen in the mass of living organisms is bound in amino acids, in the form of structural proteins (for example keratin), soluble globular proteins, conjugated proteins, for example glycoproteins, or in the form of organic nitrogen that can be incorporated as nucleic acids in DNA and RNA (Nelson and Cox, 2000)

Contaminated solid urban waste in soils contains high amounts of organic nitrogen in non-degraded waste components. One of the objectives of waste segregation and pre-treatment is to minimize emissions of nitrogen contaminants that can be produced by traditional soil practices (Andreottola and Cannas, 1992).

In order to compare the amount of Cl, N, S and also HHV in the several prepared mixes, the respective amounts are represented in Table 7, as well as some data reported by other authors in order to do a parallel with the results achieved in the present work. Some of the authors of the works mentioned in the tables studied only RDF or only pine (written in the table). Also, when it is mentioned a normative number is because the result refers to pine analysed according to each normative (each related with one element).

Table 7. Amount of N, Cl, S and HHV including data in several other studies.

Material	**N (%)**	**Cl (%)**	**S (%)**	**HHV (MJ/kg)**
Pine(100%)	0.13	0.02	0.01	19.71
RDF(5%)+Pine(95%)	0.08	0.01	0.003	20.25
RDF(10%)+Pine(90%)	0.12	0.08	0.005	20.68
RDF(15%)+Pine(85%)	0.04	0.06	0.01	21.02
Zhao et al., 2016 (RDF)	0.24	0.05		
Vounatosos et al., 2016 (RDF)	1.07	0.51	0.32	
Gallardo et al., 2014 (RDF)	0.90		0.10	21.36
C.Di Blasi et.al, 1999 (PINE)	0.21		0.02	31.11
EN 15104, 2012 (PINE)	0.20			
EN 15289, 2012 (PINE)		0.01	0.01	
EN 14918, 2012 (PINE)				20.28
https://phyllis.nl/Biomass/View/118, 1997 (PINE)	0.14		0.05	22.31
Feldmann , et al., 1988 (PINE)	0.06		0.01	20.14
Saez, et.al, 1998 (PINE)	0.51		0.15	18.75
Kurkela, 1996 (PINE)	0.10			20.17
Garcia, et al., 2014 (PINE)	0.50		<0,01	
Rabacal et al., 2013 (PINE)	0.50		<0,01	
Brás et al., 2018 *in press* (Rejected fraction)	1.18	0.49	0.22	>10

The results reported by Brás et al. (2018) refer the characterization of the rejected fraction from the MTB and the material that was the base of the production of the RDF produced and under investigation in the present work. This fraction is very heterogeneous in terms of its composition and with the presence of non-combustible fraction. The data presented by the authors is very different from the prepared RDF.

Comparing pine with RDF and pine:RDF mixes there are not markedly differences. The data in the table referring to norms EN 15104, EN 15289 and EN 14918 describe the results of pine used in the present work but characterized according to these standards. The first thing to be noticed is that the methodology followed in the present work achieved results very close to the obtained other laboratories and following standard methodologies. In fact, this arise in a high confidence degree in the overall experimental results.

Comparing pine characteristics reported by several authors show a high variability of composition probably depending from region and even tree types (wood pine, pine sawdust, ecc). Taking the data referred to RDF mixes or RDF alone, the chlorine content in the former show a similar trend to the reported by Zhao et al. (2016), 0.05%, but distant from Vounatosos (et al., 2016) that was

0.51%. Vounatosos has classified RDF as 4 (in terms of PCI or NCV), 2 (chlorine content), 1 (mercury concentration) according to European standard EN 15359:2011. The variability of the percentage of chlorine in RDF can be justified by the diversity of the materials making up the fuel itself.

In fact, it is defined as a heterogeneous fuel, and it is impossible to know with certainty the perfect composition of the single pellet. However, chlorine is mainly present in paper (due to previous bleaching) or PVC, therefore, where the percentage of chlorine in the pellet mix or in the RDF is greater, it means that the presence of plastic material prevails, although by law is mandatory to remove this kind of polymer from the fractions to prepare RDF. On the other hand, it can be noted that in the presence of only pine content in the pellet, the percentage of Cl is very low (0.02%) and is similar to that deriving from the standard EN 15289:2012 (0.01%).

For nitrogen and sulphur, the differences between the different samples examined are not so obvious. For pine-only pellets the percentage of nitrogen is 0.13%, similar to the value of Di Blasi (et al., 1999), to the standard EN 15104: 2012, to Kurkela (1996) and Feldmann et al. (1988). Even for pellets containing RDF the values are not very different from the various references. The same goes for the percentage of sulphur, where the maximum value with RDF alone is 0.32% according to the study by Vounatosos et al. (2016).

The results of the present experimental work can be considered satisfactory because the percentage of Cl, N and S is not high. Otherwise it was a problem because these parameters are very important for environmental protection, they are related to emissions of combustion gases that contribute to greenhouse gases and even to acid rain.

The high heating value (HHV) as can be seen from the table, the content is not very different with the addition of RDF in the pellet. Increases with the growth of RDF in the sample and this further affirms the idea of using the solid fuel derived from wastes, instead of fossil fuels, produced greater quantities of clean energy.

We also note a consistency of the HHV values with the other studies, both for pine-only pellets and in the presence of RDF.

4.3 CHARACTERIZATION OF ASHES

Along with the gas emissions, the use of solid fuels has as a consequence the production of ashes. These are divided between solid residues deposited on the bottom (bottom ash) and fly ash transported by the combustion gases. It is the flying ashes that are of most concern because they have higher levels of toxicity due to the high concentrations of volatile metals such as cadmium, lead and mercury, which is why it is important to capture them in such a way as to avoid their release into the atmosphere. It is essential to determine the presence of heavy metals in the ashes, because if present in large quantities they can be dangerous to human health and the environment (Zajac et al., 2019).
Two main ideas were followed: the quantification of heavy metals in the ashes and their toxicity, that is, the availability of these heavy metals to leachate to water and be spread in the environmental after final deposition. The heavy metals evaluated were the previous quantified in the rejected fractions that were used for RDF production, namely Cadmium, Chromium, Lead, Nickel, Zinc and Copper (Brás et al., 2018). Once in the experimental apparatus it was not possible to collect the fly ashes, only the bottom ashes were characterized.

