

Università degli Studi di Napoli Federico II



Department of
Chemical, Materials and Industrial Production Engineering

PhD Thesis in
Industrial Product and Process Engineering
Cycle XXXVI

Behavior of Lead during Pyrolysis of Contaminated Biomass

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Abstract

Pyrolysis of lignocellulosic biomasses is a consolidate process to obtain biofuels and biomaterials. However, the cultivation of biomasses for energetic purposes must be carefully evaluated to avoid conflicts with the cultivation of food crops. To overcome such issues, new kinds of biomasses are being considered, such as contaminated biomasses; heavy metals play a prominent role among the possible biomass contaminants. However, pyrolysis of heavy metals contaminated biomass is a scarcely investigated topic, and the information about heavy metals fate and influence during the pyrolysis process are few.

This Ph.D. thesis investigates the transformations of Pb, one of the most common soil contaminants, during pyrolysis in a wide range of pyrolysis temperatures (400-800 °C) in order to give indications on the transport mechanisms that determine its distribution into the different pyrolysis products and its possible effects on the pyrolysis mechanisms. Also, the effects of different Pb chemical forms typically found in the soil and of different mechanisms responsible of biomass contamination are investigated.

Poplar (*Populus nigra*), grown on Pb contaminated soil, is used for the experimental campaign. Pyrolysis tests are conducted at slow heating rate at three different final pyrolysis temperatures (i.e. 465, 600 and 800 °C). In order to explore the devolatilization and the chemical transformation of Pb during the pyrolysis process a reactor configuration is used where solid elutriation phenomena can be considered negligible. Poplar samples are doped to achieve a concentration of Pb of about 1000ppm with two Pb salts, $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ and $\text{Pb}(\text{NO}_3)_2$, representing the most common chemical form of Pb contamination. Moreover, in order to reproduce different source of contamination (authigenic or detrital or a mix of them) three different doping procedures are adopted, namely ion exchange, dry mixing and wet impregnation. The possible interactions with inorganics intrinsically present in the biomass have also been investigated by using both plain and demineralized poplar as feedstock for Pb doping.

All the pyrolysis products (bio-oil, biochar and gas) are characterized extensively to study the distribution of Pb, its chemical form in the solid residue and its possible effect on the pyrolysis mechanisms and products characteristics. Chromatographic techniques are used for the gas and liquid characterization, whereas biochar is analysed through elemental analysis, ashing, porosity, ICP-MS (Inductively Coupled Plasma Mass spectroscopy), XRD (x-ray diffraction) and BCR sequential extraction. The results related to biochar characterization highlighted that both the initial Pb

speciation and the type of contamination affect many biochar physical chemical properties and are relevant in Pb volatilization. From the gas and bio-oil analyses emerged that also the other pyrolysis products are influenced by the presence of Pb in terms of yield and composition.

The results of the study provide fundamental indications for the optimization of a very robust pyrolysis reactor, namely the auger reactor, typically adopted for both biochar and bio-oil production by taking into account not only the yields of the desired product but also Pb content and stability.

1 Introduction

Biomasses play a key role in the development of renewable energy and biofuels; the cultivation of biomass for energy purposes is currently regulated, in Europe, by (RED II EU Directive). This directive promotes the use of biofuels in the European States by setting a target of a minimum of 32% of renewable energy by 2030. Lignocellulosic biomass is a vegetal biomass composed mainly of cellulose, hemicellulose and lignin that account for 40-45 wt. %, 15-25 wt. % and 15-25 wt. % of the total biomass weight, respectively (Bridgwater, 1999). The exact composition of a vegetal biomass is highly variable with the plant and soil type: woody biomasses are characterized by a higher lignin content, while herbaceous biomasses are composed mostly by cellulose and hemicellulose (Vassilev et al., 2010). Lignocellulosic biomasses contain also other organic compounds called extractives, other than an inorganic fraction; extractives and inorganics are minor components of lignocellulosic biomasses, but their presence is relevant both for the living plant metabolism (Engels et al., 2011) and for the subsequent use of the biomass. The most abundant inorganic elements that naturally occur in lignocellulosic biomass are alkali and alkali-earth metals (AAEMs) (Giudicianni et al., 2021), but depending on the type of plant and its growth conditions many inorganic elements can be found in the biomass structure (Vassilev et al., 2012).

To supply the rising demand for lignocellulosic biomass while avoiding iLUC (indirect land use change) related concerns (Fritsche et al., 2010), there is the need to consider alternative biomass type, such as residual or contaminated biomasses.

The term “contaminated biomass” identifies a biomass that contains potentially harmful substances and pollutants, both of organic and inorganic nature. Lignocellulosic biomass can become contaminated when, for example, it comes from plants used in phytoremediation strategies. Phytoremediation is a remediation technique for degraded soils that involves the cultivation of specific types of plants capable not only to grow on poor quality and contaminated soils, but also to improve the soil properties, to limit the spread of contaminants and/or to uptake them from the soil. Phytoremediation techniques can be mainly classified in:

- Phytoextraction: this technique involves plants that can accumulate concentrations of contaminants in their harvestable tissues. For example, hyperaccumulators are plants that are capable to accumulate greater than normal concentrations of contaminants in their tissues by a factor of up to 1000 times when compared to non-accumulators (Rascio & Navari-Izzo, 2011). However, hyperaccumulators often are not suitable for phytoextraction since their

growth tend to be slow and cannot be harvested often. On the contrary, short rotation forestry crops, or short rotation coppice, such as poplar and willow, are more suitable for phytoextraction. In fact, despite being able to accumulate lower concentrations of contaminants in their tissues, they exhibit a fast growth and can be harvested often, giving good results in terms of soil remediation and economic return from biomass production (Abhilash et al., 2012). Phytoextraction is suitable for inorganic contaminants, especially heavy metals such as lead (Pb), zinc (Zn), copper (Cu), iron (Fe), nickel (Ni), chromium (Cr), arsenic (As), cadmium (Cd) and mercury (Hg).

- Rhizodegradation: this technique is based on the ability of plants to promote microbial activity in the rhizosphere, which is the volume of soil surrounding the roots of the plant, through the release of exudates (Berendsen et al., 2012). The soil microorganisms can then actively destroy soil pollutants, reducing soil contamination. Rhizodegradation is suitable for organic contaminants, and in particular hydrocarbons.
- Phytostabilization: this technique aims to contain and stabilize contaminants within the soil through accumulation by roots, precipitation within the rhizosphere and the establishment of a vegetative cover (Bolan et al., 2011). Moreover, phytostabilization prevents the dispersion of contaminants via dust lifting, which is a phenomenon particularly relevant in arid and windy areas, while contextually reinforcing the soil texture (Simon & Collison, 2002).

The phytoremediation of heavy metals is bound to their accumulation and immobilization in (and on) the plant tissues, that is regulated by specific biological pathways. During their life cycle, plants must acquire several inorganic elements that are essential macronutrients (N, P, K, S, Ca, and Mg) and micronutrients elements (Fe, Zn, Mn, Ni, Cu, Mo). The plants have developed highly specific mechanisms to absorb these nutrients from the soil, translocate and store them in their tissues. Usually, the absorption mechanisms are selective toward specific elements. The absorption capacity of the inorganic species depends by many factors, such as physical-chemical properties of the soil (pH, redox potential, organic matter content, cationic exchange capacity) (Calace et al., 2002), absorption reaction kinetic (Fischerová et al., 2005), inorganic species bioavailability (Fischerová et al., 2005) and chemical properties of the plant. In non-hyperaccumulator plants, the uptake of non-macronutrient inorganics does not exceed the metabolic requirements (< 10 ppm). On the other hand, hyperaccumulator plants (as anticipated) can reach accumulation levels of micronutrient inorganics and heavy metals in the range of thousands of ppm. More than 400 plants species are heavy metals hyperaccumulator (Reeves et al., 1999); most of them is specialized in Ni accumulation, around 30 plant species can absorb Co, Cu and Zn, while there is no known hyperaccumulator plant that is specialized for Pb absorption.

In general, phytoremediation is a complex matter, as can be seen from the overview reported in Table 1 (US-EPA, 2000).

There is a multitude of plants that can be successfully used for specific phytoremediation strategies targeting different pollutants, other than hyperaccumulators.

Table 1 - Overview of the phytoremediation techniques.

Mechanism	Process Goal	Media	Contaminants	Plants	Status
Phytoextraction	Contaminant extraction and capture	Soil, sediment, sludges	Metals: Ag, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Zn; Radionuclides: ⁹⁰ Sr, ¹³⁷ Cs, ²³⁹ Pu, ^{238,234} U	Indian mustard, pennycress, alyssum sunflowers, hybrid poplars	Laboratory, pilot, and field applications
Rhizofiltration	Contaminant extraction and capture	Groundwater, surface water	Metals, radionuclides	Sunflowers, Indian mustard, water hyacinth	Laboratory and pilot-scale
Phytostabilization	Contaminant containment	Soil, sediment, sludges	As, Cd, Cr, Cu, Hs, Pb, Zn	Indian mustard, hybrid poplars, grasses	Field application
Rhizodegradation	Contaminant destruction	Soil, sediment, sludges, groundwater,	Organic compounds (TPH, PAHs, pesticides chlorinated solvents, PCBs)	Red mulberry, grasses, hybrid poplar, cattail, rice	Field application
Phytodegradation	Contaminant destruction	Soil, sediment, sludges, groundwater surface water	Organic compounds, chlorinated solvents, phenols, herbicides, munitions	Algae, stonewort, hybrid poplar, black willow, bald cypress	Field demonstration
Phytovolatilization	Contaminant extraction from media and release to air	Groundwater, soil, sediment, sludges	Chlorinated solvents, some inorganics (Se, Hg, and As)	Poplars, alfalfa black locust, Indian mustard	Laboratory and field application
Hydraulic control (plume control)	Contaminant degradation or containment	Groundwater, surface water	Water-soluble organics and inorganics	Hybrid poplar, cottonwood, willow	Field demonstration
Vegetative cover (evapotranspiration cover)	Contaminant containment, erosion control	Soil, sludge, sediments	Organic and inorganic compounds	Poplars, grasses	Field application
Riparian corridors (non-point source control)	Contaminant destruction	Surface water, groundwater	Water-soluble organics and inorganics	Poplars	Field application

A plant that results versatile in phytoremediation is poplar, that has been used for the treatment of both organic and inorganic contaminants. Moreover, poplar is a short rotation coppice, which is a type of plant characterized by fast growth and that can be harvested every couple of years (Vanbeveren & Ceulemans, 2019), adding the advantage of biomass production to the phytoremediation application. Poplar is mostly used for the phytoextraction or the phytostabilization of heavy metals in contaminated soil. For example, (Pierzynski, 2015) planted poplar trees on a former mineral site contaminated with As and Cd, while (Baldantoni et al., 2014) studied the phytoremediation capacity of poplar in relation to Cu, Cd, Fe, Zn and Pb

Focusing on inorganic contaminants, and in particular on heavy metals, they can be bound to the biomass structure in different ways, depending on the type of biomass and the specific heavy metal considered. The heavy metals can be integrated into the biomass structure and chemically bound to its components, which is the main occurrence in phytoextraction, or can be deposited and physically bound to the surface or external layers of the biomass, which is the main occurrence in phytostabilization. Following the definition of (Vassilev et al., 2012), the first case will be referred to as “authigenic contamination” while the second case will be referred to as “detrital contamination”. The most usual case is a co-existence of these two types of contaminations. Occasionally, heavy metals can also be found as independent solid inclusions, both as pure metals and alloys, but often this is due to handling of the collected biomass with metal tools; in this case the contamination can be referred to as “anthropic”.

