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Physico-chemical characterization of chars produced in the co-pyrolysis of wastes and possible routes of valorisation

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Para os meus pais, António e Helena.
Para a minha irmã, Joana.
Para o meu companheiro, Sérgio.
Para o meu filho, Gabriel

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RESUMO

A presente dissertação tem como objectivo principal o estudo da valorização dos carvões obtidos na co-pirólise de resíduos de plásticos, pneus e biomassa florestal.

Os carvões pirolíticos foram submetidos a um tratamento multietápico tendo em vista a obtenção de materiais carbonosos de valor acrescentado. Realizou-se uma caracterização físico-química dos carvões tratados tendo em vista o estudo de possíveis aplicações destes materiais, nomeadamente, a possibilidade de serem utilizados como adsorventes de poluentes.

Os carvões pirolíticos brutos foram submetidos a uma extracção sequencial com solventes orgânicos de polaridade crescente seguida de uma desmineralização ácida.

Os resultados obtidos demonstraram que o procedimento multietápico realizado garantiu uma descontaminação eficiente dos carvões, permitindo a recuperação de uma fracção significativa dos óleos da pirólise e/ou de subprodutos condensados que ficaram retidos nos carvões brutos, assim como uma redução significativa do seu conteúdo em cinzas.

O procedimento de desmineralização ácida realizado permitiu também concluir que os metais pesados maioritários, assim como os mais tóxicos, estão significativamente imobilizados e retidos na matriz dos carvões, desde que não sejam aplicadas condições acídicas agressivas.

A análise elementar aos carvões permitiu determinar heteroátomos como o oxigénio, enxofre e azoto, sendo este facto indicativo da presença de grupos funcionais na superfície dos carvões, o que representa um interesse acrescido relativamente à adsorção de poluentes orgânicos e inorgânicos específicos.

As propriedades texturais e de adsorção dos carvões tratados foram determinadas e os resultados obtidos indicaram que estes carvões são predominantemente materiais meso e macroporosos, com capacidade para adsorver moléculas volumosas.

O tratamento aplicado aos carvões permitiu obter materiais carbonáceos com qualidade suficiente para serem reutilizados como adsorventes ou como percursores de carvão activado.

Palavras-chave: carvões pirolíticos, resíduos, propriedades físico-químicas, adsorção

ABSTRACT

The main goal of the present thesis is to study the valorisation of chars produced in the co-pyrolysis of plastics, forestry biomass and tire wastes.

A multistep upgrading procedure was applied to the pyrolysis chars in order to produce value-added carbon materials and the quality of the upgraded chars was evaluated by measuring some of their physico-chemical properties. An assessment of the possible routes of valorisation for the pyrolytic chars, particularly their valorisation as pollutants adsorbents, was performed.

The crude chars were submitted to a sequential solvent extraction with organic solvents of increasing polarity followed by an acidic demineralization procedure. The results obtained showed that the upgrading treatment ensures an efficient decontamination of the pyrolysis chars, allowing the recovery of a significant fraction of the pyrolysis oil and/or condensed by-products trapped in the crude chars as well as a significant reduction in the char's ash content.

The demineralization procedure also allowed to conclude that the main heavy metals as well as the most hazardous are significantly immobilized in the char matrix if aggressive acidic conditions were not used.

The upgraded chars presented heteroatoms such as oxygen, sulphur and nitrogen, indicative of the presence of polar functional groups on the chars' surface, which represents an increase interest for the adsorption of specific organic and inorganic pollutants

The textural and adsorption properties of the upgraded chars were evaluated and the results indicate that the chars are mainly mesoporous and macroporous materials, with adsorption capacity for bulky molecules.

The upgrading treatments performed over the chars allowed to obtain carbonaceous materials having sufficient quality to be reused as adsorbents or as precursors for activated carbon.

Keywords: pyrolytic chars, wastes, physico-chemical properties, adsorption

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LIST OF ABBREVIATIONS, ACRONYMS AND SYMBOLS

AAS – Atomic Absorption Spectrometry
AEBIOM – European Biomass Association
ASTM - American Society for Testing and Materials
B&C – Building and Construction
B.E.T. - Brunauer-Emmet-Teller
ELT – End-of-Life Tires
EU-27 – European Union
EPA – Environmental Protection Agency
EUROSTAT – European Statistics
HHV – High Heating Value
IUPAC – International Union of Pure and Applied Chemistry
NAFTA – North American Free Trade Agreement
LHV – Low Heating Value
L.Q. – Limit of Quantification
MSW – Municipal Solid Waste
OECD – Organization for Economic Co-operation and development
PE - Polyethylene
PE-HD - Polyethylene High Density
PE-LD – Polyethylene Low Density
PE-LLD - Polyethylene Linear Low Density
PET – Polyethylene Terephthalate
PP – Polypropylene
PS – Polystyrene
PTFE – Polytetrafluoroethylene
PVC – Polyvinyl Chloride
S_{BET} - Área específica determinada pelo modelo de B.E.T.
S.S.E. – Sequential Solvent Extraction
UEZ-LNEG – Unidade de Emissões Zero do Laboratório Nacional de Energia e Geologia
WEEE – Waste Electrical and Electronic Waste
X.R.F. – X Ray Fluorescence

1. BACKGROUND

Human activity, in its many aspects, is reflected in an increasing diversity and continued production of wastes being necessary to ensure their appropriate destination, to minimize the negative impacts on health and environment.

Waste materials are generated from manufacturing processes, industries and municipal solid wastes (MSW). Only in the European Union (EU-27) the waste produced in 2008 amounted to a total of 2.62 billion tonnes [1]. Worldwide the level of waste generated is overwhelming.

The recent Waste Framework Directive 2008/98/EC [2] of the European Parliament and of the Council of the European Union clearly states that "*measures to protect the environment and human health by preventing or reducing the adverse impacts of the generation and management of waste and by reducing overall impacts of resource use and improving the efficiency of such use*" have to be undertaken. However, landfill disposal still remain the winning option in what concerns waste management [1,3-5], being incineration the most used and implemented alternative to landfilling of non-recyclable wastes. However, these burying and burning options raise lot of controversy about the emission of toxic compounds and greenhouse gases.

To improve its image and public acceptability, waste incineration is increasingly presented as a clean, green waste-to-energy technology instead of a process of simply waste mass-burn [6,7]. However, with incineration, the organic content of wastes is completely destroyed, making more attractive the thermochemical treatment alternatives that allow the conversion of wastes into new organic products that can be used as raw materials for chemical industries in addition to energy production as substitutes of traditional fuels.

The main available thermochemical conversion technologies, besides incineration, are pyrolysis and gasification that consist in the thermal degradation of wastes in the absence of external oxygen supply or with limited oxygen supply, respectively. The formation of harmful substances can be better controlled with these thermal processes [8,9].

The thermochemical process focused in this dissertation is pyrolysis since it converts the raw waste material into three types of products: char, light molecular weight gases and heavy molecular weight compounds that condense when cooled down. The gaseous and liquid fractions are considered the most valuable products of the pyrolysis process and may be used directly as fuels or added to petroleum refinery feedstock [10].

Although pyrolysis is relatively insensitive to its input material, some wastes such as plastics, tire rubbers and lignocellulosic biomass are considered suitable raw materials to pyrolytic processes. This is due because of their combustible properties and high volatile matter content in addition to the fact that they are natural and synthetic polymers easily cracked down by pyrolysis into smaller chains of hydrocarbon gas and pyrolysis oil that have industrial and energetic interesting applications [10-12].

Generally, pyrolysis conditions are optimized in order to maximize the lighter fractions, but non-volatilization of raw materials, re-condensation and/or recombination of thermal cracking products may occur in a more or less extent leading to the production of pyrolytic char.

This solid char is mainly composed by a carbon-rich matrix that contains almost all the inorganic compounds present in the raw wastes and a significant amount of the condensed by-products formed during the pyrolysis process dispersed throughout a porous structure. Generally, the pyrolytic char does not possess properties of sufficiently high quality to be directly reused owing to the presence of oils and contaminants. To minimize the cost and increase the sustainability of the pyrolysis process, the pyrolytic char has to be upgraded and valorised as it is done with the gaseous and liquid products; otherwise it will be directed to landfill disposal.

Combustion of char is a possibility, since it provides energy inside the pyrolytic process [13]. Other interesting alternative is the valorisation as adsorbent of suitable pollutants [14]. Adsorption properties of pyrolysis chars are well known [15-19], moreover due to its porous characteristics and high carbon content, the solid char constitutes a good precursor for the manufacture of activated carbons by means of physicochemical activation [16,18,20,21].

With this background, it was decided to perform an efficient upgrading/improvement of chars obtained in the co-pyrolysis of plastics, tires and pine biomass wastes and subjected the upgraded chars to a physico-chemical characterization in order to evaluate possible routes of valorisation for the pyrolytic chars, particularly, their valorisation as pollutants adsorbents or precursors of high-quality activated carbon.

2. INTRODUCTION

2.1 Generation of plastics, tires and pine biomass wastes

2.1.1 Plastic wastes - overview of the European and Portuguese situations

World's annual production of plastic materials has reached around 265 million tonnes in 2010 with Europe representing 21.5% of the global plastics production and China overtook Europe as the biggest production region at 23.5%. USA, Canada and Mexico (NAFTA) are in the third position with 20.5% of the total production (Figure 1).

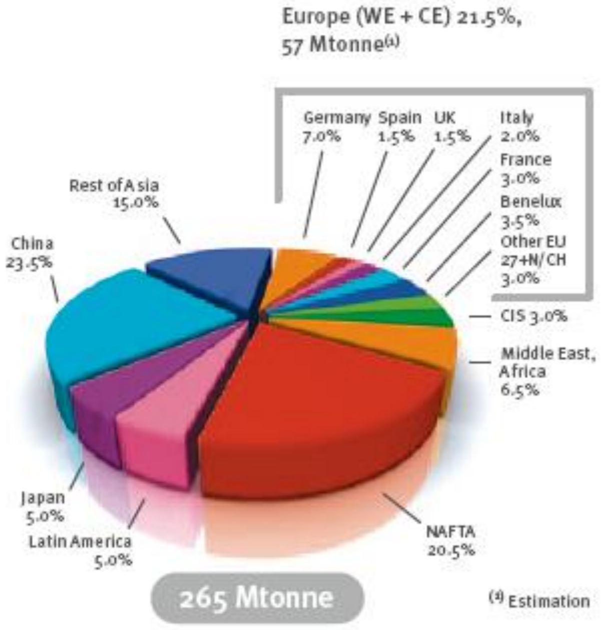

Figure 1. World Production of Plastics in 2010 [22].

There are different types of plastics with a variety of grades to help deliver specific properties for each application. The "big five" plastic types that stand out in terms of their market share are the following: polyethylene – including low density (PE-LD), linear low density (PE-LLD) and high density (PE-HD) types, polypropylene (PP), polyvinyl chloride (PVC), polystyrene (solid PS and expandable PS), polyethylene terephthalate (PET). All these plastic types together account for around 74% of the overall plastic demand in Europe. Polyethylene is in the top of resin types by market with a share of 29% (Figure 2).

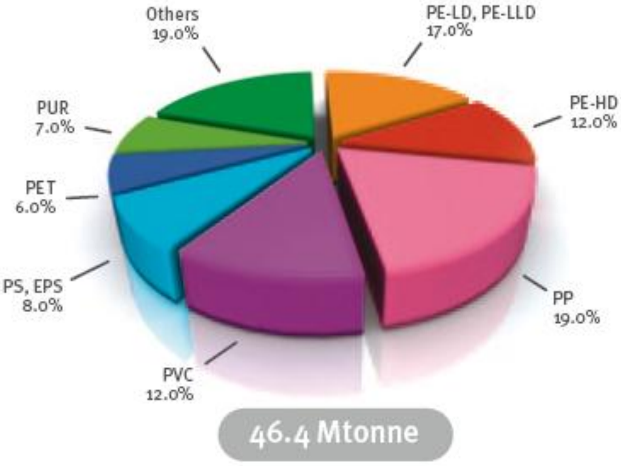

Figure 2. European Plastics Demand* by Resin Type, 2010 [22].