4.3.1 Percentage of ash content of ashes

In order to evaluate the extension of the combustion, it was characterized the ashes, namely to understand if it still had volatiles or were effectively an inorganic material resulting from the combustion. From the total masses of ash of different composition, derived from the combustion in the domestic boiler, about 1 gram of material was weighed for each sample and they were submitted to 550 °C in the muffle (according to the standard EN 15403:2011) for further determination of the ash content.
From the analysis carried out, the results were obtained are shown in Table 8.

Table 8. Average and standard deviation values of the inorganic fraction of the combustion of ashes.

Material	Ashes (%)	
	Average	STDV
Pine (100%)	71.84	6.79
(5%RDF + 95%Pine)	85.71	6.07
(10%RDF + 90%Pine)	87.22	4.81
(15%RDF + 85%Pine)	89.74	4.26

Is interesting to see that the extension of the combustion increased with the amount of RDF, that is, the inorganic fraction of the ashes in the case of 100% pine combustion was only 71.84 % while from mixes with 15% RDF the inorganic fraction was almost 90%.

This means that the material burned better with higher percentages of RDF during combustion.

It is important to keep in mind that from the fuel characterization it arose that biomass had a lower amount of ash compared with the mixes with RDF.

The lower fuel conversion in the furnace can be related with the combustion temperature and the more the temperature increases, the more the percentage of ash decreases and the more volatilization increases inside the furnace (Zajac et al., 2019).

A greater content of volatile matter means a greater quantity of material that burns in the gas phase and consequently a greater probability of producing emissions of gases and fly ash containing concentrations of metals.

On the basis of the results obtained from the present experimental work it can be deduced that from the environmental point of view, a good combustion is that deriving from the addition of RDF in the pellet sample, in particular with 15%, because it shows a percentage of inorganic matter equal at 90% compared to 72% of pine-only pellets.

4.3.2 Composition of ashes

The ash content resulting from the combustion of pellets in the domestic boiler was also characterized in terms of their metals content, in compliance with the European standard EN 15411:2011.

The Table 9 shows the concentration of the metals in the ashes obtained according with EN 15411:2011.

Table 9. Concentration of heavy metals in the ashes from the furnace and estimate of their concentration in the materials before burn (raw materials).

Element	Unit	Sample			
		Pine 100%	5%RDF:95%Pine	10%RDF:90%Pine	15%RDF:85%Pine
Pb	mg/kg$_{ash}$	0.156	3.611	2.917	2.973
	mg/kg$_{rawmaterial}$	0.001	0.059	0.071	0.088
Cd	mg/kg$_{ash}$	0.054	0.045	0.011	0.016
	mg/kg$_{rawmaterial}$	0.0004	0.0007	0.0003	0.0005
Cu	mg/kg$_{ash}$	56	99	110	206
	mg/kg$_{rawmaterial}$	0.368	1.6	2.7	6.1
Zn	mg/kg$_{ash}$	109	794	770	1043
	mg/kg$_{rawmaterial}$	0.717	13.0	18.7	30.9
Cr	mg/kg$_{ash}$	378	555	241	257
	mg/kg$_{rawmaterial}$	2.49	9.11	5.86	7.62
Ni	mg/kg$_{ash}$	90.9	68.2	21.7	10.5
	mg/kg$_{rawmaterial}$	0.598	1.12	0.527	0.313

The estimation of the amount of metals in the raw material is done knowing the percentage of ash for each mix, according to Equation 9.

$$\text{Concentration in raw material} = \text{Cmetals ash} \times \frac{\%\ \text{Ash}}{100} \qquad \text{Equation 9}$$

From the table it arises that the concentrations of the heavy metals contained in the bottom ash from the mixes burning depend of the materials.

That is, for Cd, Cr and Ni, pine seems to have higher concentrations because ashes from 100% pine have higher amounts of these metals, decreasing with the addition of RDF.

For Pb, Cu and Zn, the trend is the opposite. Taking into account the results presented in Table 9 and Table 10, and the materials variability, you can say the results are somewhat expected, except for lead and cadmium, where the concentrations were significantly lower than those reported by Zajac et al. (2019) for pine ash.

The estimate of metals in the raw materials presented in Table 9 intended to understand if the amount of metals present in the unburned material were condensate in the bottom ashes.

If the amount estimated is not similar from the reported from the raw materials (Table 9) it may be concluded that the metals may volatilize in the combustion process and be dragged with the fly ashes and therefore disperse in the gas emissions.

Once the amount of metals estimated in the raw materials (Table 9) are considerably lower than the expected (Table 10) is possible to say that the gas emissions should have high concentrations of metals. The RDF represented in Table 10 was the one used to prepare the mixes under study.

Table 10. Concentration of heavy metals in the RDF, Pine and Pine Ash.

Element	**Concentration in RDF (d.b.)** (mg/kg) (1)	**Concentration in Pine (d.b.)** (mg/kg) (2)	**Concentration in Pine Ash (d.b.)** (mg/kg) (2)(3)
Cu	23.2	145.38	140
Zn	179.3	265.05	250
Cr	16	37.25	40
Cd	0.064	5.6	6
Pb	23.9	9.41	10
Ni	2.4	47.84	40

(1) Tomé (2018); (2) Zajac et al (2019); (3) average concentration for all the temperatures studied by the authors;

Zajac et al. (2019) studied the influence of ash-forming temperature on ash content and the content of selected heavy metals in these ashes, for several type of woods.

They conclude that the increase of the burning temperature leads to a decrease in the amount of ashes produced but also that some metals decrease their concentration in the ashes when the combustion increase while others have the opposite trend.

The authors noticed that for instance Cr concentration is rather high in the ashes while Pb, Cd or Cu have lower concentrations.