One of the main issues of phytoremediation is how to treat and dispose of the harvested contaminated biomasses. Composting and compaction have been considered as possible treatments (Ghosh & Singh, 2005) to reduce the volume of the contaminated biomasses making their handling and eventual disposal easier. However, composting can promote the formation of soluble organic compounds that increase the mobility of heavy metals (Sas-Nowosielska et al., 2004). Thermochemical treatments result more appealing since they can give an economic return coupling the disposal of contaminated biomass with the production of valuable products such as energy or bio-based materials.

Combustion of contaminated biomass must be carefully approached to avoid the release of contaminants in the atmosphere; efficient purification equipment has an essential role in the combustion process of heavy metal contaminated biomass (Chalot et al., 2012). Co-combustion of contaminated biomass with coal has also been considered (Sas-Nowosielska et al., 2004).

During the gasification of contaminated biomass, the volatilization of heavy metals can hinder the properties of the produced gas and can cause equipment fouling, corrosion, and catalyst deactivation (Chai et al., 2022; Mullen & Boateng, 2013). These effects can be mitigated by purifying the produced gas before further usage (Cui et al., 2021) or consider biomass pretreatment to decrease the initial metal content of the feedstock (Yu et al., 2014).

Pyrolysis is getting more and more attention as a thermochemical treatment for contaminated biomasses (Vocciante et al., 2019) as it has two main beneficial effects: through pyrolysis, the volume of the contaminated material is greatly reduced, so its handling and disposal are simplified; moreover, pyrolysis is also a valorisation technique, since it can generate valuable products such as bio-oil and biochar from waste biomass.

2 Aim of the thesis

From a literature survey, it emerges that the presence of heavy metals influences the pyrolysis process of contaminated lignocellulosic biomasses. In particular, heavy metals seem to interfere with the pyrolysis mechanisms altering pyrolysis products yields and properties. Moreover, during pyrolysis heavy metals can react changing their chemical speciation and can be displaced among pyrolysis products, hindering their subsequent utilization.

However, pyrolysis of heavy metals contaminated biomass is still a recent topic and the knowledge on the subject is only partial. In general, the observed effects of heavy metals are correlated to their absolute concentration, disregarding any possible influence of their chemical speciation or of their bond with the biomass tissues. The main aim of this PhD thesis is to contribute to fill this knowledge gap starting from the study of Pb, one of the most widespread heavy metal contaminants, focusing on chemical speciation and contamination type.

The PhD research purpose can be summarized in three objectives:

- Evaluation of the effects of Pb speciation and contamination type on pyrolysis mechanisms in terms of products yield and properties modifications.
- Clarification of the displacement behavior of Pb during pyrolysis, focusing on the effect of Pb speciation and contamination type
- Design, realization and startup of a continuous intermediate pyrolysis system for contaminated biomass processing

3 State of the art

3.1.1 Pyrolysis

Pyrolysis can be defined as the thermochemical degradation of biomass in an oxygen free atmosphere, resulting in three kinds of products: a solid phase, called char or biochar, a condensable vapor phase, known as bio-oil, and a permanent gas phase. The pyrolysis products are determined in yields and characteristics by both the biomass composition and the operational conditions of the pyrolysis process. The main operational parameters that define the pyrolysis process are the final temperature of the process, usually called for simplicity “pyrolysis temperature”, and the heating rate of the process. Other operational parameters that affect the outcomes of pyrolysis to a lesser extent are the process pressure and the pyrolyzing agent (type and flow rate), that is the inert gas used as carrier gas.

Depending on the pyrolysis temperature and heating rate, the pyrolysis process can be categorized into:

- Slow pyrolysis, which is characterized by a heating rate not higher than 60 °C/min and final temperature that usually is between 300 and 800 °C. Common residence times for slow pyrolysis are from several minutes to hours. In slow pyrolysis conditions the yield of char is maximized.
- Fast pyrolysis, which is characterized by a heating rate higher than 100 °C/min that can go up to 1000 °C/min and higher (often referred to as flash pyrolysis), and a final temperature between 450 and 600 °C. Fast (and flash) pyrolysis typical residence times range from fractions of seconds to few minutes, and these operational conditions are meant to maximize the bio-oil yield.

The proposed classification is not particularly strict, especially regarding pyrolysis temperature. Some authors (Hornung, 2013) also introduce an “intermediate pyrolysis” that, as the name suggests, is carried out under heating rates comprised between slow and fast pyrolysis.

Looking at vegetal biomass pyrolysis, it is a quite known subject, even though the complexity and variability of biomass composition make it challenging to identify standard conditions for the process and to develop a detailed kinetic mechanism that can predict the outcome of pyrolysis (Anca-Couce, 2016; Ranzi et al., 2017). Cellulose, hemicellulose, lignin and extractives have specific degradation pathway (Anca-Couce, 2016) that strongly interact with each other and with the inorganics during pyrolysis, contributing to the complexity of the process (Giudicianni et al., 2021).

3.1.2 Effect of pyrolysis thermal conditions

3.1.2.1 Product yields

Figure 1 (Di Blasi, 2009) reports the yields of the three pyrolysis products from a wide set of experiments exploring the effects of both pyrolysis temperature and heating rate, dividing the data in slow and fast pyrolysis conditions.

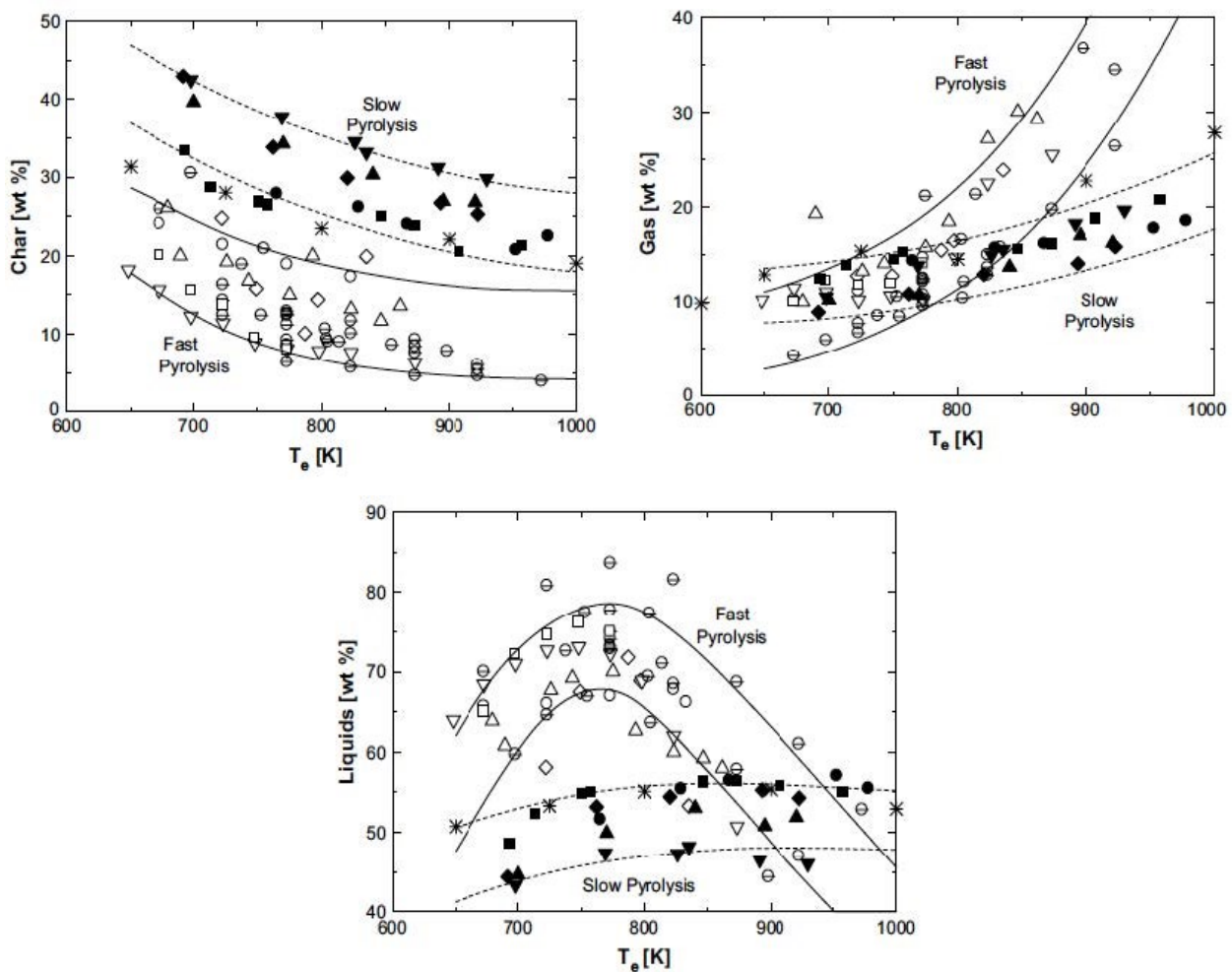


Figure 1 - Yields of pyrolysis products under different pyrolysis regimes (Di Blasi, 2009)

Char yield results higher for slow pyrolysis conditions regardless of the pyrolysis temperature. However, the char yield decreases as pyrolysis temperature increases, both for fast and slow pyrolysis. In general, depending also on the feedstock composition, biochar yield can range from 45 wt. % (slow pyrolysis at 700 K) to 5 wt. % (fast pyrolysis at 980 K).

Gas yield increases with the pyrolysis temperature regardless of the heating rate. Up to 800 K, the gas yields of slow and fast pyrolysis experiments are comparable; however, as pyrolysis temperatures further increase fast pyrolysis conditions results in a higher gas yield with a maximum of about 35 wt. % at 900 K.

Finally, liquid yields show different trends as pyrolysis temperature increases: in slow pyrolysis conditions, the liquid yield is quite independent of pyrolysis temperature, ranging from 45 wt. % to 55 wt. %. Fast pyrolysis conditions, on the other hand, allow for maximum liquid yield in a short temperature range, roughly from 720 K and 820 K. For temperatures outside this range, the liquid yield decreases sharply.