* EU27+N/CH incl. Other Plastics (~5.6 Mtonne)

Of the total plastic production in Europe (57 million tonnes) in 2010 the total generation of post-consumer plastic waste reached 24.7 million tonnes [22]. The main sources of plastic waste are typically the sectors which represent the highest plastic consumption. Figure 3 shows the contribution of the different sectors to the plastic waste stream in the EU-27, Norway and Switzerland in 2008. Packaging is the largest contributor to plastic waste at 63%, well ahead of “Others” (13%), which includes furniture, medical waste, etc. The remaining sectors include: automotive (5%), waste electrical and electronic equipment (WEEE) (5%), building and construction (B&C) (6%) and agriculture (5%).

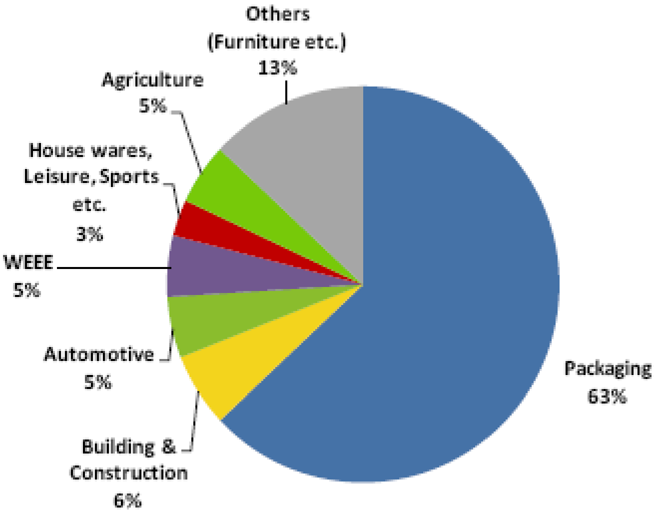

Figure 3. Proportions of post-consumer plastic waste in EU-27, Norway and Switzerland by application, 2008 [23]

In 2008, MSW accounted for approximately 40-50% of plastic waste in the EU-27 [23]. In turn, MSW are constituted by 10% of plastic waste, in average [24].

A large share (70%) of MSW plastics consists of packaging items but houseware items (toys, leisure and sport goods) or small WEEE are also discarded by households. Within the packaging plastic fraction, polyolefins are the most common polymers. According to the data of 2005, High-Density Polyethylene (HDPE), Low-Density Polyethylene (LDPE) and Polypropylene (PP) together account for around 60% of plastics in European MSW, Polyethylene Terephthalate (PET) and Polystyrene (PS) are also significant and the share of the remaining resins represents approximately 10% [25].

In Portugal, data from 2009 indicates that around 24 million tonnes of waste was generated of which 21% was MSW [26]. The total of plastic wastes sent to waste management operators in the Portuguese territory was about 400000 tones.

From the author knowledge there is no available quantitative information about the main polymers in the Portuguese plastic waste fraction. However, statistics from the Portuguese Association of Plastic Industries indicates that, in 2009 [27], ethylene and propylene polymers were the most consumed. Therefore, and considering the European trend, it is reasonable to assume that plastic wastes will present mainly HDPE, LDPE and PP in their composition.

From the total generation of post-consumer plastic waste in Europe in 2010, 10.4 million tonnes were disposed of (42.1%) and 14.3 million tonnes (57.9%) were recovered (Figure 4). Plastic wastes recovered include those diverted for incineration with energy recovery (33.6%) and those recycled (24.3%). In Figure 4, recycling of plastic wastes includes mechanical and chemical recycling (also called feedstock recycling), but the rate of chemical recycling is almost insignificant (around 0.5%).

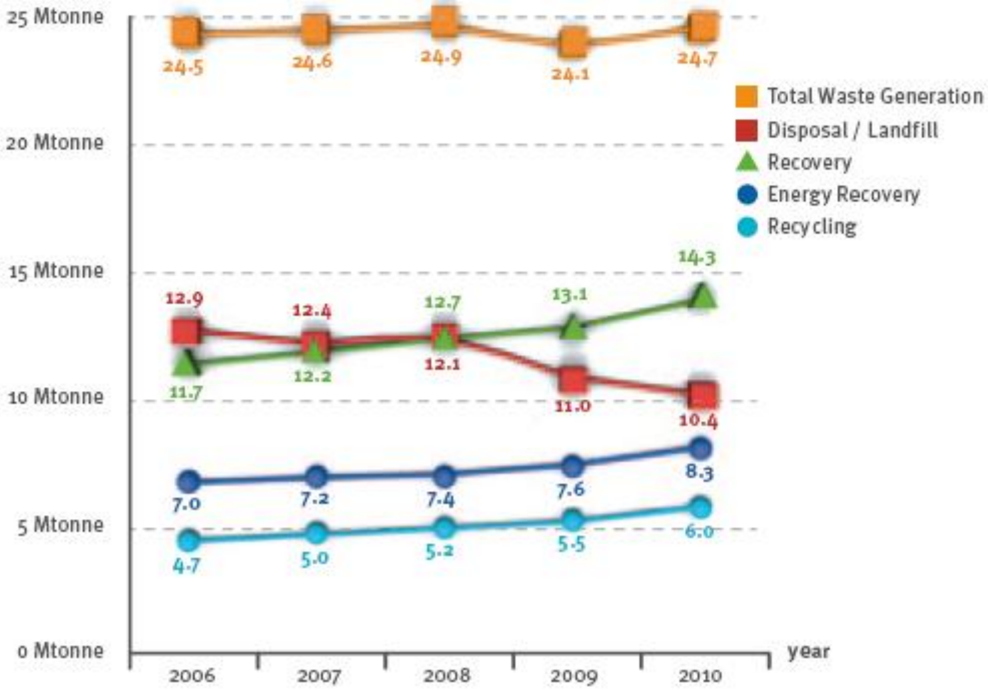

Figure 4. Total plastics waste treatments and disposal in Europe 2006 – 2010 [22].

Concerning Portugal, data from 2010 [22] indicate that 20% was recycled and around 37% was used for energy recovery by combustion from the total of plastic wastes sent to waste management operators. Consequently, 43% was forwarded to landfill disposal.

2.1.2 Tire wastes - overview of the European and Portuguese situations

About 1.4 billion new tyres are sold worldwide each year and subsequently just as many falls into the category of end-of-life tyres (ELT) [28]. In 2007, an impressive 4.6 million tonnes of ELT were generated in the USA (Table 1). Europe occupies the 2nd position in the global market with around 3.2 million tonnes of used tyres generated in 2009.

In Portugal, Valorpneu is the company that organize and manage the system for collection and ultimate disposal of used tyres and in 2010 around 94000 tonnes of used tires were collected [29].

The recovery rates for ELT tires in major markets for the year 2009 are presented in Table 1. It can be seen that 95% of ELT arising on the EU market were diverted from landfill. From the total of ELT sent to recovery processes, about half was destined for material recycling and about the same quantity was used for combustion with energy recovery.

Table 1. ELT recovery rate for 2009 in major markets [28].

	ELT recovery (tonnes)	ELT arising (tonnes)	Recovery rates (%)
EU27 + CH + NO	2494000	2621000	95
USA (2007)	4105800	4595700	89
Japan	737000	814000	91

In Portugal, data from Valorpneu for the year of 2010 [29] indicate that all the used tires collected were recovered by means of recycling (72.7%) and energetic valorisation by combustion (27.3%).

2.1.3 Pine biomass wastes – overview of the European and Portuguese situations

In 2010, forest and other wooded land covered almost 178 million hectares in the EU27, or around 40% of its lands area, with three quarters of forest area available for wood supply [30], being pine one of the dominant species in the European forests [31].

The European Association of Biomass (AEBIOM) estimates that the current potential production of primary forestry residues (e.g., logging residues, early thinnings and extracted stumps) in the EU27 is around 24891 ktoe[1] with Portugal presenting a value of 325 ktoe. Concerning the production of secondary forest residues (manufacture of wood and of products of wood and cork, except furniture, manufacture of articles of straw and plaiting materials, manufacture of paper and paper products, printing and reproduction of recorded media, manufacture of furniture, jewellery, musical instruments, toys, repair and installation of machinery and equipment), a total of 38829 ktons is attributed to the EU27 and of 1254 ktons to Portugal [30].

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[1] The ton of oil equivalent is a conventional standardized unit for measuring energy, defined on the basis for a ton of oil with a net calorific value of 41.9 MJ/kg

There is a lack of information concerning, specifically, the total production of pine biomass wastes in Europe.

According to the last Portuguese forestry inventory of 2005-2006 [32], Portugal is a country where approximately 38% of its total land area is occupied by public and private forests which corresponds to around 3 million hectares. The predominant species in the Portuguese forest are pine (32%), eucalyptus (23%) and cork oak (23%) (Figure 5).

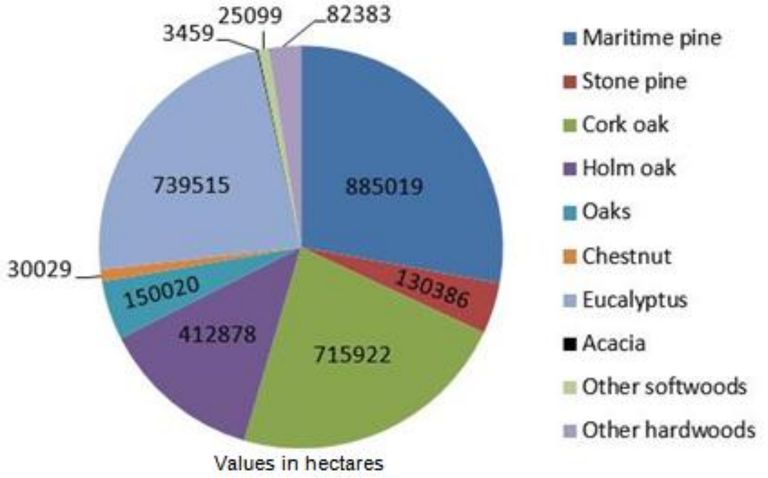


Figure 5. Portuguese forest composition in 2005-2006 [32].

The total pine biomass amounts to 55 million tonnes which corresponds to 90 million m^3 of biomass volume.

Pine was the biomass used for this study because it is the dominant variety in the Portuguese forest and it reasonable to assume that is one of the major sources of forest biomass waste (By forest biomass waste it is understood the lignocellulosic and wood materials resulting from forest cleaning and harvesting and from wood forest related industries).

Data report from 2009 about the Portuguese residues situation [26] indicates a total of 800000 tonnes of wood residues generated. Concerning the residues generated by sectors of economic activity, according to this report 900000 tonnes of residues were generated by the sectors of agriculture, forests, wood and oak, however, it is not specified if these amounts concern to biomass residues.

From the author knowledge there is no official statistics about the generation of, specifically, pine forest wastes in the national scenario but some data from different bibliographic sources dealing with this subject were found and Table 2 presents a compilation of those sources.

Table 2. Estimation of potential pine forest wastes in Portugal.