Cr is a metal that in combustion (oxidation) technologies remains in condensed (solid) phases, regardless of the oxygen potential of the system and the presence of sulphur and chlorine, while other metals or because have lower boiling point or because form volatile oxides at low temperatures, mainly move to the gas phase (Zajac et al., 2019). This is the case of Pb, Cd and Cu.

Figure 28 shows the concentration of heavy metals in the ash from the combustion test with the different mixes under study, but also the amount of ash from each test (the black line in the graphic). The increase of the combustion efficiency is clear as the RDF increases in the mix because the percentage of inorganics in the ash increases.

With this trend is also found an increase of Zn and Cu in the ashes while for Cr and Ni the behaviour is the opposite.

Pb and Cd are not representative compared with the other metals under evaluation.

Although the results aren't entirely in accordance with the achieved by Zajac et al. (2019) it endorses the need for furthers studies to evaluate the possibility of emission of heavy metals in the solid (bottom ashes) or the gaseous (fly ashes) phases.

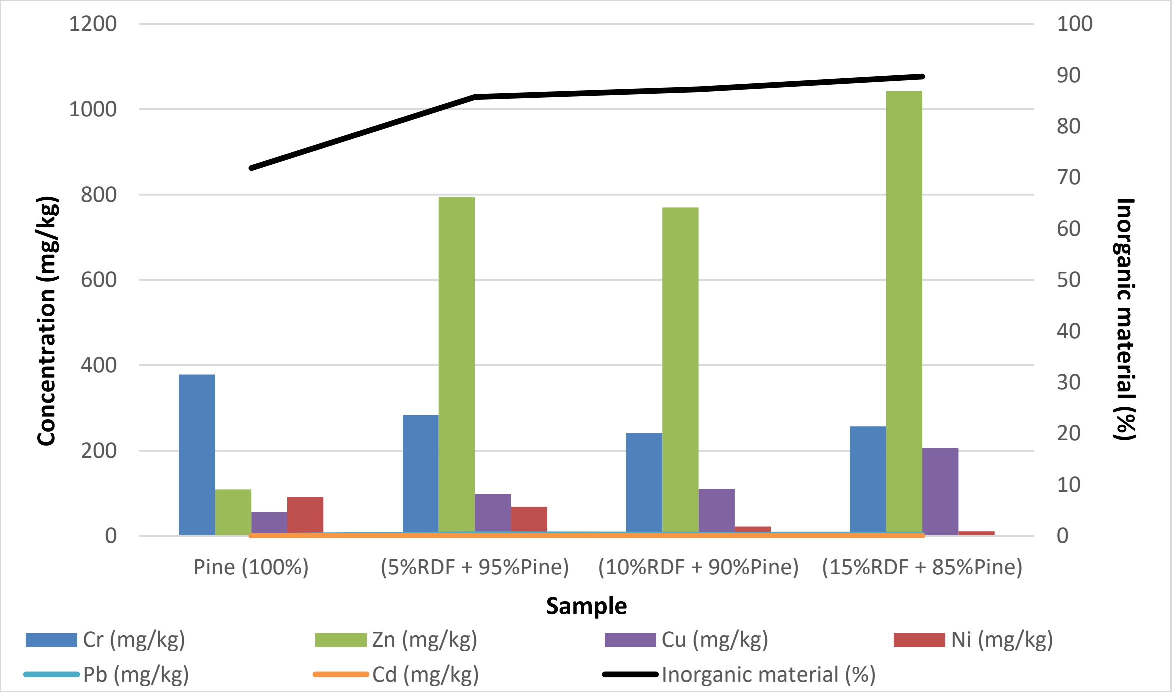


Figure 28. Amount of heavy metals in the ashes and relationship with the inorganic content of the ashes.

High concentration of metals in the RDF or Pine (for example Zn, Cr, Pb and Cd), may suggest contamination by dangerous materials such as batteries, cosmetics and paints (Sharma et al., 1997). But this is not found in this study. Analysing trace metal concentrations as described in Gallardo et al., (2014), the RDF used in this work has much lower concentrations (Table 11).

Even with reference to the Italian legislation - Genon et al. (2008), it is found that the contents in trace metals is much lower than the one established for a quality RDF, opening up good prospects of its use.

A high level of variability is found even when looking for the metal content of the rejected fraction that was used for the RDF preparation. A sampling plan should be done to accurately realize the characteristics of RDF that may be used as fuels.

Table 11. Concentration of heavy metals in different materials that are used to produce fuels.

Sample	**Cu (mg/kg)**	**Cd (mg/kg)**	**Cr (mg/kg)**	**Pb (mg/kg)**	**Zn (mg/kg)**	**Ni (mg/kg)**
Brás et al., 2018 (Rejected fraction)	18.3	0.62	16.7	25.0	547	1.48
Tomé, 2018 (RDF)	23.2	0.064	16	23.9	179.3	2.4
Zhao et al., 2016 (RDF)	15.8	0.1	2.1	4.8	25.7	2.5
Ranieri et al., 2017 (RDF)	51.82	<0.50	9.922	198.31	107.04	
Gallardo et al., 2014 (RDF)	108.92	9.8	135.49	63.86		
Genon et al., 2008 (RDF)	45-266	0.18-2.6	11.3-140	25-157	225-340	
Saez et al., 1998 (PINE)	115		70	22		
Zajaz et al., 2019 (PINE)	145.3	5.6	37.25	9.41	265.05	47.84

The result obtained by comparing the different metal contents present in the pellet sample (of different composition), with the other bibliographic studies, shows lower values of raw material in the pellet under examination.

This can be considered an advantage because as a raw material contains quantities of mineral material that can be toxic for both human health and the environment, and since after a combustion it can also produce fly ash and equally dangerous gas emissions if released into the atmosphere, getting lower concentrations is only a benefit.

4.3.3 Hazard evaluation

The level of hazard of the ashes was evaluated according to the European standard EN 12457.