3.1.2.2 Product properties

- **Char**

Char can be considered as a multiphase system composed of a carbon matrix and a mineral phase. Nowadays, the deep knowledge of the chemical and physical characteristics of char is leading to the exploration of many routes for valorizing the char potential for diverse applications other than soil amendment, such as treatment of polluted gas or liquid streams, synthesis of composite materials and many others.

The content and composition of both organic and inorganic char constituents depend on pyrolysis operational parameters, namely, temperature, heating rate, pressure, and gas and solid residence times. Pyrolysis temperature affects the chemical and physical characteristics of the char more than the other variables.

One of the most common characterizations of char is the determination of its elemental composition in terms of C, H, N and O. The composition of a various population of biomasses and chars produced under pyrolysis temperatures in the range 200-1000 °C is reported in Figure 2 (Weber & Quicker, 2018).

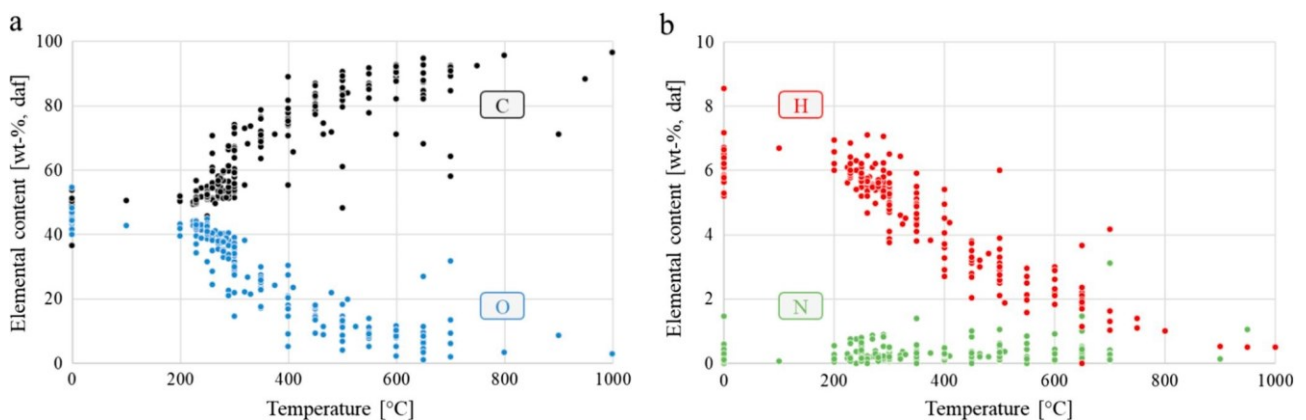


Figure 2 C, H, N, O content of carbonized woody biomass (Weber & Quicker, 2018)

The C and O contents of biomass typically range between 50 and 40 wt. % on a dry ash free basis, whereas the H content varies between 5 and 7 wt. %. The most significant changes during char production occur in the temperature range of 200–400 °C, where C and O contents are in the range

of 70–80 and 10–30 wt. %, respectively. At temperatures higher than about 700 °C, charring reactions occur, increasing the char aromaticity by growth of graphene layers and removal of heteroatoms. At these temperatures, chars may reach C and O contents of higher than 95 wt. % and lower than 5 wt. %, respectively, whereas the H content decreases to less than 2 wt. % for very high treatment temperatures. N content does not exhibit a specific trend with temperature according to the analyzed data. The inorganic content, which determines many important properties of char, increases with the pyrolysis temperature mainly due to the devolatilization of the organic matter of the biomass. The inorganic matter results more thermally stable; however, it must be considered that some inorganics can be present as volatile compounds. The textural characteristics of char in terms of porous structure evolve as the pyrolysis temperature increases and is influenced both by the organic and inorganic phases of the biomass. The char pore structure is composed by micro-, meso-, and macropores, (Gargiulo et al., 2018) which are pores with diameters smaller than 2 nm, between 2 and 50 nm, and greater than 50 nm, respectively. The non-monotonous trend of the char specific surface area with temperature results from the occurrence of devolatilization, repolymerization of entrapped condensable species, graphitization, and ash sintering phenomena. Depending on the original biomass type and heating rate, the maximum specific surface area was in the range 300–500 m²/g at temperatures between 500 and 700 °C (Weber & Quicker, 2018).

- **Bio-oil**

The composite nature of the biomass and the severe thermal treatments (in terms of time-temperature relationship) to which the biomass is subjected produce a very complex chemistry of the condensable fraction, where about 300 species were identified and grouped into primary, secondary and tertiary products (Evans & Milne, 1987). The thermal conditions of the process and the residence time of the condensable fraction in the reaction environment affect their relative contents. When matching the optimal conditions for its yield maximization, acids, alcohols, aldehydes, esters, ketones, phenols, guaiacols, syringols, sugars, furans, alkenes, and aromatics make up most of the condensable fraction (Evans & Milne, 1987). The pyrolysis products may include a variable amount of water. The water content in the condensable fraction can be controlled using multiple condensation stages, namely a fractionated condensation (Lehto et al., 2014).

Dehydrogenation/aromatization reactions that occur at very high temperature can result in larger polynuclear aromatic hydrocarbons that may condense into polycyclic aromatic hydrocarbons (PAH). (Evans & Milne, 1987) The physical properties of the bio-oil, like the high density, viscosity and surface tension, strongly depend on its water content. Bio-oil is indeed immiscible with fossil-based oils and has less than half their calorific value due to its high oxygen content. Compared to

conventional petroleum-based fuels, bio-oil is not as stable due to its heterogeneous composition, where its components can react to each other to form larger water-insoluble molecules (Gargiulo et al., 2016; Kumar et al., 2020; Lehto et al., 2014; Scholze & Meier, 2001). Bio-oils also include a non-negligible fraction of suspended solids, affecting in particular the storage and use phases.

- **Gas**

The composition of the pyrolysis gas consists mainly of CO and CO₂, with limited amounts of H₂ and CH₄ and traces of light hydrocarbons, typically C₂ and C₃. The trends of CO, CO₂, and CH₄ yields have been thoroughly studied as a function of temperature and heating rate. Below 500 °C, CO and CO₂ are the main products of primary decomposition reactions, and their yields slightly increase with temperature. Around 500 °C, CO and CO₂ yields are in the range 2–15 and 5–15 wt. %, (Neves et al., 2011) respectively. The production of CH₄ and H₂ became relevant above 500 °C, when also a sharp increase of the CO yield, ranging between 20 and 40 wt. % at around 800 °C, and a slight increase of the CO₂ yield (up to about 20 wt. % at 800 °C), was observed. Indeed, higher yields were also observed for the other minor species, such as CH₄ and H₂, respectively equal to 8 and 1 wt. % at T = 800 °C (Neves et al., 2011). Looking at the influence of the heating rate, it did not produce significant changes in the species yields at low temperature, whereas it induced higher yields of secondary species at high temperature, if combined with long enough gas residence time (Di Blasi, 2009).

3.2 Inorganic behavior during pyrolysis

Most of the features of biomass pyrolysis, like the initial decomposition temperature, the pyrolysis rate and temperature of the maximum devolatilization and the products (char, gas, and condensable fraction) distributions, as well as their composition and characteristics, highly depend on the inorganic elements in the biomass, namely AAEMs. More specifically, these inorganic elements affect, at a molecular level, the decomposition of the organic matrix during biomass pyrolysis. Among these, the most studied are Na, Ca, K and Mg because of their high concentration in lignocellulosic biomasses.

3.2.1 Effect of inorganics (mostly AAEMs) on pyrolysis process and products

Considering the effect of AAEMs on each organic component of biomass, it can be stated that AAEMs: a) anticipate the beginning of the decomposition reactions and maximum devolatilization rate temperature, b) promote the decomposition reactions that lead to the production of permanent gases and low molecular condensable species, and c) enhance the dehydration reactions of the holocellulosic components and the repolymerization reactions of unstable reaction intermediates, resulting in higher char yield. Looking at the possible catalytic effects, some authors found correlation between the electropositivity of the metal and the extent of the catalytic activity (Eom et al., 2012),

whereas other findings show that neither Ca^{2+} (Aho et al., 2013) nor Mg^{2+} (Mahadevan et al., 2016) had any catalytic effect on the yields of the pyrolysis products. With specific reference to willow biomass, (Saddawi et al., 2012) found that the samples with the highest Na^+ concentration produce comparable char yields, which appears to not be consistent with literature results. Nevertheless, it should be noted that high loading levels promote the ash retention in char, and this should be carefully taken into account when the concentration of the doping element is such as to alter significantly the ash content in the final solid residue (Z. Liu et al., 2020). For that reason, the actual effect of Na^+ on the pyrolysis mechanism should be assessed by recalculating the char yield on a dry ash-free basis.

As shown by all the above, the effect of metals on the pyrolysis of biomass is influenced by multiple factors and, although some common trends exist in the literature, as many deviations from those trends have been reported. The catalytic effects of metals can be promoted or mitigated by several factors, often interacting between them, at a multiscale level:

- Molecular scale: metal devolatilization (Leijenhurst et al., 2016) and passivation (Ramsurn & Gupta, 2012) can be caused by the chemical interactions between metal ions and the inorganic fraction and between metal ions and the organic components. The AAEMs, like Na and K in free ion form, could be easily transferred to the vapor phase when reacting with the organic volatile species released during pyrolysis (Okuno et al., 2005); the concentration of the organic species in the gas phase (linked to the devolatilization rate, carrier gas type and dilution) as well as the mass transfer limitations inside the particle directly affect the extent of these reactions (Leijenhurst et al., 2016). Additionally, some inorganic species like $\text{Ca}(\text{OH})_2$ react with the intrinsic inorganic elements in the biomass and alter their properties, making them inactive (Ramsurn & Gupta, 2012).
- Particle scale: Particle size and evolution of the porous structure of the char have been found to influence the mass and heat transfer within the biomass particle; the extent of the metals catalytic activity varies according to the residence time of the volatiles inside the particle and the intraparticle thermal gradient. Additionally, the endothermicity/exothermicity of the thermal decomposition steps that set the temperature at particle and even at reactor level is influenced by the selectivity induced by metal ions towards some decomposition mechanism. In this regime, the interaction between heat transfer and chemistry establishes the pyrolysis products (Shah et al., 2015).
- Reactor scale: firstly, the residence time of the volatiles arising from the biomass particles/bed is affected by reactor fluid dynamics. Secondly, the reactor configuration can induce thermal

gradients both inside the particle/bed and inside the gas phase, adapting the extent of the catalytic activity of the metal ions accordingly.

3.2.2 Displacement of AAEMs

The displacement of AAEMs from the biomass to the pyrolysis products is a relevant topic, and there is also a good knowledge on the transfer mechanisms that regulates the displacement itself (see Figure 3 from Leijenhurst et al., 2016). There are two main pathways that can be identified: a “chemically driven” transfer mechanism, in which the alkali metals devolatilize (by themselves or reacting with the lignocellulosic biomass components) and are then trapped into bio-oil directly; and a “mechanically driven” transfer mechanism, in which the alkali metals are found in bio-oil as solid particles (such as fine char particles or free metal particles), that are entrained by the gas flow and taken out from the reactor.