Source	Year	Ton/year
A. D. Little and Tecninvest [33]	1985	1220000
L. Barreto [34]	1980-1990	1636333
CBE [35]	1993	1400000
J. Dias [36]	2002	670000
T. Mateus [37]	2007	619650
P. Campilho [38]	2010	1560000

Data in Table 2 are quite similar and it can be assumed from these sources that, on average, around 1 million tonnes of pine biomass waste are potentially available every year. However, it should be noted that given the lack of rigorous data, the difference between the potential and the effective availability of forest residues must be significant. Thus the numbers presented in Table 2 are, presumably, under estimated.

Actually, Portugal has eight combustion power plants dedicated to energy production using exclusively residual biomass, mainly forest biomass. These power plants have the total capacity to process around 1 million ton/year of residual forest biomass [39], mainly pine and eucalyptus biomass wastes.

There is also seven cogeneration power plants located in the major industries of wood based products (mainly pulp and paper industries) with capacities to process about 700000 tonnes of forest biomass wastes.

Data from 2010 indicates that the Portuguese domestic consume (household) of pine firewood was around 1 million tonnes, mostly for heating purposes [40].

According to a study of 2007 [41], the forest residues managed by the Portuguese forest associations had the destinations indicated by Figure 6.

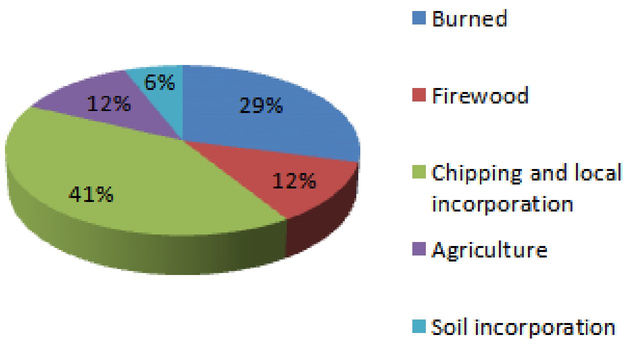


Figure 6. Forest residues management of the Portuguese forest associations, 2007 [41].

It is clear that several thousands of tonnes of forest biomass, including pine biomass, are not being properly valorised and the accumulation of large amounts of biomass wastes in the Portuguese forests dramatically increases the risk of forest fires.

2.2 Waste treatments - Overview of the current situation

Landfill and incineration (with and without energy recovery) are the most common and used methods of waste disposal throughout the world [1,3-4]. The negative environmental/sanitary/economics impacts of these burying and burning options are widely known and led to the growing of waste management alternatives, including recovery of waste materials such as recycling and composting that present an increasing trend in the last years [3,42].

Figure 7 presents the MSW treatment options in the EU-27 in the past 14 years. The tendency presented in Figure 7 is similar over the world among the industrialized/developed countries.

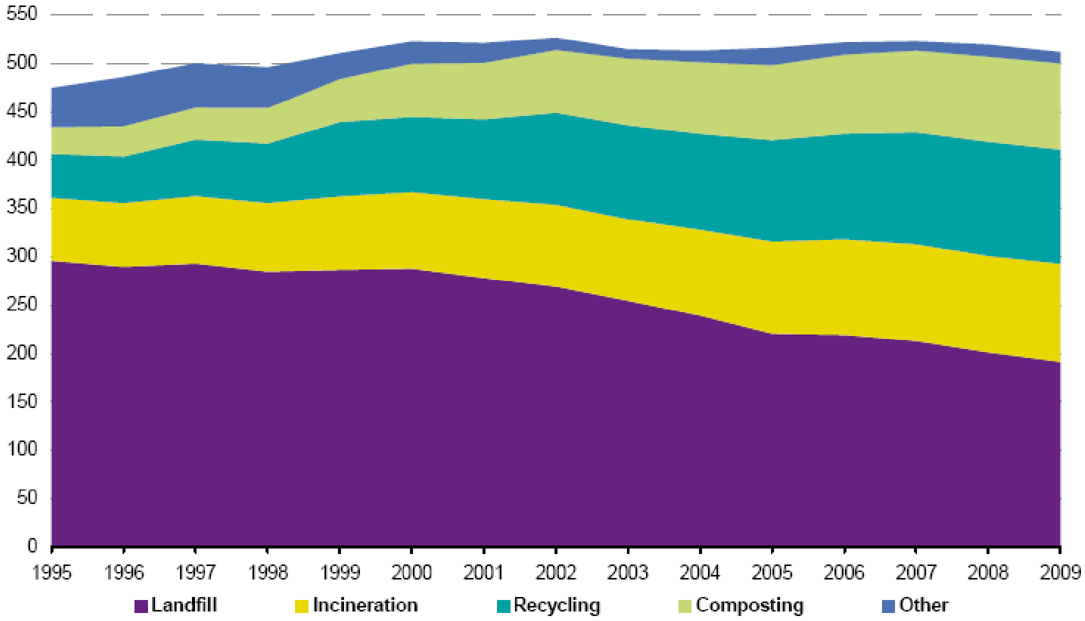


Figure 7. MSW treatment in the EU-27 (kg per capita) 1995-2009 [42].

According to OECD/Eurostat, the term recycling in Figure 7 is defined as any reprocessing of material in a production process that diverts it from the waste stream, except reuse as fuel, and the term composting is defined as a biological process that submits biodegradable waste to anaerobic or aerobic decomposition and that results in a product used on land or for the production of growing media [42].

2.2.1 Plastics, tires and pine biomass waste – possible recovery options

In the previous section it has been seen that landfill disposal still remain the most used option in what concerns general waste management, being incineration the most common and implemented alternative to landfilling of wastes.

However, the Landfill Directive 1999/31/EC [43] requires Member States to reduce the amount of biodegradable municipal waste going to landfills and the Waste Framework Directive 2008/98/EC [2] defines a waste hierarchy in which disposal should be the ultimate option and used only when wastes cannot be prevented or recovered/recycled.

Plastics, used tires and forest biomass residues are three types of wastes that present a slightly different trend in the waste management scenario since energetic valorisation by means of combustion is the preferred option of treatment, at least in the European countries. “Direct” recycling, in particular for plastic and rubber wastes also present important rates but quite below of the desirable. As demonstrated in section *2.1,* considerable amounts of plastic wastes are still diverted to landfill and huge amounts of effective and potential forest biomass wastes are currently available being not valorised.

From the existent and possible waste treatment technologies that allow a proper recovery of this type of wastes, thermochemical treatments are considered suitable since they are relatively insensitive to input materials with the possibility of treating heterogeneous and contaminated wastes with limited use of pre-treatment, allowing the valorisation of the energetic and/or organic content of wastes, thus fulfilling the requirements of the Waste Framework Directive.

The main available thermochemical conversion technologies are characterised essentially by the level of oxygen present [44]:

- Incineration, where complete combustion or oxidation occurs, often with excess air, resulting in fully oxidised products;

- Gasification, where incomplete combustion or oxidation occurs. Only a fraction of the material burns thereby generating sufficient heat to decompose thermally the rest of the material. The products are not fully oxidised and have a high heating value.

- Pyrolysis, where no combustion or oxidation takes place, but thermal degradation of the material occurs by adding heat directly or indirectly.

This is only one way of classifying thermal processes and is a considerable simplification as pyrolysis occurs in gasification, and both pyrolysis and gasification occur as intermediate steps in incineration.

Incineration/combustion, the most established and implemented thermochemical treatment of wastes, has the obvious advantage of volume reduction of wastes by about 90% and of weight reduction by 75% [45]. In addition, the energy of the hot gases generated could be used to generate steam and, consequently, to generate electricity by a steam turbine.

However, in spite of the advantages, incineration of wastes suffers from several concerns which the most important are:

- The organic content of wastes is completely destroyed being not recycled;
- Generation of large amount of gas emissions and carbon dioxide in particular, formation and reformation of toxic dioxins and furans, dusts, among others;
- Poor public image.

These drawbacks of the incineration processes make more attractive other thermochemical treatment alternatives such as the pyrolysis and gasification that also gives waste reduction by weight and volume but the oxygen-deficient atmosphere in these processes do not provide the environment needed for dioxins and furans to form or reform (pollution control) [8,9]. One of the most important advantages of pyrolysis and gasification is the conversion of wastes into other organic products that can be used as raw materials for chemical industries in addition to energy production as substitutes of traditional fuels.

Pyrolysis and gasification are thermal treatments included in the Waste Incineration Directive 2000/76/EC [46] and have to meet the mandatory emissions limits that it sets.

The thermochemical process focused in this dissertation is **pyrolysis** and will be discussed in detail in next sections.

2.3 Pyrolysis of wastes

During pyrolysis, the wastes are thermally decomposed in an inert atmosphere, giving rise to volatile matter and a carbon-rich solid residue named as pyrolytic char. The volatile matter comprises condensable vapours called pyrolysis oil at room temperatures and non-condensable (permanent) gases. Pyrolysis occurs with externally applied heat under moderated conditions of pressure and temperature.

The gaseous and condensable fractions are considered the most valuable products of the pyrolysis process since the gases have a low to medium calorific value and can be used as fuel or feedstock for chemical conversion and the condensable liquid that are constituted by heavy molecular weight compounds can be used as a fuel oil substitute or added to petroleum refinery feedstock.

Pyrolysis processes can be classified as slow, medium or fast pyrolysis. The basis for this classification is the residence time of the solid waste material within the reactor – seconds, minutes, up to hours, and correlated energy transfer and temperature distribution. Slow heating rates (5-7 K/min) maximize the char yield and high heating rates such as the ones used in fast pyrolysis (about 300ºC/min) increase the liquid fraction [47].

In spite of the already referred advantages of pyrolysis over incineration, the process is not free of drawbacks. The exhaust gases still have to be cleaned-up, although the air pollution control systems are less costly and complex and the pyrolytic oils/tars could be very complex mixtures containing toxic and carcinogenic compounds depending on the pyrolysis feedstock.

2.3.1 Pyrolysis of polymeric materials

2.3.1.1 Polymers

Polymeric materials can be classified based on their origin into natural and synthetic. Based on physical properties, polymers can be classified into elastomers (or rubbers), plastics, and fibers. Plastics can be further subdivided into thermoplastics (whose deformation at elevated temperatures is reversible) and thermosets (which undergo irreversible changes when heated). Polymers can also be classified in terms of their chemical composition. The main carbonaceous polymers with no heteroatoms are polyolefins, polydienes, and aromatic hydrocarbon polymers (typically styrenics). The main polyolefins are thermoplastics: polyethylene (PE) and polypropylene (PP), which are two of the three most widely used synthetic polymers, as already referred; polydienes are generally elastomeric and contain one double bond per repeating unit and the most important aromatic hydrocarbon polymers are based on polystyrene.

The most important oxygen-containing polymers are cellulosics, polyacrylics, and polyesters being cellulosics the most important oxygen-containing natural materials, mostly wood and paper products [48].

2.3.1.2 Thermal decomposition of polymers

Four general mechanisms common in polymer thermal decomposition are illustrated in Figure 8. These reactions can be divided into those involving atoms in the main polymer chain and those involving principally side chains or groups. While the decomposition of some polymers can be explained by one of these general mechanisms, others involve combinations of these four general mechanisms.

Among simple thermoplastics, the most common reaction mechanism involves the breaking of bonds in the main polymer chain. These chain scissions may occur at the chain end or at random locations in the chain. End chain scissions result in the production of monomer, and the process is often known as unzipping (typical in polystyrene). Random-chain scissions generally result in the generation of both monomers and oligomers (polymer units with 10 or fewer monomer units) as well as a variety of other chemical species (like in PE and PP). The type and distribution of volatile products depend on the relative volatility of the resulting molecules.

Cross-linking is another reaction involving the main chain. It generally occurs after some stripping of substituents and involves the creation of bonds between two adjacent polymer chains. This process is very important in the formation of chars, since it generates a structure with a higher molecular weight that is less easily volatilized.