A study that focuses in particular on the properties of ash and the potential re-use of two types of waste (RSU and RDF) as fuels, that followed the TCLP (toxicity characteristic leaching procedure), showed that the low ash generated by the combustion of MSW and RDF can be classified as non-hazardous materials, but both types of fly ash require post-treatment due to higher contents of heavy metals (Ni-Bin et al., 1999).

The leaching procedure is a method of sample extraction for chemical analysis, used as an analytical method to simulate leaching.

The methodology of this test is important to determine if a waste is dangerous, if it can be classified as a waste to be disposed of in a hazardous landfill or in a common municipal landfill. It also determines the presence of possible contaminants in the waste that can lead to risks for public and environmental health. We followed European standard EN 12457-4:2002 "Waste characterization" - Leaching - Conformity test for the leaching of granular waste and sludge - Part 4:Single stage test, with a liquid / solid ratio of 10 l/kg, for materials with particles smaller than 10 mm (with or without reduction in size). This standard specifies a conformity test which provides information on the leaching of granular waste and sludge under the specified test conditions, and in particular with a liquid/solid ratio of 10 l/kg of dry substance. It applies to waste smaller than 10 mm with or without reduction in size. According to the EN 12457-4 standard, some factors influencing the leaching of contaminants from waste are the pH, the ratio between liquid and solid, the reduction in size that leads to a change in the pH of the eluate and the properties of the waste.

Also, the temperature influences the solubility of the components, in particular the waste containing degradable organic matter can be influenced by biological processes that depend on the temperature (EN 12457-4, 2002).

The hazard assessment is done according to the Decree Law 183/2009 of May 23, that establishes the legal regime for landfills, the technical characteristics and the requirements to be observed in the design, licensing, construction, exploitation, closure and post-closure of landfills, transposing the Directive 1999/31/CE of April 26, 1999, relating to landfills.

In this legal document are defined the limit values for leaching non-hazardous waste and are specified in Table 12.

Table 12. Leaching limit values according to the D.L.183/2009 (Annex IV, Table 4).

Leaching limit values (D.L.183/2009)	
Component	**Concentration (mg/kg)**
Cd	2
Cr	20
Pb	10
Ni	10
Zn	50
Cu	50

Some physical and chemical parameters of the leachate solution are represented in Table 13 and in Figure 29, namely pH, conductivity and temperature.

Table 13. average and standard deviation value of pH, conductivity and temperature.

Materials	**pH**		**Conductivity (mS/cm)**		**Temperature (°C)**	
	Average	STDV	Average	STDV	Average	STDV
Pine (100%)	12.44	0.13	10.19	0.21	20.60	0.28
(5%RDF + 95%Pine)	11.21	0.32	4.21	0.20	20.55	0.07
(10%RDF + 90%Pine)	10.78	0.22	3.59	0.11	20.80	0.00
(15%RDF + 85%Pine)	10.48	0.19	2.90	0.27	21.35	0.07

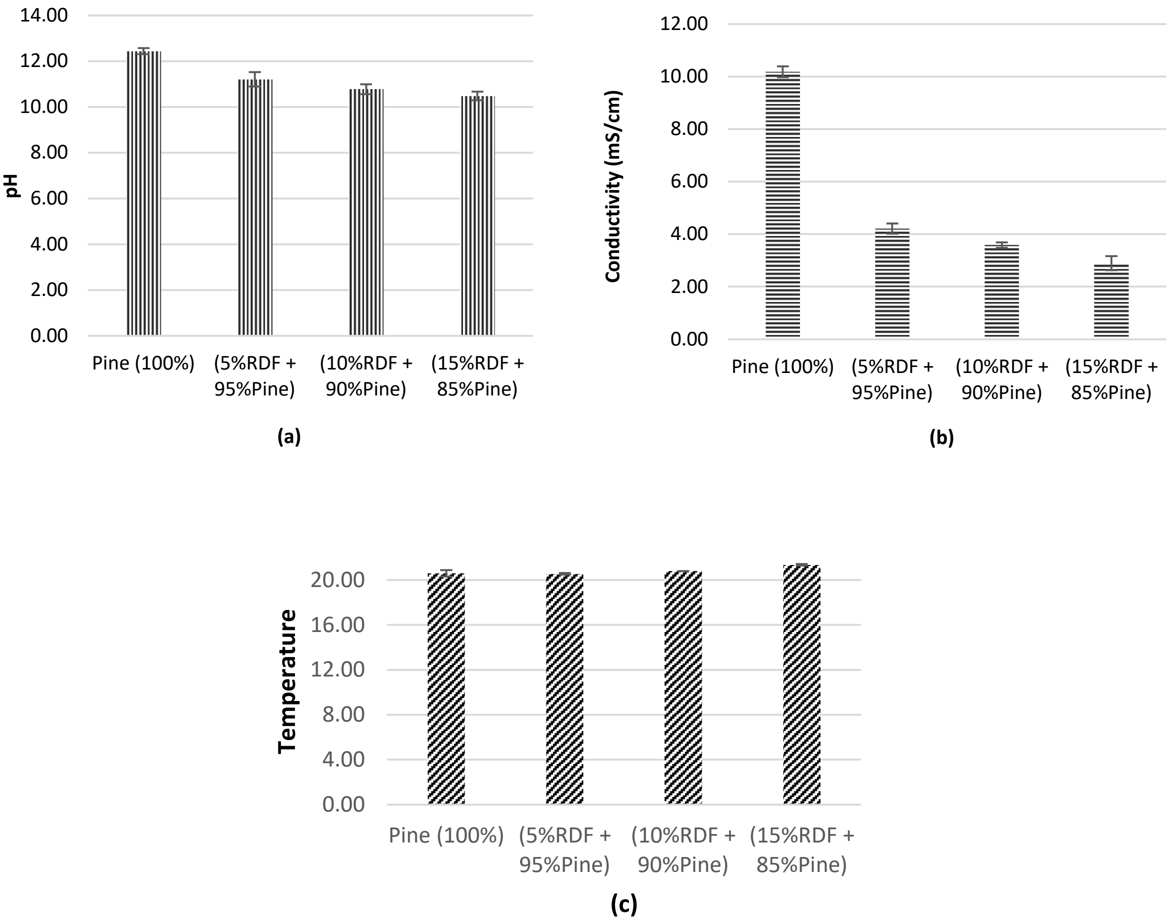


Figure 29. Characteristics of the bottom ashes in leaching solutions (a) pH, (b) conductivity, (c) temperature.