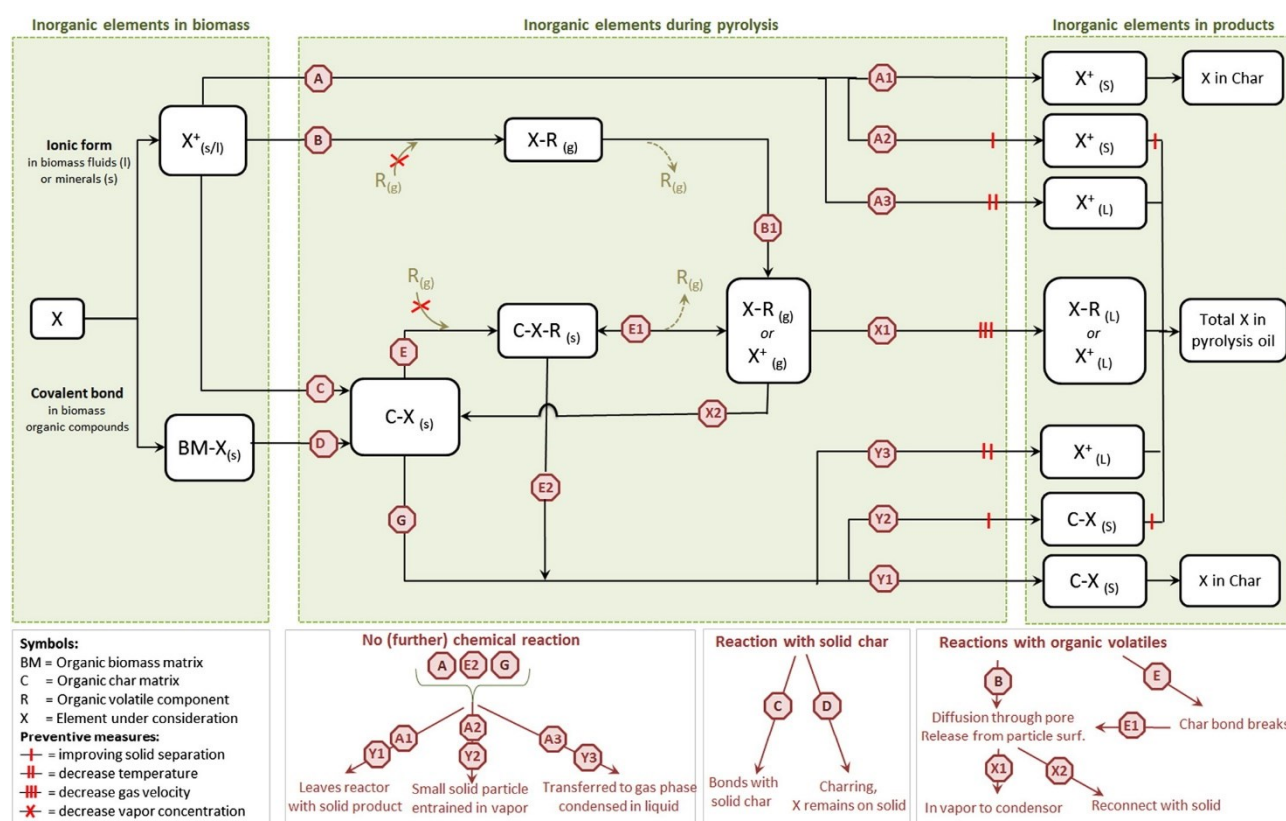


Figure 3 Schematic representation of the main transfer routes for inorganic matter from biomass to pyrolysis oil (Leijenhurst et al., 2016)

Chemically driven transfer mechanisms are mainly dependent from the initial chemical speciation of the inorganics, the biomass composition and the pyrolysis operational conditions, such as pyrolysis temperature.

Mechanically driven transfer mechanisms are particularly relevant in fast pyrolysis, that usually involves a reactor configuration (e.g. fluidized bed reactors) characterized by high gas flow velocity

and, consequently, probable physical elutriation of contaminated fine char particles (Jendoubi et al., 2011).

Another kind of solid particle that can be produced in fast pyrolysis is aerosol particles. Aerosol formation was observed both for the biomass components (cellulose and lignin) and for a real biomass (red oak) (Tiarks et al., 2019), following the “boiling ejection” of a molten intermediate phase that is generated during fast pyrolysis. Boiling ejection was confirmed by (Teixeira et al., 2016) for cellulose and Ca doped cellulose. The authors attributed the formation of bigger aerosol particles to boiling ejection, while observed a different mechanism responsible for the formation of sub-micronic aerosol, which is tied to the occurrence of bubbles in the molten intermediate phase. When the bubbles burst, small droplets of molten phase are scattered away from the main particle. To have a complete overview of the possible aerosol sources, also the possibility of secondary aerosol formation must be taken into consideration: some volatile organic compounds formed during pyrolysis can react to form condensed or solid phase particles (Fawaz et al., 2020). However, the formation of secondary aerosols is unlikely to contribute to inorganics, such as heavy metals, displacement.

3.3 Heavy metals behavior during pyrolysis

When other components are added, like in the case of heavy metals for hyperaccumulators, the pyrolysis process becomes even more complicated; heavy metals can, in fact, exhibit some catalytic effects during pyrolysis, changing both products yields and properties. Moreover, they can migrate into different pyrolysis products causing issues with their use or further processing. Even though pyrolysis seems one of the most promising treatments for contaminated biomass, there are only few studies on various kinds of pyrolysis reactors. Most of these studies focus on the final distribution of heavy metals in the pyrolysis products taking into account the effect of the reactor (and of the entire pyrolysis plant) configuration and of the operational conditions (Z. Liu et al., 2020).

Most of the studies on pyrolysis of contaminated biomass use real hyperaccumulator biomasses (*Avicennia marina* (He, et al., 2019a), *Sedum plumbizincicola* (Zhong et al., 2016) *Brassica juncea* (Huang et al., 2018)) or energy crops/short rotation coppice from phytoremediation sites (poplar (Giudicianni et al., 2017), poplar and willow (Stals, et al., 2010a) as feedstock. In some cases, the biomass is artificially loaded with heavy metal through different doping procedures (e.g. impregnation (Han et al., 2018), ion exchange (Mayer et al., 2012)) to achieve high heavy metal concentrations in order to facilitate the detection of heavy metals in pyrolysis products and enhance their possible effect on the process. On the other hand, the observed results could be affected by the metal salt employed, the doping methodology considered and/or the concentration of heavy metals

(that often is much higher for doped biomasses than for real phytoremediation biomasses). Consequently, the results could differ from the case of real phytoremediation residues.

Table 2 reports an overview of literature papers that deal with pyrolysis of heavy metals contaminated biomass, listing the main characteristics of the considered biomasses and pyrolysis operational conditions.

Table 2 Overview of literature papers dealing with pyrolysis of heavy metals contaminated biomass

Contamination type	Biomass type	Heavy metal	Pyrolysis conditions	Reactor type	Pyrolysis temperature	Reference
doping	Corn stover	Ni, Zn, Cu, Co, Cr (citrate and acetate)	Fast, N ₂	Fluidized bed Spouted bed	600 °C	(Koppolu et al., 2003, 2004)
natural	Avicennia marina	Cr, Fe, Cu, Zn, As, Pb	10 and 60 °C/min, He	Tube furnace	300, 400, 500, 600, 700, 800 °C	(He, et al., 2019a; He, et al., 2019b)
natural	Populus nigra and Arundo donax	Cd, Cu, Pb, Zn	4 °C/min, steam	Jacketed	380, 430, 480, 600 °C	(Grottola et al., 2019)
doping	Willow	Zn, Pb (nitrate and sulfate)	20 °C/min, He	TGA/Py-Ms system	800-900 °C	(Mayer et al., 2012)
doping	Eucaliptus debarked	Zn, Co, Fe, Ni, Cu (nitrate)	Fast, N ₂	Tube furnace	500 °C	(Eibner et al., 2015)
doping	Arundo donax and Broussonetia papyrifera	Cd, Cu, Pb (nitrate)	10 °C/min, N ₂	Tube furnace	450 °C	(Han et al., 2018)
natural	Sorghum bicolor	Ni, Zn	20 °C/min, N ₂ Flash, N ₂	Tube furnace Semi-continuous	450 °C 450 °C	(Al Chami et al., 2014)
natural	Tobacco	Cu, Cd, Zn	10 °C/min	Semi-continuous	500 °C	(Gonsalvesh et al., 2016)
natural	Brassica juncea	Zn, Pb, Cd	10 °C/min, N ₂	Muffle	350, 550, 750 °C	(Huang et al., 2018)
natural	Willow	Zn, Cd, Pb	Flash, N ₂	Semi-continuous	350, 450, 550 °C	(Stals, et al., 2010b)
natural	Poplar	Cd, Cu, Pb, Zn	Fast, N ₂	Screw	290, 450, 800 °C	(Bert et al., 2017)
doping	Water hyacinth	Pb (nitrate)	30 °C/min, N ₂	Fixed bed	275, 375, 450, 550 °C	(Jiu et al., 2015)
natural	Sedum plumbizincicola	Zn, Cd, Pb	Fast, N ₂	Tube furnace	450, 550, 650, 750 °C	(Zhong et al., 2016)

3.3.1 Influence of heavy metals on pyrolysis process and products

The interpretation of heavy metals contaminated biomass pyrolysis studies is complicated if one considers that the presence of HMs induces modifications of the plant chemistry, both in the inorganic and the organic fractions. Consequently, it is challenging to understand if the observed effects are due to the presence of HMs or to the changes in the biomass, induced by their presence during plant growth. In this regard, a crucial aspect that needs to be addressed in the first place is to assess how these metals are present in the biomass structure, i.e. in which chemical form they appear and to which biomass component they are bound. The most common forms of appearance of heavy metals

in vegetal biomasses were reviewed in (Vassilev et al., 2012), showing that they can be found both as organic or inorganic compounds, directly bound to biomass principal components, or even dispersed in the fluid phase of the plants as cations. This type of evaluation is quite difficult, since usually the analytical techniques involved in inorganic detection involve pretreatments that modify both the biomass structure and the inorganic phase chemistry. For example, ashing is a common pretreatment for the analysis of the inorganic fraction of solid fuels and is widely applied also to biomass. By ashing, the organic matter of the biomass is oxidized and removed, but in the meantime the inorganic matter also undergoes several physical and chemical transformations depending on the ashing temperature (Reinmöller et al., 2023). High temperature ashing, at a temperature of 815 °C, also causes the partial decomposition of the inorganic fraction, and inorganics are found mainly in form of oxides. To avoid the decomposition of the inorganic fraction, other ashing procedures have been tested: medium temperature ashing at 550 °C and low temperature ashing in oxygen plasma at 100-150 °C (Suárez-García et al., 2002). These procedures were found to produce lower amounts of inorganic oxides, especially in the case of low temperature ashing, but in the meantime were responsible for the formation of inorganic salts such as nitrates, sulfates and carbonates.