The main reaction types involving side chains or groups are elimination reactions and cyclization reactions. In elimination reactions, the bonds connecting side groups of the polymer chain to the chain itself are broken, with the side groups often reacting with other eliminated side groups. The products of these reactions are generally small enough to be volatile. In cyclization reactions, two adjacent side groups react to form a bond between them, resulting in the production of a cyclic structure. This process is also important in char formation because the residue is much richer in carbon than the original polymer.

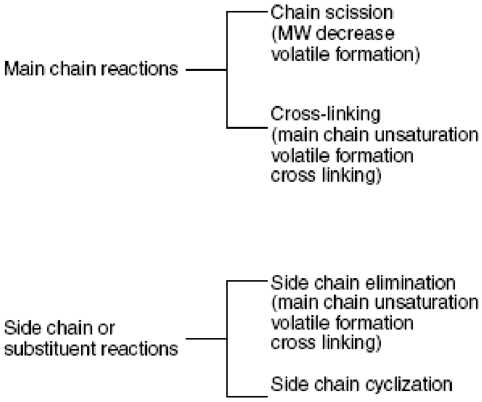


Figure 8. General polymer thermal decomposition mechanisms [48].

The decomposition of cellulose involves at least four processes in addition to simple desorption of physically bound water. The first is the cross-linking of cellulose chains, with the evolution of water (dehydration). The second concurrent reaction is the unzipping of the cellulose chain. Laevoglucosan is formed from the monomer unit. The third reaction is the decomposition of the dehydrated product (dehydrocellulose) to yield char and volatile products. Finally, the laevoglucosan can further decompose to yield smaller volatile products, including tars and, eventually, carbon monoxide.

Some laevoglucosan may also repolymerize. Wood is made up of 40-50% cellulose, 15-25% hemicellulose, and 15-30% lignin. The yields of gaseous products and kinetic data indicate that the decomposition may be regarded as the superposition of the individual constituent's decomposition mechanisms. On heating, the hemicellulose decomposes first (475 to 535 K), followed by cellulose (525 to 625 K), and lignin (555 to 775 K). The decomposition of lignin contributes significantly to the overall char yield [48].

2.3.1.3 Pyrolysis of plastic, tires and pine biomass wastes

Plastics, tire rubber and lignocellulosic biomass are considered suitable raw materials to pyrolytic processes due to their chemical composition (mainly carbon and hydrogen as in crude oil), combustible properties and high volatile matter content in addition to the fact that they are natural and synthetic polymers easily cracked down by pyrolysis into smaller polymeric chains of hydrocarbon gas and pyrolysis oil that have industrial and energetic interesting applications [10-12].

Pyrolysis of plastics wastes and used tires has been widely studied [11-12,16,49-67] with the aim to obtain liquids with diesel/gasoline hydrocarbons-range and also with high value chemicals.

The pyrolysis of lignocellulosic biomass has been also subject of study [68] being the liquids obtained highly complex mixtures of oxygenated aliphatic and aromatic compounds as it is typical in bio-oils from biomass pyrolysis. In particular, the pyrolysis of pine biomass has been already studied [69-72] and the main conclusions are that the pyrolytic oil obtained can be used as feedstock for synthesis of fine chemicals, adhesives, fertilizers, etc., but if an alternative to traditional fuels is to be considered the bio-oil is so oxygenated that has to be subjected to an upgrading, usually an hydrogenation.

To overcome this issue concerning the quality of the bio-oils, strategies involving the co-pyrolysis of plastics with pine biomass have been undertaken [73-79], with the primary goal of improving the hydrogenation during thermal co-processing of polymer wastes with wood biomass leading to an increase of liquid production quantity and quality.

The same approach was considered by Miranda *et al*. [80-81] that studied the co-pyrolysis of tires and plastic wastes in order to improve liquid yields and its fuel properties.

Cao *et al*. [82] investigate the characteristics of oils produced from the co-pyrolysis of woody biomass and tire and observed that exists hydrogen transfer among the pyrolysis vapours and a synergistic effect that improve the quality of the oil.

Concerning the pyrolysis of mixtures composed by the three wastes (plastics, rubber tire and forestry biomass) there is only one work from Paradela *et al*. [83] that studied the synergetic effects and the advantages of their co-pyrolysis. The authors conclude that the liquid yield as well as its composition is significantly affected by the plastic content in the waste mixture.

2.3.1.4 Char by-product of the co-pyrolysis of plastic, tires and pine biomass wastes

Generally, pyrolysis conditions are optimized in order to maximize the gaseous and liquid fractions, since these are the products considered as the most interesting from an economical point of view.

However, and as explained in section *2.3.1.2*, non-volatilization of raw materials, recondensation, repolymerization and/or recombination of thermal cracking products may occur in a more or less extent leading to the production of pyrolytic char.

The individual pyrolysis of tires usually lead to char's yield of 30-50% [50,56-58,60,63-64,66,83] that is mainly constituted by the carbon black ("negro de fumo" in the Portuguese terminology) used as filler in tire production [84], and the pyrolysis of pine biomass may produce 10-40% of chars [69-73,76-79], depending on pyrolysis conditions.

The production of char in thermoplastic pyrolysis is usually quite low [48,51-55,58-62,65,67] and resulting from secondary tar-cracking reactions (for this reason it is many times called as coke, since char is the designation for a primary pyrolysis product as for biomass and tire pyrolysis), but there are exceptions, such as the pyrolysis of polystyrene that in certain conditions, like batch systems, may give significant char's yield due to the formation of non-volatile polyaromatics residues resulting of secondary reactions of instable aromatic intermediate products [61-62,85-86].

Concerning the co-pyrolysis of plastics with pine biomass, it is observed in the literature [73-79] that the char's yield may range between 7-32%, occurring an increase in the char's yield with the increasing of biomass proportion in the mixture.

The same trend is observed in mixtures with tires and plastics in which the char's yield increase from 10% to 50% with the increase of tire content from 0% to100% [81].

In the work from Paradela *et al*. [83], the co-pyrolysis of the three wastes give rises to char formation in the range of around 0-30% with the decrease of plastics content in the mixture from 100% to 20%.

2.3.1.4.1. Valorisation of pyrolysis char by-product

The solid chars obtained in the pyrolysis of polymeric and biomass wastes are mainly composed by a carbon-rich matrix that contains almost all the inorganic compounds present in the raw wastes and a significant amount of the condensed by-products formed during the pyrolysis process dispersed, usually, throughout a porous structure. Generally, the pyrolytic char does not possess properties of sufficiently high quality to be reused owing to the presence of oils and contaminants.

In pyrolysis processes where a significant production of char by-product is observed, as in the pyrolysis of plastics, tires and pine biomass waste mixtures, the char has to be upgraded and valorised as are the gaseous and liquid products in order to minimize the cost and increase the sustainability of the pyrolysis process. The combustion of char is the more suggested alternative, since it is a fast and easy solution that provides energy for the pyrolytic process [13] and because these chars have calorific values in the order of 30-40 MJ/kg [77,79-81]. However, combustion has the drawbacks previously referred (gas cleaning, contaminant emissions,…).

A more interesting and noble alternative is the valorisation as adsorbent of suitable pollutants since the adsorption properties of pyrolysis chars from different raw materials are well known [15-19]. In particular, tire char adsorption properties have been extensively studied [16,19,87-91] being the main conclusions that these chars are carbon materials with mesoporous/macroporous properties appropriate for the adsorption of bulky molecules.

Also, the chars from pine biomass pyrolysis have been applied in adsorption studies [18,92-95] with good results for heavy metals and aromatic compounds.

Studies concerning adsorption studies from raw pyrolysis chars of thermoplastics were not found since, as referred before, the yields of chars from the pyrolysis of these materials are usually low. Also, these chars present characteristics closer to carbonaceous residues designated as coke than to typical porous chars [61] and although coke could be upgraded to activated carbon [96], from the author knowledge there is no evidences that the upgrading of pyrolysis coke to activated carbon from thermoplastics has ever been contemplated.

Adsorption properties of raw chars obtained in the co-pyrolysis of plastics, tire and biomass wastes are not known given the lack of studies dealing with the subject and only recently Bernardo *et al*. [97-99] provided information about the composition and risk assessment of those types of chars.

3. THESIS' AIMS

The Introduction section shows that the interest in the recovery and upgrading of wastes such as plastics, forestry biomass and used tyres is growing since high amounts of these wastes are presently produced. The information presented in the previously section lead to the following main conclusions:

- In the European and Portuguese scenario, it was seen that polyethylene and polypropylene are the plastics present in higher amounts in the plastic fraction of the Municipal Solid Wastes (MSW), being Polystyrene also a significant contributor;
- Pine forestry biomass is the dominant variety in the Portuguese forest and it reasonable to assume that is one of the major sources of forest biomass wastes;
- Huge amounts of end-of-life tires are generated each year around the world, therefore is of the most importance to find strategies for the valorisation of these wastes;
- The unsustainability and disadvantages of the two major waste management options used, landfill and incineration, make more attractive thermochemical treatment alternatives such as pyrolysis;
- As wastes pyrolysis to produce valuable gaseous and liquid products is growing in importance, it is anticipated that large amounts of char pyrolysis by-product will be available. To minimize the cost and increase the sustainability of the pyrolysis process the char has to be upgraded and valorised as are the gaseous and liquid products.

With this background, it was decided to perform an efficient multistep upgrading/improvement of chars obtained in the co-pyrolysis of plastics (mixture of PE, PP and PS), tires and pine biomass wastes and subjected the upgraded chars to a physico-chemical characterization in order to evaluate possible routes of valorisation for the pyrolytic chars, particularly, their valorisation as pollutants adsorbents or precursors of high-quality activated carbon.

To achieve this main goal, several specific objectives were defined:

1. Characterization of the raw wastes (plastics, tires and pine biomass) submitted to pyrolysis experiments.
2. Co-pyrolysis of different waste mixtures and collection of the char by-products.
3. Multistep upgrading treatment.
   3.1. Submit the crude chars to a sequential solvent extraction with organic solvents of increasing polarity and evaluation of the extraction efficiency;
   3.2. Perform a heat treatment in the extracted chars;
   3.3. Demineralization procedure – acidic washing/leaching;
4. Physico-chemical characterization of the chars.
   4.1. Perform a thermal and elemental analysis in the chars;
   4.2. Determination of the inorganic content of the chars and evaluation of the efficiency of the demineralization procedure;
   4.3. Evaluation of the textural and adsorption properties of the upgraded chars.

4. MATERIAL AND METHODS

The main core of the Materials and Methods section of this Master Thesis is based on a manuscript submitted in October-2011 to the scientific Journal of Hazardous Materials from Elsevier entitled “Physico-chemical properties of chars obtained in the co-pyrolysis of waste mixtures” of which the first author is Maria Bernardo.

4.1 Plastics, used tires and pine biomass samples

Plastics were a mixture of polyethylene (PE), polypropylene (PP) and polystyrene (PS) from a recycling company in the form of pellets with around 2-5 mm of diameter.

Figure 9 presents a picture of the plastics used. It can be seen PS green particles, PP in the form of black pellets and PE grey pellets.

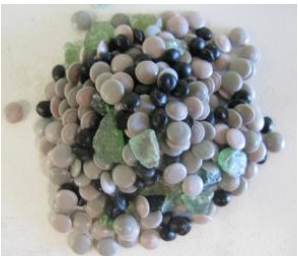


Figure 9. Plastic wastes used in the pyrolysis experiments.

The tire samples used were in the form of strips with around 2 cm of length and 1-2 mm of diameter (Figure 10) and were provided by a recycling plant of scrap tires.

Figure 10. Scrap tires used in the pyrolysis experiments.

Pinus pinaster or Maritime Pine was the pine biomass species used and was in the form of shredded pieces (Figure 11) obtained from forestry residues having the same granulometry of scrap tires.