It is interesting to notice that the leaching solution from the pine ashes has higher pH and conductivity. The addition of RDF decreases these parameters in the leaching solutions. In fact, wood is a more complex material that probably arise to the production of higher content of oxides (Ca, Mg, Na and even heavy metals oxides) remaining after wood burning and that have alkaline behaviour. For the same reason higher contents of soluble ions may be transferred to the leachate solution what control the higher conductivity of pine ashes. Table 14 shows the data evaluated in the leaching solutions in terms of heavy metals.

Table 14. Leaching values obtained from experimental work and method quality parameters.

Element	**Method limits (mg/kg)**		**Leaching values (mg/kg_{ash})**			
	LOD	LOQ	Pine (100%)	RDF(5%) + Pine(95%)	RDF (10%) + Pine(90%)	RDF (15%) + Pine(85%)
Cd	0.00046	0.00015	nd	nd	nd	nd
Cr	0.056	0.19	16.2	nd	nd	nd
Pb	0.0026	0.0087	nd	0.289	0.029	0.016
Ni	0.063	0.21	nd	nd	nd	nd
Zn	0.030	0.10	3.76	4.30	2.22	1.62
Cu	0.10	0.33	nd	0.743	0.347	nd

LOD (limit of detection); LOQ (limit of quantification); nd (not detected).

As can be seen by Table 14, the concentration of the metals leached from the ashes, for each composition of pellets are lower than the limit values of leaching dictated by the Decree Law.

This means that the ashes can be defined as non-hazardous and non-toxic to the environment and man. The concentration values of the metals were obtained using two atomic absorption spectrophotometers; one works on spectral bandwidths in mg and the other in µg, connected to a software from which the calibration curve of the concentration of the single metals is obtained (Pb, Cd, Cu, Ni, Zn, Cr).

However, this curve differs from the standard concentration values because there is the probability of error, therefore the LOD indicates the lowest concentration that can be detected but not necessarily quantified, with LOQ the lowest concentration that can be quantitatively determined with accuracy and precision and with nd the concentration from the undetected negative value.

5. CONCLUSIONS

The present study stems from the need to partially compensate for the problem of increasingly uncontrollable waste disposal throughout the world.

Often the disposal methods are not enough, but those of the recycling are added in such a way as to be able to re-use some of the waste that would otherwise be stored in landfills or incinerated.

The resources that are in waste, material or energy, must be valorized increasing the recycling strategies. One of the methodologies that can be follow is the energetic valorisation, after a series of mechanical and biological treatments of undifferentiated waste, for the production of solid fuel derived from the waste itself (RDF).

This experimental work is dedicated, in particular, to the potential use of RDF, seen as an energy source for combustion in biomass power plants.

It has multiple environmental and energy benefits. In terms of waste management it leads to the promotion of separate waste collection and the reduction of waste in landfills, in terms of emissions it reduces the CO_2 and greenhouse gas content, from an economic point of view it guarantees the saving of fossil fuels and their importation from other countries, but the great advantage manifests itself in energy terms by producing clean energy in large quantities.

It was thought in fact to investigate this study by combining the use of RDF with pine, in the form of pellets, in order to evaluate the ability to replace some biomass by prepared RDF in biomass power plants.

After a complete analysis in all the pellet compositions (pine 100%, 95% pine:5% RDF, 90% pine:10% RDF, 85% pine:15% RDF) of all the verified parameters (humidity, ash, material volatile, fixed carbon, chlorine, nitrogen, sulphur, higher calorific value, heavy metals) it was concluded that, in energy and environmental terms, the benefits deriving from the use of the RDF and pine mix are many.

The content of chlorine, sulphur and nitrogen, with the addition of 15% of RDF in the pellet, shows low values (0.06%, 0.04%, 0.005%) and this result is positive because otherwise it turned out to be a serious problem for the environment, as these substances are linked to combustion gas emissions, contribute to the production of greenhouse gases and acidic rain.

Even the value of HHV, with the increase in the RDF content in the pellet (21.02 MJ/Kg with 15% RDF), is a great advantage, because in replacement of traditional fossil fuel it produces more energy.

As regards the ash characterization, after the combustion of each pellet composition in the domestic boiler, the results were equally reassuring because from the quantification of the heavy metals contained in the ash and their toxicity, it can be seen that the concentration of metals is lower than the leaching limits for non-hazardous wastes, according to the Decree Law 183/2009 and therefore the ashes are not dangerous and non-toxic.

From the analysis of the concentrations of metals, following combustion and unburned material, it allowed to understand that, despite the danger to the environment and to human health of heavy metal's emissions, such as Pb, Zn, Cr and Cd, it was found out that their concentrations are low and similar to the evaluated for biomass pellets and, therefore, they do not cause increased concern.

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ANNEXES

Annex A - Proximate Analysis

This section will present the totality of the proximate analysis of the different pellets compositions. The results are shown in the following tables.

A1 Humidity

Table A1. basic parameters for each mix composition.

	$m_{capsule}$ (g)	$m_{initial\ of\ pellet}$ (g)	$m_{after\ drying\ of\ pellet\ +\ capsule}$ (105°C) (g)	$m_{after\ drying\ of\ pellet}$ (105°C) (g)	Humidity (%)
Pine1(100%)	46.1854	4.9279	50.7733	4.5879	6.8995
Pine2(100%)	46.8151	4.9914	51.4677	4.6526	6.7877
Pine3(100%)	41.6636	5.0894	46.406	4.7424	6.8181
Rdf(5%)+Pine(95%)	39.1677	4.9647	43.574	4.4063	11.2474
Rdf(5%)+Pine(95%)	64.7400	5.0231	69.1917	4.4517	11.3754
Rdf(5%)+Pine(95%)	71.3102	5.0794	75.7654	4.4552	12.2889
Rdf(10%)+Pine(90%)	71.2322	4.9918	75.7074	4.4752	10.3490
Rdf(10%)+Pine(90%)	70.7615	5.0097	75.1128	4.3513	13.1425
Rdf(10%)+Pine(90%)	72.6372	5.0611	77.0323	4.3951	13.1592
Rdf(15%)+Pine(85%)	67.4008	5.0391	71.7254	4.3246	14.1791
Rdf(15%)+Pine(85%)	72.0355	5.0212	76.3609	4.3254	13.8572
Rdf(15%)+Pine(85%)	67.8435	4.9638	72.125	4.2815	13.7455

Table A2. average and standard deviation value of the humidity parameter for each mix composition.