During the pyrolysis process, heavy metals can interact with the decomposition mechanisms of the biomass components, affecting pyrolysis products yield and properties. The direct study of the catalytic effects of heavy metals is usually conducted on heavily enriched biomasses, with concentrations that are much higher than in naturally contaminated biomasses. In one of these studies (Eibner et al., 2015), for example, the authors investigated the effect of impregnation with metals salts on eucalyptus pyrolysis, reaching concentrations of heavy metals between 2.5 wt. % and 7.1 wt. %. The introduction of Ni, Cu, Zn, Fe and other heavy metals resulted in the modification of the decomposition pathway of the cellulose, altering bio-oil and gas compositions.

In general, the possible catalytic effects of heavy metals are expressed phenomenologically, based on the observed differences in yields and properties of pyrolysis products. However, the literature paper that contains direct comparisons between contaminated and control biomass samples are few, as reported in Table 3 (Giudicianni et al., 2021).

Table 3 Effect of heavy metals on pyrolysis products yields

Pyrolysis regime	Feedstock	Metal Contamination	T (°C)	Sample	Yield (wt %)			Reference
					Gas	Condensable fraction	Char	
fast	fir sawdast	Cu	450	(a)	10	50	40	(W. J. Liu et al., 2012)
			450	(b)	25	42	33	
			500	(a)	17	55	30	
			500	(b)	27	47	27	
			550	(a)	28	52	27	
			550	(b)	30	44	25	
			600	(a)	22	50	25	
			600	(b)	35	42	20	
slow	<i>Sorghum bicolor</i>	Zn, Ni	450	(a)	12	30	50	(Al Chami et al., 2014)
450			(b)	5	33	55		
450			(a)	45	16	31		
450			(b)	48	21	22		
fast	water hyacinth	Pb	375	(a)	2.5	57	47.5	(Jiu et al., 2015)
			375	(b)	32	22.5	47	
			450	(a)	7.5	60	35	
			450	(b)	22	37.5	42	
			550	(a)	10	55	32	
			550	(b)	25	38	37	
			300	(a)	5.5	33	61.6	
			300	(b)	4.4	35.3	60.2	
slow	<i>Avicennia marina</i>	Cd, Cu, Zn, Pb, As, Ni	400	(a)	16	43.6	40.4	(He, et al., 2019a)
			400	(b)	14.4	46.8	38.8	
			500	(a)	20.9	46.9	32.1	
			500	(b)	18	51.2	30.9	
			600	(a)	23	46.8	30.2	
			600	(b)	20.1	51.2	28.3	
			700	(a)	25.1	46.2	28.8	
			700	(b)	21.9	51.3	26.8	
			800	(a)	26.7	45.4	27.9	
			800	(b)	23.2	50.8	25.9	

It's not possible to identify a common trend in the products yields variation of contaminated biomass compared to control biomass. Depending on biomass characteristics, pyrolysis conditions and heavy metals chemical form, concentration and contamination type, the yields of all pyrolysis products can vary widely. For example, (Jiu et al., 2015) reported a drastic decrease (15-30 wt. %) in gas yield in water hyacinth biomass treated with lead nitrate, and a corresponding increase in bio-oil yield (17-35 wt. %); the char yield also decreased, but in a lower amount. A similar behavior was observed for copper sulphate contaminated fir sawdust (W. J. Liu et al., 2012). On the other hand, the pyrolysis of

naturally contaminated *Avicennia marina* (He, et al., 2019b) resulted in the opposite behavior, characterized by a mild increase in gas and char yields and a decrease in bio-oil yield; all the observed yield variations are lower than 5 wt. %.

The information on the effect of heavy metals on pyrolysis product properties with respect to a control biomass is even less available, and even more difficult to schematize, than what is reported above for the yield. The most reported data regards the bio-oil composition; in both cases reported in (Jiu et al., 2015) and (W. J. Liu et al., 2012), the addition to the biomass of heavy metals (Pb and Cu, respectively) changed the bio-oil composition by promoting the formation of some species and inhibiting the production of other species, often with conflicting results. For example, Pb is found to increase the production of acetic acid while Cu causes a reduction of the same compound.

3.3.2 Chemical speciation and displacement of heavy metals:

Since pyrolysis of heavy metals contaminated biomass is a quite new topic, there is very little information about the transformation that heavy metals undergo at high temperature and about the transport mechanisms that displace them into the different pyrolysis products.

Some more extensive studies were conducted on heavy metals chemical reactions during combustion; this is a matter of relevance, for example, to operate municipal waste incinerators safely (Monkhouse, 2011). Anyway, during combustion the prevalent reactions of heavy metals involve oxygen, so these results cannot be trivially extended to pyrolysis, when oxygen in its molecular form is absent from the reactive atmosphere. Regarding heavy metals chemistry in pyrolysis, the few results that are available in literature are based on animal residue or wastewater treatment residues pyrolysis instead of lignocellulosic biomass, because of their higher metal content (Chanaka Udayanga et al., 2018). Since the biomass composition is quite different between vegetable and animal derived biomass, also in this case the results cannot be generalized for all pyrolysis applications.

Finally, regarding the transport mechanisms of heavy metals during pyrolysis, there is little to no information available. On the other hand, there is a good knowledge of transfer mechanisms of alkali and alkali-earth metals during pyrolysis, as described in the previous paragraph. It is reasonable to think that similar transfer mechanisms also apply to heavy metals, even if there is no clear evidence for this in the available scientific literature.

3.3.2.1 Influence of pyrolysis temperature and heating rate

Thermal pyrolysis conditions are extremely relevant for the speciation and displacement of heavy metals. While the majority of the available studies on the subject explore a range of pyrolysis

temperatures, it is difficult to find a direct comparison between different heating rates. Usually, the focus is either on slow or fast pyrolysis.

The studies on slow pyrolysis usually aim to find the optimal pyrolysis temperature to retain the heavy metals in the char in a form that results chemically and physically stable (Gonsalvesh et al., 2016; Grottola et al., 2019; He, Strezov, Kan, Weldekidan, Asumadu-Sarkodie, et al., 2019; Huang et al., 2018). Assessing the stability of the heavy metals in the char is of fundamental importance because this allow to use the contaminated char for further applications, may them be soil amendments or wastewater treatments, without the risk of releasing the contaminants back into the environment. To this purpose, usually the produced char is subjected to several leaching tests to determine both the mobility (US-EPA Method 1311) of the heavy metals and their bioavailability (ISO 14870:2001), which represent the tendency of heavy metals to be released from the char and their ability to harm live beings (plants or animals), respectively.

On the other hand, fast pyrolysis results in a higher bio-oil yield; thus, the usual aim of studies on fast pyrolysis of contaminated biomass is to assess the possibility of obtaining a bio-oil free from heavy metals, that can be either used directly for combustion or further treated for the production of more refined bio-fuels and other chemicals (Stals, et al., 2010b).

Thermal pyrolysis conditions, together with biomass properties, influence greatly the displacement of heavy metals in pyrolysis products. This aspect is usually taken into account considering the amount of heavy metals retained in char and, less frequently, in bio-oil and gas phase.

A general overview of the effect of pyrolysis temperature and heating rate on the retention in char of some heavy metals is reported in Figure 4 and Table 4 (Giudicianni et al., 2021).

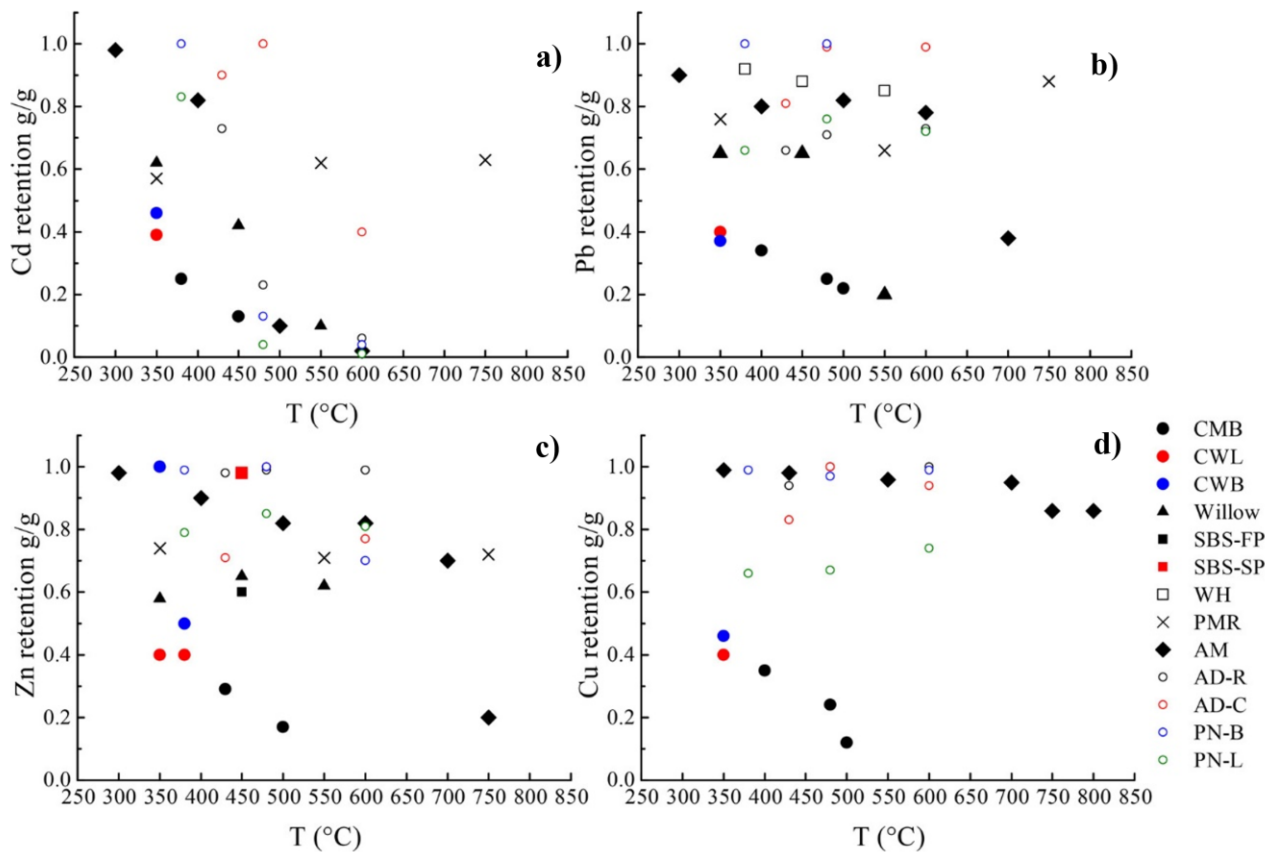


Figure 4 HMs retention in the char obtained under different pyrolysis temperatures from different biomasses listed in Table 4 (Giudicianni et al., 2021)

Table 4 Nomenclature of Figure 4 legend.