Figure 11. Pine biomass used in the pyrolysis experiments.

Table 3 presents the elemental and proximate analysis of the waste samples used in this work. These analyses were performed at UEZ-LNEG.

Table 3. Elemental and proximate analysis of plastics, tires and pine biomass used in this work. Analysis performed in the materials as received.

	Tire rubber	Pine biomass	PE	PP	PS
LHV (MJ/kg daf) (ASTM D 2015 and D 5865)	n.d.	n.d.	43.3	35.1	37.4
HHV (MJ/kg daf) (ASTM D 2015 and D 5865)	38.5	20.2	46.4	37.6	39.0
Proximate Analysis					
Fixed Carbon (% w/w)[b]	33.5	13.6	0.1	0.1	0.2
Volatiles (% w/w) (950ºC/NP 3423[a])	61.6	74.5	99.8	82.6	99.5
Ash (% w/w) (800ºC and 750ºC)	2.9	0.3	0.1	17.2	0.0
Moisture (%w/w) (105ºC)	2.0	11.6	0.0	0.1	0.3
Elemental Analysis					
Carbon Content (% daf)	86.1	50.6	84.8	70.5	86.1
Hydrogen Content (% daf)	7.2	6.4	14.5	11.6	7.4
Sulphur Content (% daf)	1.5	0.2	0.3	<LQ	<LQ
Nitrogen Content (% daf)	0.2	0.2	0.3	0.5	6.1
Chlorine Content (% daf)	-	0.07	-	-	-
Oxygen Content (% daf)	0.1	42.5[b]	-	-	-

[a]Portuguese standard for the determination of volatiles; [b]Estimated by difference; LHV – Low Heating Value; HHV – High Heating Value; daf – dry ash free; n.d. – not determined; LQ – limit of quantification

A microwave acid digestion based in the EPA 3052 method [100] was used to digest the plastics, pine biomass and tire wastes. A broad group of selected heavy metals were quantified in the digested samples using a Thermo Elemental Solaar atomic absorption spectrometry (AAS) equipment. The selected heavy metals were: Cadmium (Cd), Lead (Pb), Zinc (Zn), Copper (Cu), Chromium (Cr), Nickel (Ni), Molybdenum (Mo), Barium (Ba), Mercury (Hg), Arsenic (As), Selenium (Se), Antimony (Sb), Potassium (K), Manganese (Mn), Iron (Fe), Sodium (Na), Calcium (Ca), Aluminium (Al) and Magnesium (Mg).

4.2 Pyrolysis experiments and char samples

Pyrolysis experiments were carried out in stirred batch autoclaves of 1 and 5 litres, built in Hastelloy C276 (Parr Instruments) (Figure 12) using an initial nitrogen pressure of 0.41 MPa, a reaction time of 15 min and a temperature of 420 ºC. In these pyrolysis reactors the heat transfer from the furnace to the autoclave is a slow process with heating rates of around 5ºC/min until the desired temperature of 420ºC is reached. Therefore, the residence time of the materials inside the autoclave is significantly higher than the reaction time at the temperature chosen.

Figure 12. Stirred batch autoclaves of 1 and 5 litres from Parr Instruments used to perform the pyrolysis assays.

This part of the study was performed at UEZ-LNEG and details of the pyrolysis installation and experiments can be found in previous works [54,62,77,81,83].

The char samples studied in this work were obtained from the pyrolysis of three different waste mixtures, as indicated in Table 4.

Table 4. Composition of the three waste mixtures submitted to pyrolysis.

Waste mixture	Composition
1	30% (w/w) pine biomass + 30% (w/w) used tires + 40% (w/w) plastics
2	50% (w/w) pine biomass + 50% (w/w) plastics
3	50% (w/w) used tires + 50% (w/w) plastics

Plastic wastes were a mixture of 56% (w/w) polyethylene, 27% (w/w) polypropylene and 17% (w/w) polystyrene, simulating the composition of the plastic fraction present in the Portuguese MSW [83,101].

4.3 Upgrading of pyrolysis chars

4.3.1 Sequential Solvent Extraction (SSE)

The chars obtained in the pyrolysis experiments were a carbonized viscous pasty residue impregnated with the pyrolysis oil. In order to remove and recover these pyrolysis liquid products trapped in the raw chars, a sequential solvent extraction (SSE) was performed: extraction with hexane followed by extraction with a mixture of 1:1 (v:v) hexane:acetone and a final extraction with acetone. The solvent extractions were performed using the Soxhlet method adapted from EPA 3540C Method [102] during

16h at a rate of 4 cycles/h. The solvents were eliminated from the crude extract solutions using a vacuum rotary evaporator. All extracts were equilibrated to room temperature and weighed to determine the extraction yields.

4.3.2 Heat treatment and demineralization procedure

After SSE has been performed, the extracted chars were heated at a temperature of 350ºC, during 2 hours in a muffle furnace, in order to eliminate solvent residues, and some condensed organic products that were not removed by the solvents and that can obstruct the char pores.

The last step of the upgrading treatment was a demineralization procedure in order to decrease the ash content of the chars: the samples were treated with 1M hydrochloric acid (HCl), at 60ºC, during 60 min, with continuous stirring in two successive washing stages. The acid to char ratio was of 100 ml/g. At the end of the acidic washing steps, the mixtures were allowed to settle and then filtrated to separate the pyrolytic char which was further washed several times with deionized water to remove residual acid and solubilize salts. Finally, the washed char samples were oven-dried at 110ºC, for 24h. The amount of inorganic species leached in each of the acidic washing steps was monitored by using the Thermo Elemental Solaar AAS equipment.

4.4 Physico-chemical characterization of chars

The chars were submitted to a thermo gravimetric analysis that consists in measuring the progressive weight loss associated with the combustion of samples in a muffle furnace from room temperature up to 750ºC with increments of 50ºC, remaining 10 min at each temperature stage. This thermal analysis allow to define the composition of the upgraded chars in terms of the volatility of their components: volatile organic compounds were those volatilized up to 250 ºC; the weight loss registered between 250ºC and 350ºC was attributed to semi-volatile compounds, while the weight decrease observed from 350 ºC to 600 ºC was assigned to the volatilization and combustion of heavy organic compounds denominated fixed carbon; the residue non-combusted above 600 ºC that presented a stable weight was considered to be ashes.

Elemental analysis of the upgraded chars was performed at UEZ-LNEG with a LECO elemental analyser. Carbon, hydrogen and nitrogen were determined according the ASTM D5373 standard [103]. Sulphur determination followed the procedure defined in ASTM D4239 standard [104].

The apparent density of the upgraded chars was estimated as the weight obtained from the char occupying a given volume.

The mineral content of the chars was determined according to the following procedure: the chars were submitted to a previous digestion performed with hydrogen peroxide 30% (v/v) in a heated bath at a temperature of 95ºC followed by *aqua regia* (HCl:HNO3, 3:1, v/v) at the same temperature. Finally, a microwave acidic digestion (ETHOS 1600-Milestone equipment) with *aqua regia* in closed PTFE vessels was used to complete the solubilization of the inorganic components of the samples. The metals were quantified in the digested samples using the AAS equipment.

4.5 Textural and adsorption properties of the upgraded chars

The textural properties of the upgraded chars were evaluated by adsorption of N_2 at 77K using an ASAP 2010 Micromeritics apparatus. Adsorption measurements were made after outgassing the samples under vacuum for at least 3h at 300ºC.

The isotherms were used to calculate the apparent surface area (S_{BET}) through the B.E.T. equation and the total pore volume, mesopore volume and pore size distribution through the Barrett, Joyner, and Halenda (BJH) method (ASAP 2010 Micromeritics software version 4.0).

The volume and pore size distribution for meso and macropores were determined with a mercury porosimeter Micromeritics AutoPore IV 9500 with the software version 1.07. The combination of gas adsorption and mercury intrusion data enables the complete pore volume distribution of the samples to be evaluated.

The methylene blue test was performed to assess the adsorption capacity of moderate size pollutant molecules by the upgraded pyrolysis char [105]. It involves the addition of a standard methylene blue solution with a concentration of 120 mg/L to a sample of pyrolytic char until no further colour reduction occurs by stirring the mixture for 5 minutes.

5. RESULTS AND DISCUSSION

The main core of the Results and Discussion section of this Master Thesis is based on two works:

- The paper “Characterization of chars produced in the co-pyrolysis of different wastes: Decontamination study“ already published in the scientific Journal of Hazardous Materials from Elsevier of which the first author is Maria Bernardo;
- The manuscript submitted in October-2011 to the same Journal entitled “Physico-chemical properties of chars obtained in the co-pyrolysis of waste mixtures” of which the first author is Maria Bernardo.

5.1 Mineral composition of the raw wastes

Table 5 shows the content of heavy metals in the raw wastes. A wide range of heavy metals was chosen to be quantified in order to give complete information about the metal content. The mean and standard deviation of duplicates are shown.

Table 5. Mineral composition of raw wastes.

Metals (mg/kg)	Plastics	Pine Biomass	Tyres
Zn	9.2±1.0	22.9±1.3	31193±441
Pb	4.8±1.0	4.3±0.004	14.5±1.0
Cu	<1.0	19.1±1.6	<1.0
Hg	5.4±1.0	0.13±0.04	0.10±0.02
As	<0.1	<0.1	1.00±0.03
Se	0.3±0.2	0.6±0.1	0.5±0.01
Sb	0.28±0.01	0.18±0.01	1.20±0.18
Ba	<11.3	<11.3	21.7±3.1
Cd	<0.6	<0.6	<0.6
Cr	<4.5	<4.5	<4.5
Ni	<1.8	<1.8	<1.8
Mo	<33.5	<33.5	<33.5
Ca	852±140	859±283	2402±91
K	<2.6	1050±173	738±16
Mg	19.1±0.7	212±6	333±19
Na	63.9±8.3	146±16	167±31
Al	<1.5	<1.5	150±35
Fe	<15.8	<15.8	97.7±18.6
Mn	<1.6	11.3±0.1	2.7±1.0

The heavy metals Cd, Cr, Ni and Mo were not detected in any of the raw wastes.

Alkali metals are present in high amounts, in particular the content of Ca were significant for all the three wastes.

From the metals of concern because of their toxicity, Pb, Zn and Hg were detected in the plastics with significant concentrations. However, it was previously observed by the author [98-99] that chars obtained from the co-pyrolysis of waste mixtures with these plastics did not present Hg at detectable amounts which means that, probably, Hg suffered volatilization during pyrolysis given the fact that most mercury compounds when exposed to reducing conditions are readily decomposed to metallic Hg [106] that volatilizes around 350ºC.

The high ash content of polypropylene plastic waste of 17.2 % (Table 3) is not consistent with the mineral composition determined in plastics by AAS. A possible explanation is the heterogeneity of the sample or an incomplete solubilization of inorganic species in the acidic digestion.

As expected, the major elements in pine biomass are alkali metals, but toxic elements were also detected in significant amounts, such as Zn, Cu and Mn.

Zn was present in major amounts (around 31 g/kg) in tires since zinc oxide, sometimes along with magnesium oxide, is added as an activator during the vulcanizing process [107]. This waste also presented detectable amounts of other elements that were not detected in plastics and biomass such as Ba, As and Fe. Tires were the waste, excluding polypropylene, with higher ash content (Table 3). Therefore, it is expected a higher level of inorganic elements in its composition.

For comparative purposes and to add more information about the mineral composition of plastics, it is presented Table 6 with the qualitative metal content of these wastes given by UEZ-LNEG, determined by X-ray Fluorescence (X.R.F.) [62].

Table 6. Qualitative metal content in plastic wastes determined by X.R.F.