	Humidity (%)	
	Average	**STDV**
Pine (100%)	6.84	0.06
(5%RDF + 95%Pine)	11.64	0.57
(10%RDF + 90%Pine)	12.22	1.62
(15%RDF + 85%Pine)	13.93	0.23

A2 Ashes

Table A3. basic parameters for each mix composition.

	$m_{capsule}$ (g)	$m_{after\ drying\ of\ pellet}$ (105°C) (g)	$m_{after\ drying\ of\ pellet}$ (550°C) (g)	$m_{after\ calcination\ of\ pellet}$ (g)	Ashes (%)
Pine1(100%)	46.1854	4.5879	46.2174	0.0320	0.6975
Pine2(100%)	46.8151	4.6526	46.8454	0.0303	0.6512
Pine3(100%)	41.6636	4.7424	41.6932	0.0296	0.6242
Rdf(5%)+Pine(95%)	39.1677	4.4063	39.2407	0.0730	1.6567
Rdf(5%)+Pine(95%)	64.7400	4.4517	64.8111	0.0711	1.5971
Rdf(5%)+Pine(95%)	71.3102	4.4552	71.3845	0.0743	1.6677
Rdf(10%)+Pine(90%)	71.2322	4.4752	71.3405	0.1083	2.4200
Rdf(10%)+Pine(90%)	70.7615	4.3513	70.8704	0.1089	2.5027
Rdf(10%)+Pine(90%)	72.6372	4.3951	72.7410	0.1038	2.3617
Rdf(15%)+Pine(85%)	67.4008	4.3246	67.5247	0.1239	2.8650
Rdf(15%)+Pine(85%)	72.0355	4.3254	72.1729	0.1374	3.1766
Rdf(15%)+Pine(85%)	67.8435	4.2815	67.9660	0.1225	2.8611

Table A4. average and standard deviation value of ashes for each mix composition.

	Ashes (%)	
	Average	**STDV**
Pine (100%)	0.66	0.04
(5%RDF + 95%Pine)	1.64	0.04
(10%RDF + 90%Pine)	2.43	0.07
(15%RDF + 85%Pine)	2.97	0.18

A3 Volatile solids

Table A5. basic parameters for each mix composition.

	$m_{capsule}$ (g)	m_{pellet} (g)	$m_{(capsule+pellet) before drying}$ (g)	$m_{after drying of pellet}$ (900 °C)(g)	Volatile solids (%)
Pine1(100%)	12.6325	4.0321	16.6646	13.2682	77.40
Pine2(100%)	12.6325	3.3056	15.9381	13.1616	77.16
Pine3(100%)	12.6327	3.1423	15.7750	13.1314	77.29
Rdf(5%)+Pine(95%)	12.6329	2.9690	15.6019	13.1190	71.99
Rdf(5%)+Pine(95%)	12.6328	3.1164	15.7492	13.1372	72.18
Rdf(5%)+Pine(95%)	12.6331	2.8556	15.4887	13.0945	72.21
Rdf(10%)+Pine(90%)	12.6336	3.1958	15.8294	13.1651	71.15
Rdf(10%)+Pine(90%)	12.6335	3.0133	15.6468	13.1466	70.76
Rdf(10%)+Pine(90%)	12.6336	3.244	15.8776	13.1777	71.01
Rdf(15%)+Pine(85%)	12.6334	2.9633	15.5967	13.1492	68.67
Rdf(15%)+Pine(85%)	12.6335	2.9715	15.6050	13.1467	68.80
Rdf(15%)+Pine(85%)	12.6334	3.1495	15.7829	13.1866	68.51

Table A6. average and standard deviation value of volatile solids for each mix composition.

	Volatile solids (%)	
	Average	**STDV**
Pine (100%)	77.28	0.12
(5%RDF + 95%Pine)	72.12	0.12
(10%RDF + 90%Pine)	70.97	0.20
(15%RDF + 85%Pine)	68.66	0.15

A4 Fixed carbon

Table A7. average value of volatile solids, humidity, ashes from which the fixed carbon is derived, for each mix composition.

	Average volatile solids (%)	Average humidity (%)	Average ashes (%)	Fixed carbon (%)
Pine(100%)	77.28	6.84	0.66	15.22
Rdf(5%)+Pine(95%)	72.12	11.64	1.64	14.60
Rdf(10%)+Pine(90%)	70.97	12.22	2.43	14.38
Rdf(15%)+Pine(85%)	68.66	13.93	2.97	14.45

Table A8. average and standard deviation value of fixed carbon for each mix composition.

	Fixed carbon (%)	
	Average	STDV
Pine (100%)	15.22	0.44
(5%RDF + 95%Pine)	14.60	0.50
(10%RDF + 90%Pine)	14.38	0.60
(15%RDF + 85%Pine)	14.45	0.04

Annex B - Analysis of the ashes

This section will show the standard calibration curves and calibration curves of the concentration of single metals (Pb, Cd, Cr, Zn, Ni, Cu), in according with the standard EN 12457-4:2002 and the EN 15411:2001 using two atomic absorption spectrometers, connected to a software.

B1 Calibration of Pb

Table B1. standard concentration and average absorbance value of the Pb.