Feedstock ID	Feedstock	Pyrolysis regime
CMB	maatheide birch	Fast
CS	sunflower	Fast
CWL	willow leaves	Fast
CWB	willow branches	Fast
Willow	willow	Flash
SBS-FP	sorghum bicolor	Fast
SBS-SP	sorghum bicolor	Slow
WH	water hyacinth	Slow
PMR	Brassica juncea	Slow
AM	Avicennia marina	Slow
AD-R	Arundo donax rhizomes	Slow
AD-C	Arundo donax culms	Slow
PN-B	Populus nigra branches	Slow
PN-L	Populus nigra leaves	Slow

Each heavy metal has a different behavior with pyrolysis temperature; as a general trend, metals retention in biochar decreases as pyrolysis temperature increases. The heating rate of the process also appear to be relevant, even if there are few studies that focus on this aspect. For example, (Al Chami

et al., 2014) compared the pyrolysis of an herbaceous biomass from phytoremediation, *Sorghum bicolor* contaminated with Ni and Zn, in slow (20 °C/min) and flash pyrolysis conditions. As a result, in slow pyrolysis conditions the totality of the heavy metals (>98 wt. %) is retained in the char, while in flash pyrolysis conditions only 50 wt. % of Ni and 60 wt. % of Zn are found in the char.

The same trend can be observed in Figure 5 for Fe, Cu, Zn and Pb by comparing (He, et al., 2019a) and (He, et al., 2019b), which tested *Avicennia marina* pyrolyzed at different temperatures with a heating rate of 10 and 60 °C/min. For all the considered metals, the retention in char is lower with a higher heating rate, even remaining in slow pyrolysis conditions.

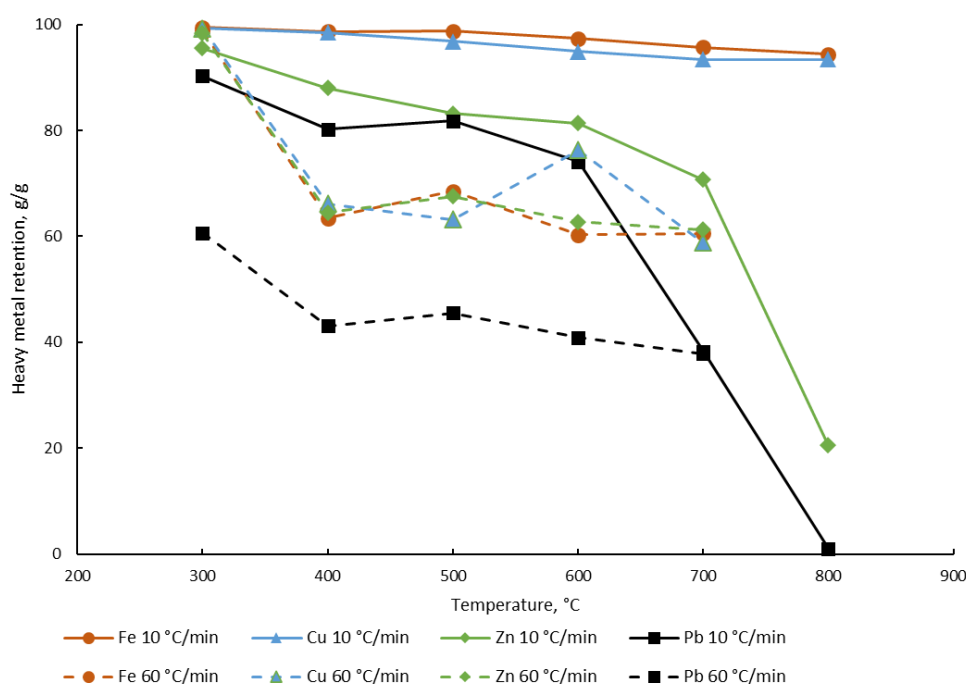


Figure 5 Heavy metals retention in chars from *Avicennia marina* pyrolyzed at different temperatures with a heating rate of 10 and 60 °C/min

Different trends can be observed:

- At 60 °C/min, the retention of all the considered heavy metals decreases between 300 and 400 °C, and then remains quite stable up to 800 °C. Fe, Zn and Cu retention decreases from around 100 wt. % at 300 °C to 65 wt. % at 400 °C, while Pb is characterized by lower retention (between 60 and 40 wt. %).
- At 10 °C/min the considered heavy metals exhibit two separate behaviors: Fe and Cu result more stable and are retained almost entirely in the char up to 800 °C; on the other hand, the retention of Zn and Pb remains quite high (around 80 wt. %) up to 600-700 °C, and then drops sharply. This could be due to reaching the volatilization temperature of the heavy metals in their specific chemical form.

Among the heavy metals, Cd seems to be the most volatile. As reported by (Giudicianni et al., 2017) for contaminated poplar wood, at 500 °C almost all Cd is released between gas and bio-oil, with only around 10 wt. % of Cd retained in char. In the case of sedum plumbizincicola fast pyrolysis (Zhong et al., 2016) even at 450 °C more than 95 wt. % of Cd is volatilized. Cr and As have similar behavior, but their retention drops only to 50-40 wt. % between 500 and 800°C (He, et al., 2019a).

The volatilization temperatures of heavy metals during pyrolysis can vary widely and seems to be influenced by the biomass composition. This is supported by the fact that the observed volatilization temperatures are lower than that of many possible heavy metals chemical speciation (Bert et al., 2017), thus suggesting that heavy metals can be present in different chemical form or react with other inorganic elements during the pyrolysis process. For instance, the volatilization temperatures of pure most heavy metals range from 767 °C for Cd to 2900 °C for Ni; an exception is represented by Hg and As that volatilize at 357 and 615 °C, respectively. Other chemical heavy metals forms that result really stable are metal oxides, that vaporize at temperatures higher than 1000 °C, while metallic salts as nitrates, sulfates and chlorides tend to decompose and/or volatilize at low temperatures (Perry & Green, 2008). However, there is no clear evidence on how the interaction with biomass components can affect these behaviors.

Another important aspect to be considered regards the stability of the heavy metals retained in the biochar. This feature can be investigated following different leaching procedures, usually aimed at determining the mobility and bioavailability of the heavy metals. Assessing the mobility and bioavailability of heavy metals is a fundamental step to the subsequent use of biochar derived from contaminated biomass pyrolysis according to the local legislations. However, this aspect is definitely under-investigated and the available literature data are not easy to compare, since the leaching solutions employed can differ from case to case. Moreover, the biomass composition, the initial heavy metal speciation and the pyrolysis reactor configuration and operational condition add more variability to this determination. (Stals, et al., 2010a) reported that Zn, Cd and Pb during flash pyrolysis of contaminated willow wood evolve towards less mobile chemical forms; similar results are obtained by (Grottola et al., 2019) for Zn, Cd, Pb and Cu during slow pyrolysis of contaminated poplar wood. Also (Gong et al., 2018) observed a general decrease in heavy metals mobility with the increase of pyrolysis temperature during slow pyrolysis of contaminated stems; however, in this case Pb behavior was not affected for temperatures higher than 400 °C, resulting immobilized for about 40 % of the initial Pb content. Regarding bioavailability, it also results to decrease as pyrolysis temperature increases for most heavy metals, as observed by (He, et al., 2019a); the authors reported a different trend for Cd and Pb, which showed an increase in bioavailability for temperature higher

than 600 °C and 400 °C, respectively.

Another analytical technique based on heavy metals extraction that is used to classify the extracted metals in classes based on their mobility is the BCR sequential extraction. BCR sequential extraction procedure was developed for heavy metal speciation analysis in soils (Ure et al., 1993), categorizing the heavy metals in 4 classes with increasing stability (F1, F2, F3, F4) based on their content in different leaching solutions. The occurrence of heavy metals in the different fractions depends on their chemical speciation and is directly related to the extent of heavy metals bioavailability and ecotoxicity, identifying any possible subsequent use of the contaminated char (Zheng et al., 2019).

BCR sequential extraction procedure has been applied extensively to other kind of samples, including pyrolysis residue of sewage sludge (Paz-Ferreiro et al., 2018) and industrial sludge (Chanaka et al., 2019). In recent times, the application to lignocellulosic contaminated biomass and derived biochars is gaining popularity. However, many studies consider different sequential extraction techniques (Tessier sequential extraction (Tessier et al., 1979) or other modified extraction procedures), making the available literature data difficult to compare. The available data from BCR sequential extraction applied to vegetal contaminated biomass suggests that, in general, a higher pyrolysis temperature promotes the stabilization and immobilization of heavy metals in char. (Gong et al., 2018; Huang et al., 2018; Y. Zhang et al., 2020). However, the occurrence in the different fractions follows a different trend with temperature for each heavy metal (Huang et al., 2018) and the same metal can show a different behavior depending on biomass properties and pyrolysis operational conditions. For instance, (Gong et al., 2018) reported that the pyrolysis of contaminated ramie stems caused the distribution of Pb between F3 and F4 fractions almost entirely without significative variations in the temperature range 300-700 °C. On the other hand, (Huang et al., 2018) observed a massive presence of Pb in F2 fraction (40 % of the total Pb) at 350 °C that decreased to 10 % at 750 °C; in this case, also F3 fraction showed a similar decrease when passing from 350 °C to 750 °C, with a corresponding increase of F4 fraction. These results confirm the huge variability of heavy metals speciation, that can affect the possible utilization of contaminated char.

While most of the studies on heavy metals contaminated biomasses focus on biochar for the evaluation of metals displacement, there is scarce data available regarding the fate of the heavy metals that leave the solid phase. In general, whether the heavy metals that are not retained in the biochar ends in the gas phase or in the bio-oil seems to be regulated by the intrinsic affinity of the considered heavy metal with the two products, other than by operational parameters such as pyrolysis temperature and by the biomass characteristics. The available literature data are in disagreement with each other. For instance, (He, et al., 2019a) observed that, during the pyrolysis of contaminated *Avicennia marina*, the majority of heavy metals that are not retained in the biochar has a greater

affinity with the gas phase: regardless of the pyrolysis temperature, the migration in the bio-oil account for less than 10 % of the total metal content. There are some exceptions, though: Pb and Zn, only in the case of slow pyrolysis at 800 °C, are found for 30 % of their content in the bio-oil; on the other hand, the amount of Cd not retained in the biochar is displaced for the most part in the bio-oil for all the considered pyrolysis temperature. Different results were obtained for fast pyrolysis of *Sedum plumbizincicola* (Zhong et al., 2016): neither Zn, Cd nor Pb were detected in the gas phase in the temperature range 450-750 °C. On the contrary, (Stals, et al., 2010a) did not find any Pb in the bio-oil produced from the flash pyrolysis of willow. However, this result is affected by the interaction between Pb and the sand that is used as a heat carrier in the employed pyrolysis reactor, so it could be misleading.