	PE	PP	PS
Major metals	Titanium (Ti)	Calcium (Ca)	-
Minor metals	Lead (Pb) Calcium (Ca) Silica (Si) Aluminium (Al) Magnesium (Mg)	Lead (Pb) Zinc (Zn) Titanium (Ti) Calcium (Ca) Potassium (K) Iron (Fe) Silicon (Si) Aluminium (Al)	Iron (Fe) Silica (Si) Aluminium (Al Magnesium(Mg) Sodium (Na)
Trace metals	Zinc (Zn) Potassium (K) Sodium (Na)	Strontium (Sr) Chromium(Cr) Potassium (K) Magnesium (Mg)	Titanium (Ti) Zinc (Zn)

It can be seen that several other metals that were not determined by AAS are present in the plastics, like Titanium (Ti), Silica (Si) and Strontium (Sr). Titanium dioxide is commonly used as pigment in plastics; in fact, plastic additives are, usually, the major source for metals contamination in plastic wastes [108].

The high ash content of Polypropylene (PP) is probably derived from high calcium content, the metal with major amounts in this waste.

5.2 Pyrolysis chars

The yields of products obtained in each of the co-pyrolysis experiment are presented in Table 7. The chars obtained from the co-pyrolysis of waste mixtures 1, 2 and 3 will be from now on named as char 1, 2 and 3, respectively.

The yield of liquids presented in Table 7 corresponds to the free liquid decanted from the autoclave.

Comparing the results it can be concluded that the addition of tires to the waste mixture increased the chars yield. The pyrolysis of waste mixture 3 (the binary mixture with 50% of tires) did not produce any free liquid products since they were all soaked in the char. Taking into account that a relatively slow pyrolysis was carried out, it was expected a significant yield of chars in the waste mixtures with pine biomass and tires, since when these materials are individually pyrolysed in these conditions, char contents between 30-50% are obtained [77,83]. The pyrolysis of plastics in these conditions usually does not lead to a significant char yield [62,77,83].

Table 7. Yields of products obtained in the co-pyrolysis of the three waste mixtures.

Waste Mixture	Co-pyrolysis reaction products
1	10% (w/w) gases + 60% (w/w) liquids + 25% (w/w) chars + 5% losses
2	12% (w/w) gases + 54% (w/w) liquids + 22% (w/w) chars + 12% losses
3	2% (w/w) gases + 97% (w/w) chars + 1% losses

The results given from the thermo-gravimetric analysis of the crude chars are presented in Table 8 and it can be seen that the volatile content of the chars are significant which is indicative of their impregnation with significant amounts of the pyrolysis liquid products.

Char 2 presents the higher content in volatile and semi-volatile organic matter and Char 3 presents the higher content in heavy compounds, namely fixed carbon and ashes. Chars 1 and 3 present the higher ash content since they were obtained from mixtures with wastes of high inorganic content, namely tires and polypropylene.

Table 8. Composition of crude chars in terms of the volatility of their components.

	Char 1	Char 2	Char 3
Volatiles (% w/w)	36.4	43.7	25.5
Semi-volatiles (% w/w)	14.9	15.7	9.3
Fixed carbon (% w/w)	46.4	40.0	62.5
Ashes (% w/w)	2.35	0.64	2.73

5.3 Upgrading of pyrolysis chars

5.3.1 Sequential Solvent Extraction (SSE)

Bernardo *et al*. [97-99] have previously demonstrated that the chars obtained in the co-pyrolysis of plastics, biomass and tire wastes have to be submitted to an organic decontamination in order to reduce their toxicity. The authors concluded that a sequential extraction with solvents of increasing polarity can provide a better removal of the pyrolysis liquid-phase products from the char than an individual extraction with any of those solvents.

In this work, the same approach was applied to the three chars obtained and the results concerning the sequential solvent extractions are presented in Figure 13.

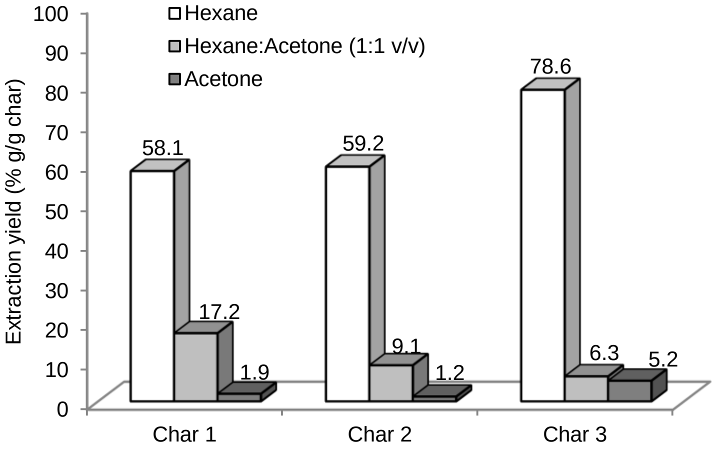


Figure 13. Extraction yields of the chars obtained in each extraction step.

The extraction yields obtained in the different extraction steps show that most of the organic products present in the three chars are non-polar and therefore soluble in pure hexane. Only residual amounts are polar enough to resist the extraction with hexane:acetone (1:1 v/v), being recovered with pure acetone.

The global extraction yields (ratio between the total mass of extracts obtained in the three extraction steps and the mass of char sample) of the sequential extractions was of 66% for char 1, 63% for char 2 and 81% for char 3. The highest extraction yield obtained for char 3 confirms that the pyrolysis liquid oils of mixture 3 were completely retained in the char.

These results show that this procedure not only ensures an efficient decontamination of the chars but also allows the recovery of a significant fraction of the pyrolysis oil and/or condensed by-products, improving the yield of the liquid products.

The results from the thermo-gravimetric analysis of the extracted chars are presented in Table 9. Comparing with the data in Table 8 it can be concluded that the sequential solvent extractions allow to remove mainly the volatile matter from the crude chars and, consequently, the heavier components corresponds to higher relative mass fractions in the extracted chars. It seems that the semi-volatile content of the chars were not significantly affected by the organic extractions.

Table 9. Composition of extracted chars in terms of the volatility of their components.

	Char 1 after SSE	Char 2 after SSE	Char 3 after SSE
Volatiles (% w/w)	2.62	5.36	1.18
Semi-volatiles (% w/w)	12.4	9.92	14.2
Fixed carbon (% w/w)	81.3	83.3	75.9
Ashes (% w/w)	3.66	1.39	8.68

SSE – Sequential solvent extraction

5.3.1.1 Metal distribution in the chars after the SSE

In order to know which were the metals present in higher amounts in the ashes of the three chars, the inorganic content of the chars after the SSE was determined. Figure 14 shows the metal distribution in each of the chars representing only the metals with concentrations above 0.5% (w/w).

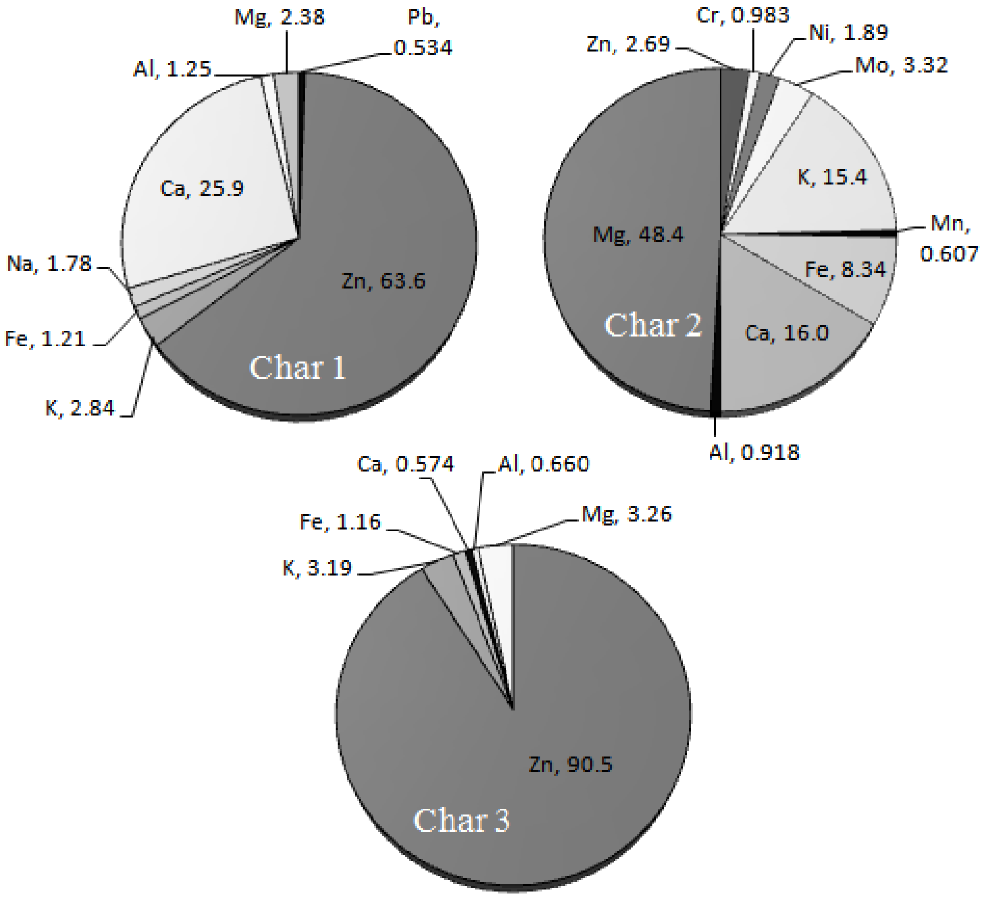


Figure 14. Metal distribution (in % w/w) in the chars after the SSE.

From the results shown in Figure 14, it is clear that the metal present in higher amount in the chars from the waste mixtures 1 and 3 is Zn. As mentioned above, these waste mixtures included used tires in their composition (Table 4) and this material is the source of Zn.

In char 1, Ca is the element more abundant after Zn, presenting a relatively high concentration (25.9%) for an individual element.

In the case of char 2, obtained from the co-pyrolysis of the waste mixture with plastics and biomass, the metal prevalent is Mg. The principal source of Mg was the pine biomass (Table 5). Also, Ca, K and Fe are significant elements in this char. This char also presented quantifiable amounts of Cr, Ni and Mo which were not detected in raw wastes (Table 5). The autoclaves where pyrolysis experiments were performed are built in Hastelloy C276 which is a nickel-molybdenum-chromium wrought alloy. A possible explanation for the presence of these metals is the contamination of the pyrolysis products by some release of heavy metals from the pyrolysis autoclaves.