Pb	
Standard Concentration (µg/L)	**Average Absorbance**
0	0.0000
2	0.0058
10	0.0350
30	0.1003
40	0.1267

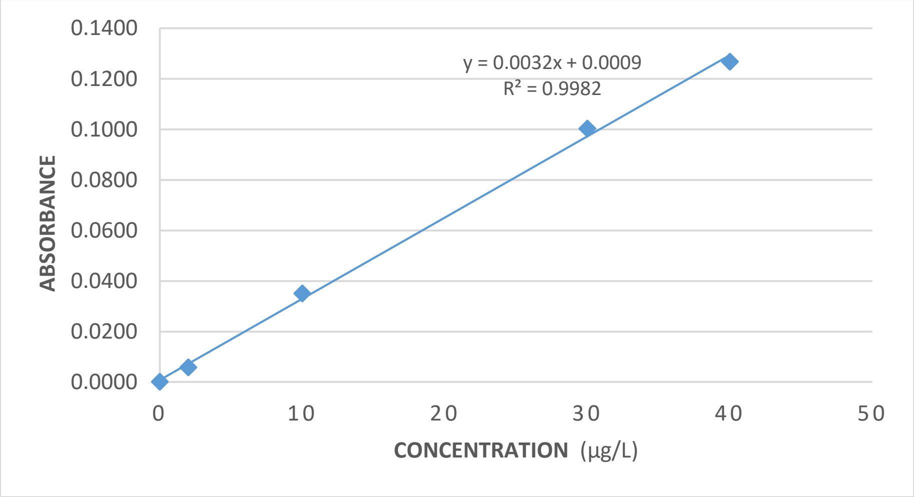

Figure B1. calibration curve of the Pb (µg/L).

B2 Calibration of Cd

Table B2. standard concentration and average absorbance value of the Cd.

Cd	
Standard Concentration (µg/L)	**Average Absorbance**
0	0.0000
0.5	0.0210
1.0	0.0410
2.0	0.0798

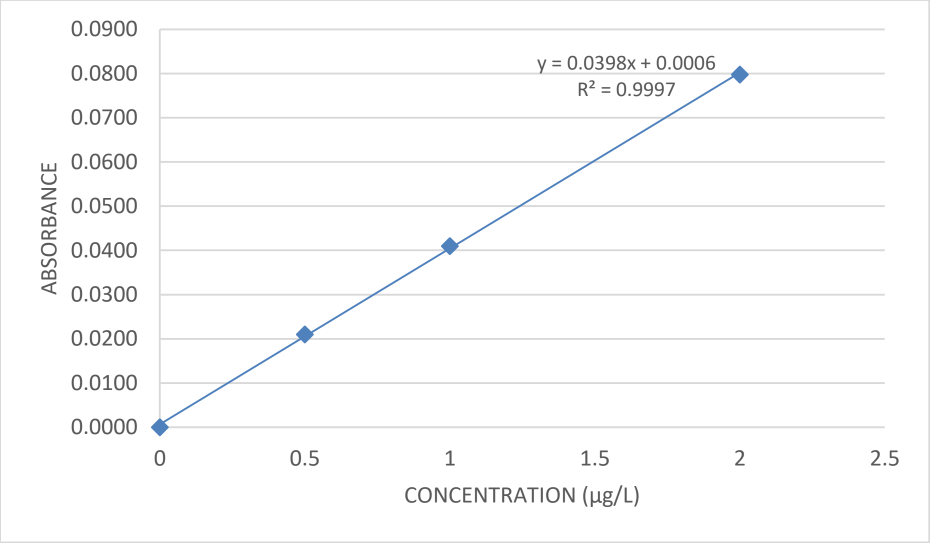

Figure B2. calibration curve of the Cd (µg/L).

B3 Calibration of Cr

Table B3. standard concentration and average absorbance value of the Cr.

Cr	
Standard Concentration (mg/L)	**Average Absorbance**
1.00	0.0216
2.00	0.0427
3.00	0.0632
4.00	0.0833
5.00	0.1048

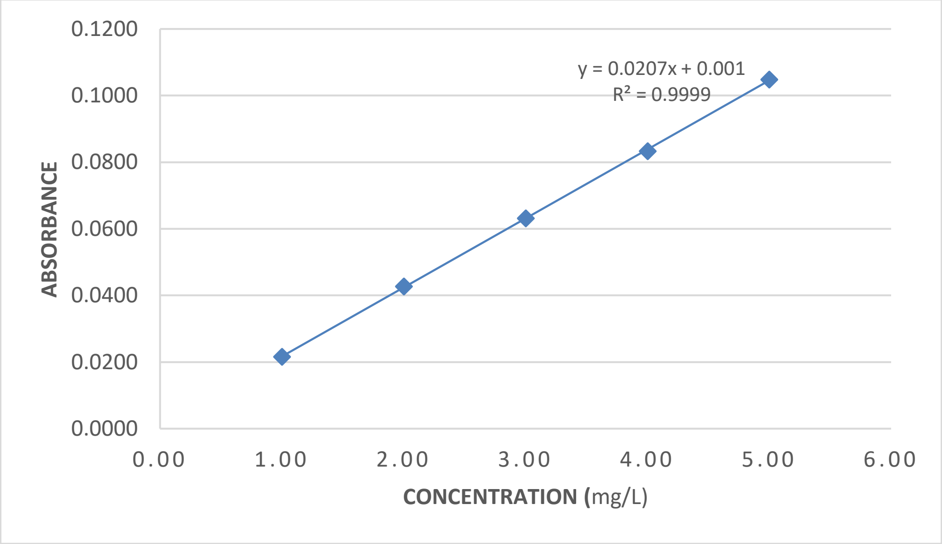

Figure B3. calibration curve of the Cr (mg/L).

B4 Calibration of Zn

Table B4. standard concentration and average absorbance value of the Zn.