3.3.2.2 Influence of pyrolysis atmosphere and gas flow rate

Most of the considered studies on heavy metals contaminated biomass pyrolysis use inert gases, such as N₂, He or Ar, to reach the oxygen free atmosphere needed for pyrolysis. The possibility of steam assisted pyrolysis was considered for the treatment of contaminated *Arundo donax* (Grottola et al., 2019) and *Populus nigra* (Giudicianni et al., 2017). In both cases, different parts of the plant were used: rhizomes and culms for *Arundo donax*, branches and leaves for *populus nigra*. The considered heavy metals, Cd, Pb, Cu and Zn, are retained in char in different amounts for each considered feedstock, confirming the importance of the feedstock biomass structure. To gain insight on the influence of pyrolysis atmosphere, the results of these studies can be compared with (Han et al., 2018) and (Bert et al., 2017), that consider the pyrolysis of contaminated *Arundo donax* and poplar, respectively, under N₂ atmosphere. As for the *Arundo donax*, steam pyrolysis of both rhizomes and culms result in slightly higher recovery of Cd, and Cu at 450 °C when compared to conventional inert atmosphere pyrolysis. On the other hand, Pb recovery in rhizomes and culms is, respectively, lower and higher than the Pb recovery in N₂ atmosphere. Considering poplar, Cu and Zn recovery follow the same trend with pyrolysis temperature regardless of the pyrolysis atmosphere: Cu remains stable for all the considered temperatures, resulting in a recovery near to 100 %; Zn shows high recovery at lower temperatures, and it starts decreasing when pyrolysis temperature exceeds 600 °C. As for Pb and Cd, they both result more stable, especially at high pyrolysis temperatures, when the samples are pyrolyzed under N₂ atmosphere.

It must be considered that the exposed results are difficult to attribute to the exclusive effect of the pyrolysis atmosphere. In fact, the considered studies differ also for reactor configuration, thermal conditions and contamination levels.

The effect of gas flow rate is also often overlooked when dealing with heavy metals contaminated biomass pyrolysis. In general, a higher flow rate impacts mostly two aspects: the retention time of the vapor phase, that is tied to the products yields and properties, and the entrainment of small biomass or char particles (Kim et al., 2016). Obviously, in these regards also the reactor configuration plays a major role; moreover, often the range of possible operational gas flow is also tied to the reactor configuration. (Yousaf et al., 2018) reports an overview of the effects of the main operational parameters, including gas flow rate, on heavy metals contaminated biomass. It is shown that the retention in char of all the considered heavy metals, including Cd, Cr, Cu, Ni, Pb and Zn, has a non-monotonous trend with the gas flow rate in the considered range (20-200 mL/min) having a maximum between 50 and 100 mL/min. However, there is no clear explanation for this phenomenon.

3.3.2.3 Influence of pyrolysis system

The reactor type results to be relevant for pyrolysis of contaminated biomass, especially in the case of fast pyrolysis. There are many different reactor configurations that are suitable for fast pyrolysis, such as fluidized bed reactors, auger reactors, ablative reactors or rotating cone reactors; different reactor types correspond to various issues when it comes to clean bio-oil production and collection, with solid particle elutriation playing a prominent role.

Some specific issues are tied to the presence of a solid heat carrier, that is necessary for many reactor configurations (e.g. sand for fluidized bed) or useful to reach high heating rates (e.g. steel balls or sand for screw reactors). As reported by (Lievens et al., 2008), the distribution of Cd and Cu among the pyrolysis products is highly influenced by the interactions with the sand used as heat carrier: the heavy metals can react with sand forming silicates, which are thermally stable compounds. Consequently, the heavy metals displacements observed in the study cannot be explained only considering the thermal conditions of the pyrolysis process.

The final distribution of inorganics in the pyrolysis products can be influenced also by the gas treatment and condensation section. (Stals, et al., 2010a) found that the introduction of hot vapor filters not only reduces the amount of heavy metals, specifically Zn and Cd, contained in the bio-oil, but also causes alterations of the bio-oil composition. The effect of the condensation section configuration was reported by (Jendoubi et al., 2011): by actuating a fractional condensation and collecting separately heavy oil fraction, light oil fraction and aerosols, the authors observed a different distribution of AAEMs in the three bio-oil fractions, depending also on the metal nature and intrinsic affinity. To the best of my knowledge, this kind of observation is not available for heavy metals, but it is likely that fractional condensation could also affect their displacement.

Table 5 reports the findings of (Elliott et al., 2017) that analyzed the solid content of bio-oil produced from different fast pyrolysis systems.

Table 5 Solid content of bio-oil produced from different fast pyrolysis systems (Elliott et al., 2017)

Reactor type	Temperature (°C)	Feed rate (kg/h)	Bio-oil solid content (wt. %)
Fluidized bed	475	0.18-0.39	0.5
Fluidized bed	480-500	0.4-1.7	1.6
Fluidized bed	480-500	1	0.51
Fluidized bed	480	0.8	0.4
Fluidized bed	525	0.85	0.11
Fluidized bed	500	0.5	0.03
Fluidized bed	500	8	0.22
Fluidized bed with Hot Vapor Filter	500	0.09-0.12	0.08
Fluidized bed with Hot Vapor Filter	500	0.42	0.07
Entrained bed with Hot Vapor Filter	530	2-5	0.02
Screw	485-500	0.24-0.86	0.5
Twin screw	500	10	0.8
Screw	550	0.24	0.33
Screw	400	0.68-0.36	0.32
Ablative	542	10	0.37
Ablative	750	20	0.5

The quantity of solid particles in bio-oil varies widely depending on the specific reactor configuration, even when considering pyrolysis reactors of the same type, as can be seen for fluidized bed reactors. This reactor configuration, that is also one of the most diffused for fast pyrolysis, can be often equipped with a hot vapor filtration section to remove the solid particles entrained in the gas flow. As reported in Table 5, this addition can greatly reduce the solid particles occurrence in bio-oil up to 0.02 %. The authors also found that the alkali and alkali earth metals concentration in the produced bio-oil was correlated with the bio-oil solid contentment, as reported in Figure 6, thus confirming that solid particle elutriation is a transfer mechanism relevant for inorganic displacement.

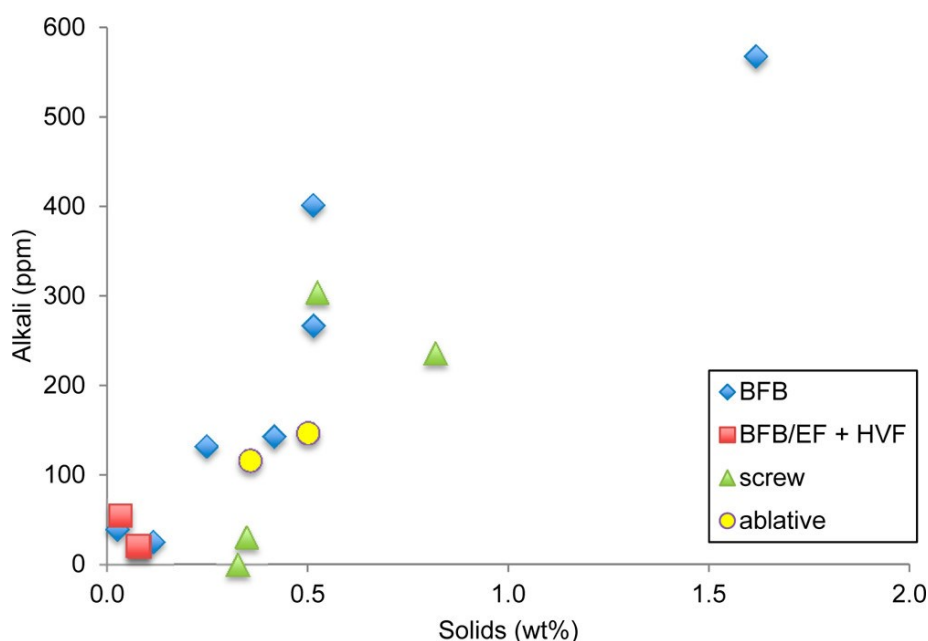


Figure 6 Alkali and alkali earth metals concentration in bio-oil from different reactors as function of the bio-oil solid content

3.3.2.4 Interactions with other elements

Another aspect that must be considered is the possibility of interactions between heavy metals and other chemical species, that can further affect their displacement. Heavy metals can react with other compounds and ions during the pyrolysis process forming metallic salts and complexes characterized by higher or lower volatilization temperatures than the original form. For example, the presence of chlorine (Cl) in the biomass could lead to the formation of metal chlorides, a family of compounds that are characterized by low volatilization temperatures. (Bert et al., 2017) performed pyrolysis experiments at 450 °C and 800 °C using as feedstocks plain poplar wood chips and metal-enriched poplar wood chips. They observed higher volatilization of Zn and Pb at 800 °C for the biomass with the higher chlorine content (145 mg/kg and <20 mg/kg for the plain and the metal-enriched biomass, respectively). According to Bert et al., the higher presence of chlorine lead to the formation of $ZnCl_2$ and of $PbCl_2$; these metal chlorides volatilize at temperatures between 200 and 650 °C and between 550 and 700 °C, respectively, which are consistent with the authors' hypothesis. On the other hand, the presence of sulfur (S) could contribute to the stabilization of heavy metals enhancing their retention in the char. As reported in (Jiu et al., 2015), the Pb retained in char after the pyrolysis of water hyacinth at 450 °C was found mainly as PbO and PbS, confirming the thermal stability of PbS at least up to 450 °C. Evidence of the presence of CdS in the char are reported by (Huang et al., 2018).

(Shi et al., 2017) reported a positive effect on Pb when water hyacinth was treated with phosphate (P) salts before pyrolysis. This effect is attributed to the formation of Pb minerals such as pyromorphite ($\text{Pb}_5(\text{PO}_4)_3\text{Cl}$) and lead-substituted hydroxyapatite ($\text{Ca}_2\text{Pb}_8(\text{PO}_4)_6(\text{OH})_2$). The mentioned minerals result thermally stable, with a recovery of Pb in char that goes from 83 % to 94 % as pyrolysis temperature increases from 300 °C to 600 °C. Also, the stability of Pb retained in char results higher than in the control biomass, suggesting that the formation of Pb-P minerals also enhances the chemical stability of Pb.

Heavy metals could react also with elements that belong to the pyrolysis system, such as the reactor material or the solid heat carrier, when employed. For example, (Stals, et al., 2010a) reported the interaction between Cd and Cu and the silicates of the sand employed as heat carrier. In particular, the authors proposed the reaction of metal chlorides and silica (SiO_2) in presence of oxygen or water that can form metal silicates complex. A similar behavior was proposed for Zn, which is thought to react directly with the quartz pyrolysis reactor.

3.3.2.5 Influence of biomass pretreatments

Common biomass pretreatments include feedstock size modification (grinding and pelletizing), chemical treatments (leaching) and the addition of compounds that can affect the pyrolysis process. However, there is no clear information about the effect of such pretreatments on heavy metals in contaminated biomass.