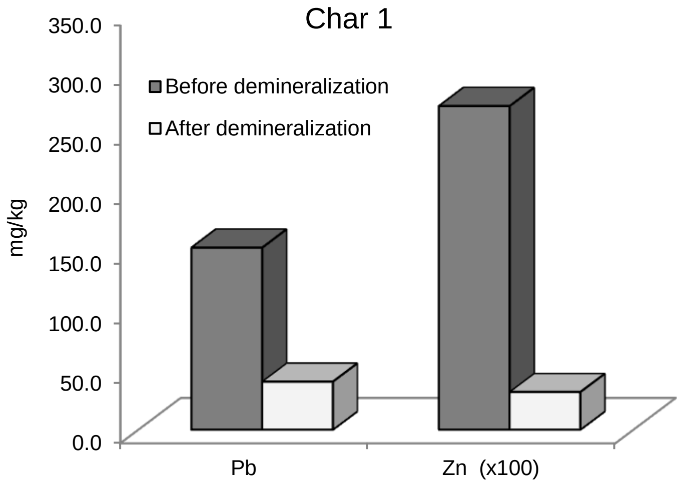
5.3.2 Demineralization of chars

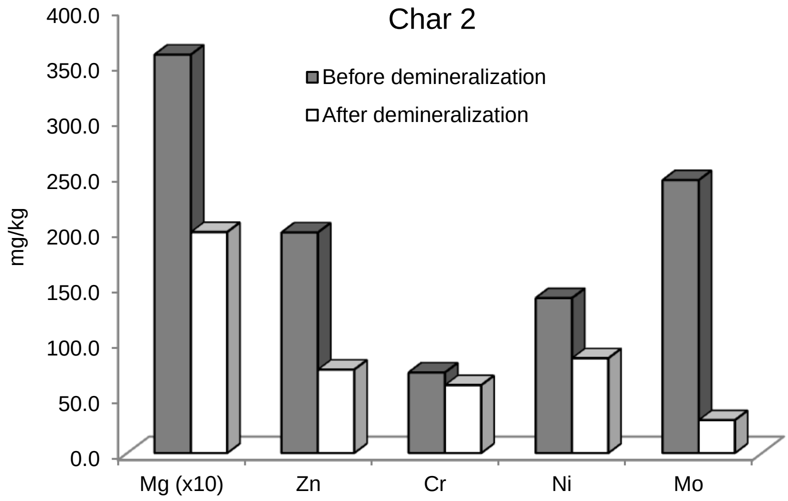
The high ash contents and their composition, particularly in chars 1 and 3, are not compatible with a safe reutilization or valorisation of these materials as adsorbents for liquid-phase applications since there is the possibility of heavy metal leaching, which restricts the applications of the chars.

Taking this into account, a demineralization procedure was applied to the chars in order to decrease the ash content, but before this procedure was performed the extracted chars remain at 350ºC during 2 hours in order to eliminate solvent residues, and some semi-volatile matter that were still present in the chars after SSE.

The main inorganic components as well as the heavy metals of concern present in the chars where used as control elements of the demineralization process. Thus for char 1, the leaching of Zn and Pb was monitored; Mg, Zn, Cr, Ni and Mo were the control elements used for char 2, while for char 3 only Zn leaching was studied.

Figure 15 shows the concentrations of the metals in the chars before and after the demineralization procedure and Table 10 shows the removal efficiencies of the metals studied.





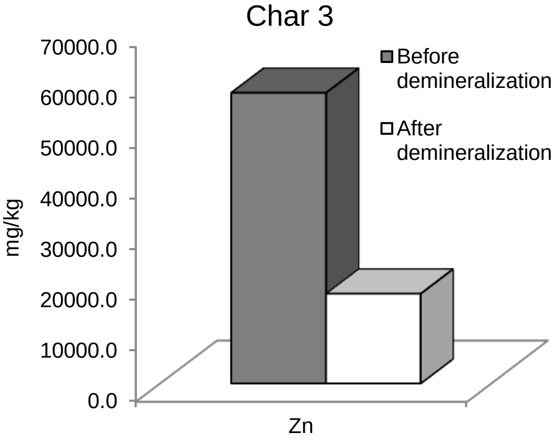


Figure 15. Concentrations of the metals in the chars before and after the demineralization procedure.

Table 10. Removal efficiencies of the metals considered in the demineralization procedure.

Metals	Removal efficiencies (%)		
	Char 1	Char 2	Char 3
Pb	73.6	-	-
Zn	88.3	62.1	69.1
Mg	-	44.4	-
Cr	-	15.7	-
Ni	-	38.8	-
Mo	-	87.9	-

Zn was effectively removed by HCl from the chars 1, 2 and 3 presenting removal efficiencies of 88.3%, 62.1% and of 69.1%, respectively. These results indicate that char overall composition and structure may also affect the removal efficiency of individual components regardless of their initial concentrations. In chars 1 and 3 it is possible that some Zn is in the form of Zinc Sulphide (ZnS or sphalerite), since ZnS has its origin in the sulfidation of ZnO added to control the rubber vulcanization process in tires manufacturing [109]. What is evident is that Zn is in a form extractable with HCl, whether as ZnS, ZnO or even as sulphate or silicate.

Pb was significantly removed from char 1 showing that Pb is in a form soluble in hot HCl such as galena (PbS) [110].

If a reuse of chars 1 and 3 for water treatment applications is to be considered, the pH range has to be taken into account since these zinc and lead sulphides are insoluble for pH values above 5-6 [111].

Char 2 presented high removal efficiency for Mo, but not so much for Mg, Cr and Ni what may indicate that these elements are in a form resistant to acidic lixiviation.

Usually, chars from biomass pyrolysis have high levels of oxygen in the form of oxygen functionalities (carboxylic acid, phenolic, hydroxyl, among others) [112], thus most of the metals may exist bounded onto these polar groups within the organic matrix. Also, there are evidences of some interactions in biomass chars of alkali metals with SiO_2 to form silicates [113].

The leaching resistance of Mg in pyrolysis chars from different residues was also noted by Hwang *et al*. [114-115]. According to these authors, textural parameters of the char such as the specific surface area and pore structure can also be a reason to restrain metal leaching. The low HCl leachability of Mg could also be indicative that this element is associated with silicates [116].

Given the fact that pyrolysis chars are carbonaceous materials similar to coal and giving the lack of information about the modes of occurrence of metallic elements in pyrolysis chars, it is reasonable to use the extensive knowledge about coal to make assumptions in pyrolysis chars.

Riley *et al*. [110] and Wang *et al*. [116-117] assumed that in carbonaceous materials like coal, some metals such as Ni and Cr might be strongly associated with the organically matrix and they are not easily solubilised with acids (except ion-exchanged elements such as the ionically bounded with polar organic groups) and/or they are matrix-encapsulated as fine mineral particles to which an acid solution has hardly access. How these elements are incorporated with the organic matter is not clear.

According Huggins and Huffman [118] chromium appears to occur in most bituminous coals in only two major forms: as Cr^{3+} in organic association and as Cr^{3+} in illite.

There is also the possibility that in char 2, chromium trioxide was formed during pyrolysis, being very hard to extract because of its high stability and insolubility in water, acid, and bases [119].

Concerning Ni, it is not clear the modes of occurrence in coal. According Finkelman *et al*. [120], it may be either organically bound or associated with sulphides but given the low removal efficiency of this element from the chars probably is strongly associated with the organic matrix.

The results obtained with char 2 indicate that this material may have a positive effect on the immobilization of metals, therefore its use in the adsorption of ionic pollutants by ion-exchanged mechanism it’s a possibility to be studied.

5.4 Physico-chemical characterization of the upgraded chars

The results given by the thermo-gravimetric analysis of the upgraded chars are shown in Table 11.

Table 11. Characterization of the chars after the upgrading treatment (SSE followed by demineralisation treatment).

	Char 1 upgraded	Char 2 upgraded	Char 3 upgraded
Volatiles (% w/w)	(2.62)2.23	(5.36)5.61	(1.18)1.78
Semi-volatiles (% w/w)	(12.4)4.82	(9.92)3.01	(14.2)0.40
Fixed carbon (% w/w)	(81.3)91.8	(83.3)91.2	(75.9)94.7
Ashes (% w/w)	(3.66)1.11	(1.39)0.20	(8.68)3.16
Carbon Content (% w/w)	79.0	67.2	87.7
Hydrogen Content (% w/w)	1.8	2.2	0.6
Nitrogen Content (% w/w)	1.0	1.2	0.6
Sulphur Content (% w/w)	0.44	0.10	0.74
Oxygen Content (% w/w)[a]	17.8	29.3	10.4
HHV (kJ/g)[b]	27.9	23.0	30.2
Apparent density (g/cm^3)	0.474	0.499	0.358

Values in parenthesis - before demineralization procedure, [a] by difference,
[b] HHV – High Heating Value (calculated according to Eq. 1)

Comparing the ash contents before and after the demineralization treatment, chars 1, 2 and 3 presented a reduction in the ash content of around 70%, 86% and 64%, respectively. These results show that the demineralisation procedure was efficient in the removal of most inorganic contaminants.

The heat treatment at 350ºC applied to the chars after the sequential solvent extraction procedure was efficient in decreasing the semi-volatile matter; however the volatile matter was not greatly affected.

Chars 1 and 2 presented higher amounts of volatile and semi-volatile matter than char 3, which is consistent with the higher values of apparent density presented by those chars.

Concerning the elemental analysis, whose results are also presented in Table 11, it can be seen that the three chars present high carbon content and chars 1 and 3, from the co-pyrolysis of waste mixtures with tires, presented higher sulphur content. Sulphur comes from the tire waste as a result of the vulcanisation process, as already referred, and the presence of this element in the chars strengthens the hypothesis that some of the metals might have formed sulphides that were incorporated into the char.

Chars 1 and 2 that resulted from pyrolysis of mixtures containing pine biomass presented higher amounts of oxygen and nitrogen, which can be indicative of the presence of polar functional groups on the char surface [121] and corroborates the theory that some of the metals in char 2 may exist bounded onto the polar groups through a ion-exchanged mechanism [93].

The high heating values (HHV) of the upgraded chars presented in Table 11 were estimated using the results from the ash content and the elemental analysis according to the Eq. 1 proposed by Channiwala and Parikh [122]:

$$\text{HHV (in kJ/g)} = 0.3491C + 1.1783H - 0.1034O - 0.0211\text{Ashes} + 0.1005S - 0.0151N \qquad \text{(Eq.1)}$$

Char 2 presents the lowest HHV because of the higher content of oxygen. The calculated HHV for chars 1 and 3 indicate that these materials have calorific values comparable to other solid fuels such as coal [122] making their combustion for energy recovery also a possible valorisation alternative.

5.5 Textural and adsorption properties of the upgraded chars

Figure 16 presents the N_2 adsorption-desorption isotherms of the chars at 77 K. For char 2, the amount adsorbed of N_2 is very small in the entire relative pressure (P/P_0) range, which indicates that this char is almost a non-porous material. According to the IUPAC classification, chars 1 and 3 exhibit isotherms of type II, typical of non-porous or macroporous adsorbents [123]. However, the hysteresis loop present in the isotherms of those chars is usually associated with capillary condensation in mesopores structures. This type of hysteresis loop is characteristic of aggregates of plate-like particles giving rise to slit-shaped pores [123].

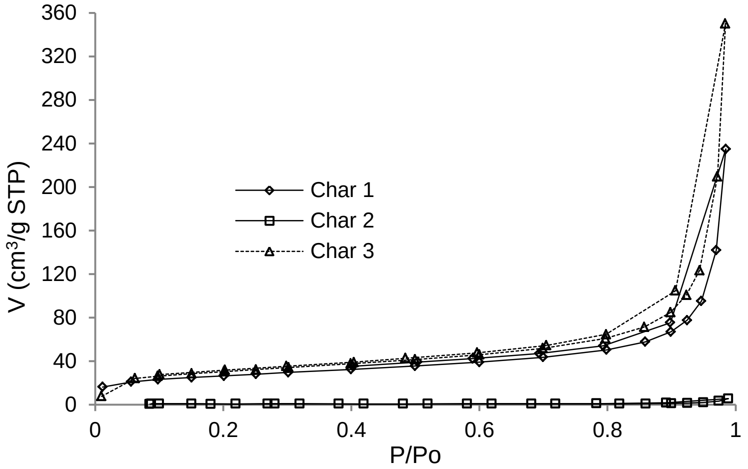


Figure 16. N_2 adsorption-desorption isotherms of the upgraded chars at 77 K.

The textural parameters given by the N_2 isotherms are presented in Table 12. The mesoporosity of chars 1 and 3 can be confirmed with the average pore diameter (mesopores are in the range 0.002-0.05 µm) and the mesopore volume. The low values of BET surface areas of these chars are in agreement with the fact that these samples are resulting from a pyrolysis process with no further activation step. Therefore, it is expected that some residual volatile matter may block the incipient porosity of the chars [15].