Zn	
Standard Concentration (mg/L)	**Average Absorbance**
0.10	0.0162
0.20	0.0317
0.40	0.0593
0.80	0.1129
1.00	0.1381

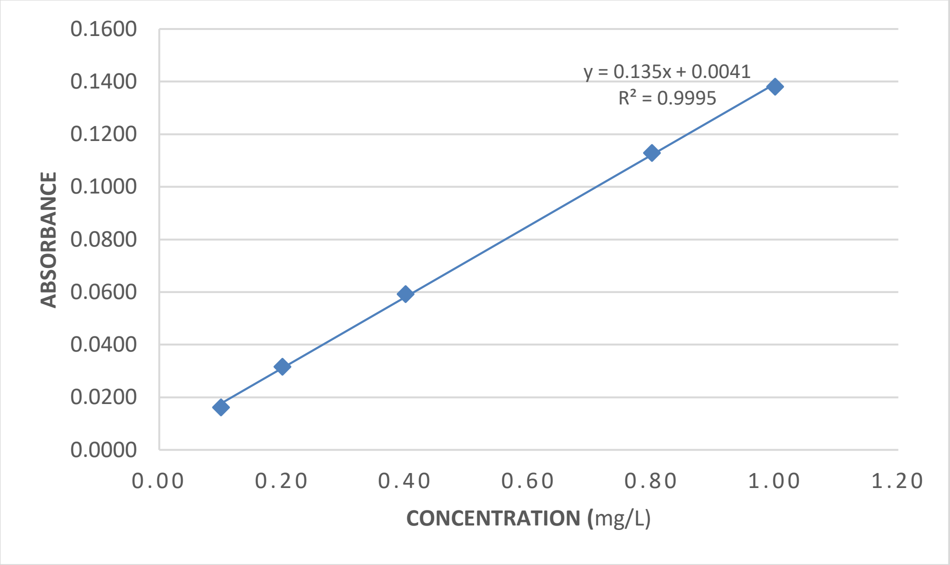

Figure B4. calibration curve of the Zn (mg/L).

B5 Calibration of Ni

Table B5. standard concentration and average absorbance value of the Ni.

Ni	
Standard Concentration (mg/L)	**Average Absorbance**
0.40	0.0113
0.80	0.0229
1.20	0.0328
1.60	0.0441
2.00	0.0538

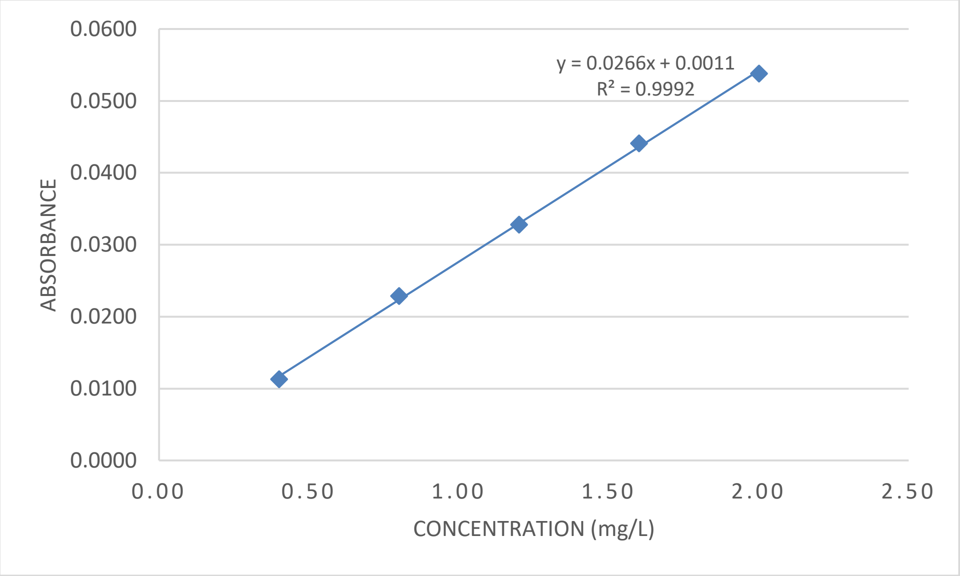

Figure B5. calibration curve of the Ni (mg/L).

Calibration of Cu

Table B6. standard concentration and average absorbance value of the Cu.

Cu	
Standard Concentration (mg/L)	**Average Absorbance**
1	0.0439
2	0.0897
3	0.1305
4	0.1755
5	0.2167

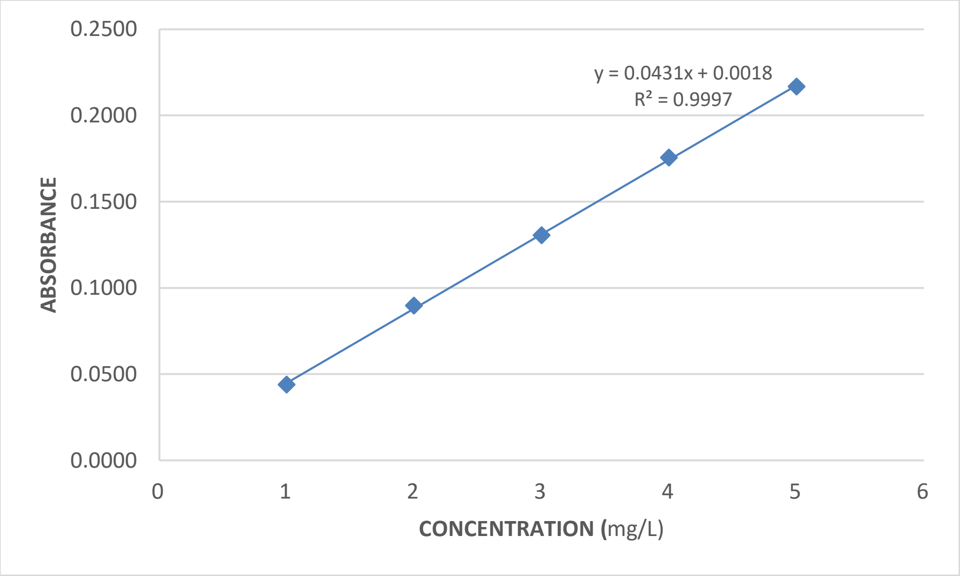

Figure B6. Calibration curve of the Cu (mg/L).