Table 12. Textural characterization and methylene blue number of the upgraded chars.

Sample	From N_2 adsorption-desorption isotherms				From Hg porosimetry			Methylene blue number (mg/g)
	S_{BET} (m^2/g)	Total pore volume (cm^3/g)	Mesopore volume (cm^3/g)	Average pore diameter (µm)	Total pore volume (ml/g)	Mesopore volume (ml/g)	Macropore volume (ml/g)	
Char 1	91.4	0.363	0.354	0.018	2.04	0.51	1.53	13.8
Char 2	2.032	0.009	n.c	n.c	1.51	0.04	1.47	3.59
Char 3	105	0.542	0.544	0.019	2.09	0.73	1.36	22.2

n.c – not calculated

Given the fact that char 2 does not present micro- and mesopores, it is not possible its characterization by N_2 adsorption. Thus, mercury porosimetry was used as a complementary technique.

Figure 17 presents the results obtained with mercury porosimetry and shows that char 2 presents porosity in the macropore range, more specifically it is an interparticle porosity due to the high pore size diameter at which occurs the mercury intrusion. This char was also the one that presented the highest apparent density and higher content of volatile matter (Table 11) which is indicative that this char still contains a significant amount of condensed volatiles obstructing the pores. Further/Other treatment for devolatilization/activation might lead to pore widening.

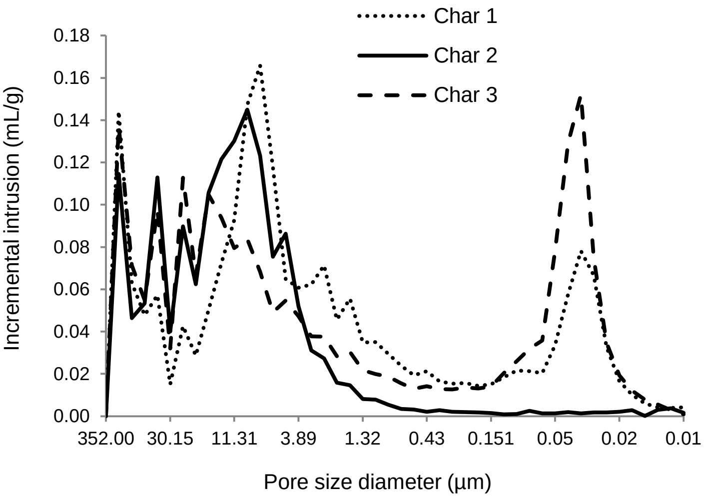


Figure 17. Incremental intrusion *vs* pore size for mercury porosimetry.

For chars 1 and 3, the results from mercury porosimetry are in good agreement with those obtained by N_2 isotherms since peaks of mercury intrusion in the mesopore and macropore range are observed. The pore volume distribution for these chars (Table 12) shows that macropores prevail over mesopores: 75% and 65.1% of macropores for chars 1 and 3, respectively. The macroporosity are probable due to the aggregates of plate like particles as indicated by the N_2 adsorption-desorption studies.

It is clear that the chars resulting from the co-pyrolysis of waste mixtures with tires present better textural properties; chars from the individual pyrolysis of tires are mostly constituted of carbon black and this carbonaceous material presents, typically, porous surfaces [124-125].

The methylene blue numbers obtained for the three upgraded chars are also presented in Table 12. The methylene blue adsorption test reveals the adsorptive properties of a carbon towards a larger molecule and this dye often serves as a model compound for removing large organic contaminants from aqueous solutions. Since these chars were found to be mesoporous and macroporous materials, they should have good adsorption properties towards bulky molecules.

The methylene blue numbers obtained, in particular for chars 1 and 3, are comparable or even higher than those obtained for various adsorbents referred in the literature, such as activated carbon prepared from different precursors, bioadsorbents, agricultural solid wastes, fly ashes, among others [126].

As expected, char 2 presented the lowest methylene blue number given its lower surface area and non-porosity.

6. CONCLUSIONS

In this work an upgrading treatment was carried out in crude chars from the co-pyrolysis of different mixtures of plastics, biomass and tire wastes in order to produce value-added carbon materials.

Submitting the chars to sequential solvent extractions with solvents of increasing polarity resulted in the removal/recovery of significant amounts of the pyrolysis oils.

The chars present high ash contents, particularly those resulting from the waste mixtures with tires that are not compatible within a safe reutilization or valorisation of these materials. In order to decrease the ash content of the chars, a demineralization procedure was successfully applied and high efficiency removals of the majority of the metallic elements were achieved.

The demineralization study allowed to conclude that the main heavy metals as well as the most hazardous are significantly immobilized in the char matrix if aggressive acidic conditions were not used.

Heteroatoms such as oxygen, sulphur and nitrogen are present in the upgraded chars; therefore it can be inferred the presence of polar functional groups on the chars' surface, which represents an increase interest for the adsorption of specific organic and inorganic pollutants.

The upgraded chars are mainly mesoporous and macroporous, thus they can be used for several purposes. The large pore sizes enable a high adsorption capacity as well as a good selectivity towards bulky molecules such as dyes, proteins, polycyclic aromatic hydrocarbons, dioxins, among others.

It should be stressed that no activation treatment was performed in the chars. Therefore, they present relatively low surface areas.

As future work it is suggested to perform leaching studies of these chars with solutions at different pH values in order to study the stability of the inorganic species.

It will be also interesting submit the chars obtained from waste mixtures with pine biomass to other or further treatment in order to provide a more effective devolatilization/activation of the pores.

It is suggested to perform aqueous adsorption tests on inorganic solutes such as Cu, Pb, Cd, As, among others, in particular with the chars obtained from waste mixtures with pine biomass. With the chars obtained from waste mixtures with tires, and given their porosity properties, it is suggested to test their adsorption properties through bulky non-polar contaminants such as polycyclic aromatic hydrocarbons or even some dyes.

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8. ANNEXES

8.1 Thermo-gravimetric analysis of the crude chars

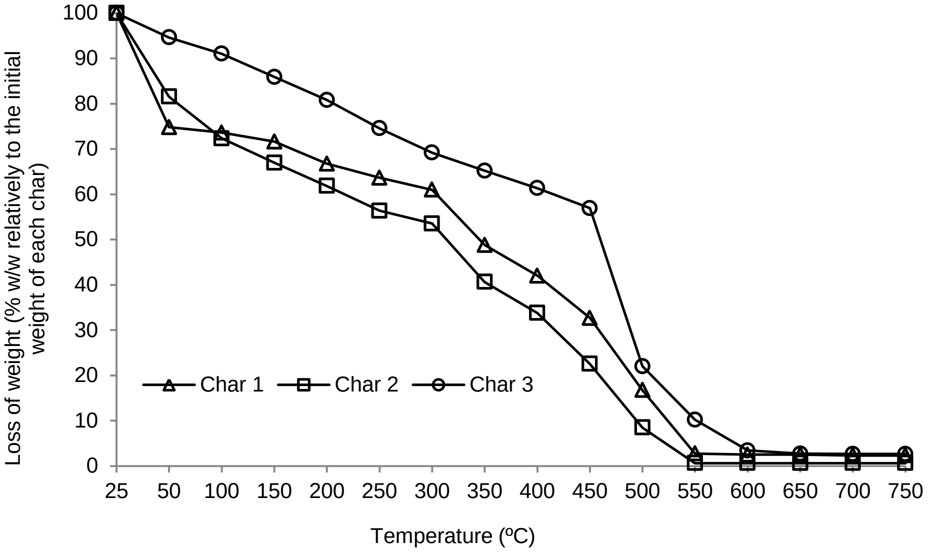

Figure 18. Loss of weight (% w/w relatively to the initial weight of each crude char), by combustion in a microwave furnace up to 750 ºC.

8.2 Thermo-gravimetric analysis of chars after the Sequential Solvent Extraction (SSE)

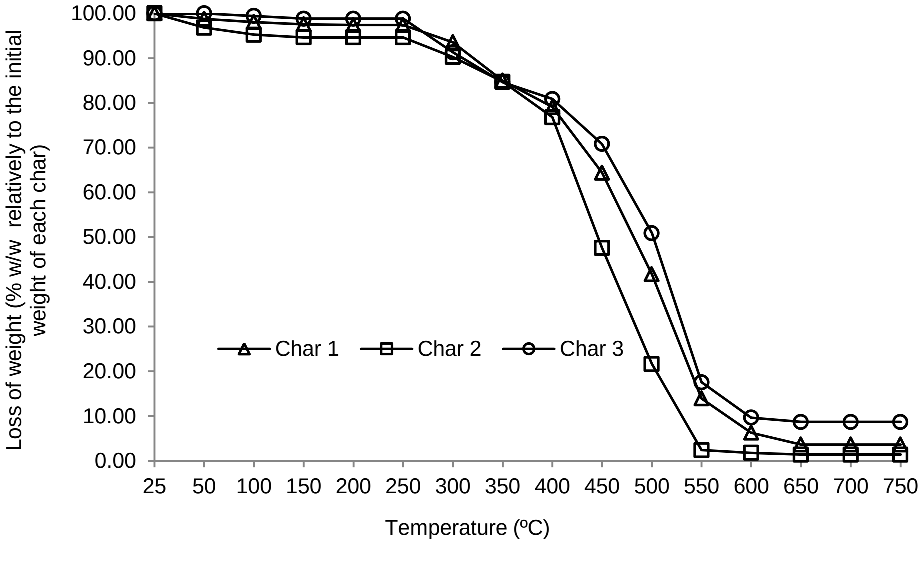

Figure 19. Loss of weight (% w/w relatively to the initial weight of each char after the SSE), by combustion in a microwave furnace up to 750 ºC.

8.3 Thermo-gravimetric analysis of chars after the upgrading treatment (SSE followed by demineralisation treatment)

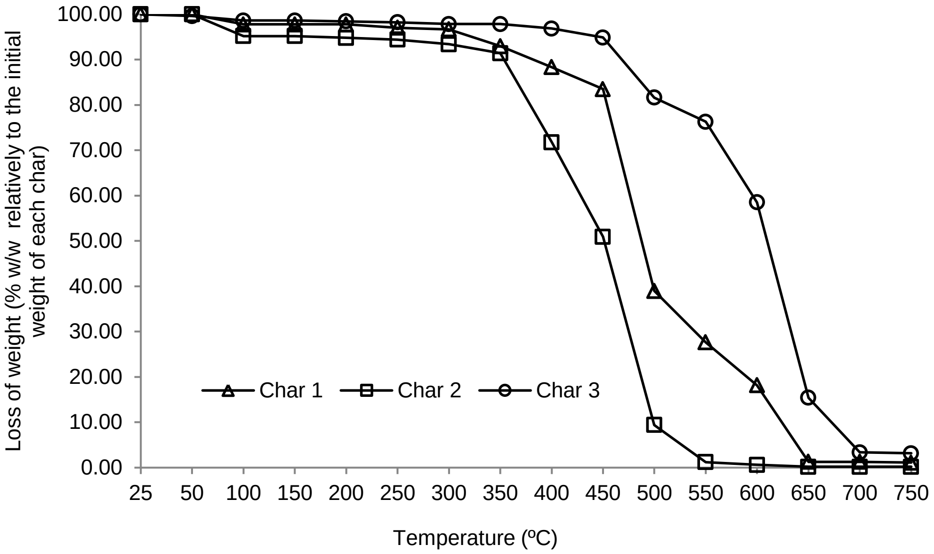

Figure 20. Loss of weight (% w/w relatively to the initial weight of each char after the upgrading treatment), by combustion in a microwave furnace up to 750 ºC.