The reduction of biomass particle size by grinding is often employed before fast pyrolysis process, impacting the products yield. In fact, smaller particles are characterized by a more uniform temperature and an improved heat transfer, experiencing faster heating rates and promoting the production of bio-oil. At the same time, these conditions can promote the formation of aerosols. Moreover, the smaller particles can be easily entrained in the gas flow, which is usually high due to fast pyrolysis reactors configuration. Both these phenomena are tied to the migration of inorganics in the bio-oil (Leijenhurst et al., 2016), so it is plausible that they are also relevant for heavy metals displacement, lowering their retention in char. However, the few available information does not provide a clear picture of particle size influence on heavy metals displacement (Yousaf et al., 2018).

Leaching is a pretreatment that is used to remove part of the inorganic fraction from the biomass, aiming to improve the quality of the bio-oil produced during pyrolysis (Wigley et al., 2016); this procedure is also referred to as demineralization. Demineralization can be carried out with different solutions, ranging from water to acid solutions. It was found that water leaching removes a considerable amount of alkali and part of the alkali-earth metals, while has small effect on heavy

metal content: as reported in (Wigley et al., 2015), water leaching does not affect the Zn content of *Pinus radiata*, and Fe content is lightly reduced. However, it is sufficient to remove around 70 % of the initial K content of the biomass. When switching to acid leaching, all the AAEMs considered are removed almost entirely from the biomass except for Ca, Fe content is further reduced and even Zn is removed for the most part. In general, water leaching is effective for heavy metals removal only when dealing with detrital contamination since the metal particles on the surface of the biomass are washed away regardless of the employed solvent. To specifically deal with heavy metals contamination, also other leaching solutions have been considered. For example, Dastyar et al. (2019) tested ionic liquid leaching on contaminated willow using triethylammonium hydrogen sulfate ([TEA][HSO₄]) and found that this treatment is effective for the removal of many heavy metals. In optimized conditions (Dastyar et al., 2019), ionic liquid leaching removes more than 70 % of Cu, Zn, Fe and Cd. However, this treatment is not effective towards Cr and Pb, with the first being removed only for 20 % of its initial content and the latter being totally unaffected from the leaching. It must be also considered that leaching demineralization procedures, when carried out with aggressive solutions such as acid solutions and ionic liquid, alter the biomass structure. This makes it difficult to attribute the observed changes in pyrolysis products yields and properties to the removal of heavy metals rather than to the biomass structural and chemical modifications.

A promising pretreatment for heavy metals contaminated biomasses could be adding other inorganic components to the biomass following different procedures. In fact, the pyrolysis of heavy metals contaminated biomass treated with specific inorganic salts could promote the immobilization of heavy metals in char. As reported in (He et al., 2021), the co-pyrolysis of *Avicennia marina* from a phytoremediation site and magnesium carbonate (MgCO₃) in a ratio of 2:1 (w/w) had a positive effect on the retention of heavy metals in char at high temperature. In particular, the addition of magnesium salt increased the recovery of Pb and Zn in char from 1% and 20% at 800 °C (He, et al., 2019a) to more than 50% and 56% at 900 °C, respectively. The same authors also investigated the effect of biomass pretreatment by impregnation with ferric salts, FeCl and Fe(NO₃)₃ (He et al., 2020). The impregnation with ferric salts resulted in a stabilization of Zn, Cr and Pb at high pyrolysis temperature, increasing their retention in char when compared to the control biomass. This effect was attributed to the formation of metal complexes between other heavy metals and Fe. Alongside the stabilization effect of Fe, there are also the potential effect of the anions of the ferric salts. Cl⁻ and NO₃⁻ can also be retained in the biomass structure, and, as stated in the previous paragraph, they could lead to enhanced heavy metals volatilization. Moreover, ferric salts solutions are also good leaching solutions for the removal of Cd from the biomass, with different results depending on the specific salt employed: FeCl solution removed more than 90 % of the initial Cd biomass content.

The addition of other metals during pyrolysis of heavy metals contaminated biomasses has also a stabilization effect on the metals retained in char. However, the observed results are not clear: the impregnation with FeCl and $\text{Fe}(\text{NO}_3)_3$ increases the leachability of heavy metals from char, but this is probably due to the interaction between heavy metals and salt anions (He et al., 2020); on the other hand, the addition of MgCO_3 results in a decrease in the leachability of heavy metals, but this effect is attributed to the modification induced on the char structure more than to a direct interaction between Mg and other metals (He et al., 2021).

3.4 Pyrolysis reactors configuration

Numerous reactor solutions have been used for years to carry out biomass pyrolysis in a variety of operating conditions. Reactors for pyrolysis, in which the two dominant mechanisms of heat transport are convective and conductive, can be classified, according to the pathway of the gas and solid phases, in:

- Plug flow: unidirectional motion for gas and solid.
- Partial back mixed: unidirectional motion for the gas but not for the solid, which is subject to back mixing phenomena.
- Tumbling: the solid is subjected to continuous rotations and tumbling inside a rotating chamber inside a cylindrical tunnel.
- Entrained: the solid is transported by the gas.

In addition, the different pyrolysis technologies are generally classified into two main categories, based on the heating mode:

- directly heated reactors;
- indirectly heated reactors.

In the former, the biomass is heated by direct contact with the pyrolysis medium, which may consist of hot gases, heated solids, superheated steam or electromagnetic radiation. In the latter, the biomass is heated through the reactor walls.

The typical reactors used to realize biomass pyrolysis are fixed bed reactors, fluidized bed reactors, circulating fluidized bed reactors, entrained flow reactor, ablative pyrolyzer, rotating cone reactors, rotary kiln reactors and screw reactors.

The following is a brief description of the different reactor types:

- **Fixed Bed Reactor:** A stream of hot inert gas is blown through a solid bed of biomass particles, that are heated up by the gas itself. This reactor configuration does not need any heat transfer medium, facilitating pyrolysis products collection.
- **Fluidized Bed Reactor:** A stream of inert gas is blown through a solid granular bed, which behaves as a fluid and acts as a heat transfer medium. These hot particles, vigorously mixed, heat up very quickly the biomass particles fed to the reactor, which undergo pyrolysis in a state of optimal mixing with uniform temperature distribution. This justifies one of the main advantages of such a configuration, i.e. the uniform quality of the product, which is difficult to achieve in other reactor configuration. The separation of solid heat transfer particles from the solid pyrolysis residue obtained represents, instead, one of the main limitations of this technology.
- **Circulating fluidized bed reactor:** Unlike the fluidized bed reactor, the solid heat transfer medium is dragged outside the reactor together with the char, and sent to a combustion chamber, where the char burns. The advantage is related to the direct heat input by recirculating hot sand from the char combustion chamber to the pyrolysis one.
- **Entrained flow reactor:** Biomass particles are entrained in high-velocity jets of hot gas. The main features of such a reactor are the high heat and mass transfer and the absence of moving mechanical parts. Char exits the pyrolysis reactor and is then separated through cyclones before the condensation of the pyrolysis vapors.
- **Ablative pyrolyzer:** Heat transfer occurs from the heated reactor walls to the biomass particles in contact with them under pressure generated either by centrifugal force or mechanically. The pyrolysis front moves unidirectionally along the radius of the particle. When a particle is mechanically moved from one part of the reactor to another, the residual oil film partly provides the necessary lubrication to the subsequent biomass particles that contact the wall and partly evaporates and then collected and condensed to form bio-oil. The reaction rate is strongly influenced by the pressure, the relative velocity of the biomass on the reactor walls, and the temperatures of the reactor walls. Inert gas flow is not required. In addition, the process is limited by the rate at which heat is delivered to the reactor walls, rather than the rate at which heat is absorbed by the biomass, and for this reason, even quite large particles can be processed.
- **Rotating Cone:** A rapid heat transfer occurs from the solid surface of a rotating cone to small biomass particles that are mixed with hot sand to make the heat exchange more efficient. Such a reactor features two fluid beds: one inside the cone, which allows for multi-pass conversion for the biomass particles, and a second fluid bed around the cone, which contains sand and

char. Between the two fluid beds there is a connection via orifices. The carbon particles left in the second bed are burned and the energy is used to heat the reactor. The transport of the hot sand to the inside of the cone is done by a small lifting system. The advantage of this system is that no inert gas flow is required. The disadvantage is the need for small particle sizes.

- Rotary Kiln Reactor: It consists of a cylindrical reactor that rotates along its axis; it can be oriented horizontally or be slightly inclined, to facilitate the biomass movement toward the exit of the reactor. The biomass is usually heated directly under a stream of hot inert gas or hot vapor. The biomass particles are constantly shaken and mixed by the reactor rotation and by the hot gas flow, ensuring good mass and energy transfer phenomena.
- Screw (auger) Reactor: It consists of a fixed cylindrical reactor in which a screw mounted on a rotating shaft transports the biomass from the inlet to the outlet of the reactor with variable speed depending on the rotational speed of the drive shaft. Biomass can be heated directly, by flowing an inert hot gas into the reactor or by inserting previously heated sand or steel balls, and/or indirectly, by heat transfer through the walls. The reactor walls can be heated by external furnaces or by heat exchange with a heated fluid flowing in a shell (or annulus) outside the reactor. The screw, in addition to mechanically transporting the material, also promotes heat exchange between the material and the reactor walls and/or carrier gas.

4 Materials and methods

4.1 Biomass choice

There are several types of plants that can be used in phytoremediation with different effects and behaviors towards specific heavy metals, ranging from herbaceous to lignocellulosic biomasses. Aiming to use phytoremediation residues for energy purposes, the focus of this work is on lignocellulosic biomass and, in particular, on short rotation coppice (SRC) biomass, which are trees characterized by a fast growth and high wood yields that can be harvested every couple of years (Vanbeverem & Ceulemans, 2019).

The SRC biomass used for the experimental campaign is poplar (*populus nigra*) that was grown on a contaminated soil in Marcianise (CE), Italy. The contaminated site is under management from Ecobat, a company that recycles vehicles batteries, so the soil is mostly contaminated by lead (Pb). The main effect of poplar on Pb is phytostabilization instead of phytoextraction (Radojčić Redovniković et al., 2017); consequently, the employed biomass has moderate levels of Pb contamination as will be further discussed in the following paragraphs.

The chosen biomass was used in two sets of pyrolysis experiments, characterized by different treatments of the feedstock.

The first set of experiments aimed to assess the effect of the initial lead chemical speciation on lignocellulosic biomass pyrolysis. To this aim, the biomass was doped with two different Pb salts: lead acetate tri-hydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$) and lead nitrate ($\text{Pb}(\text{NO}_3)_2$). Lead acetate was employed because heavy metals have been found bound to organic acids of the biomass; among the organic acids, acetates have a higher solubility and are therefore more suited for biomass doping (Koppolu & Clements, 2003). Lead nitrate was considered because of its widespread use in biomass doping procedures (see Table 2).

The second set of experiments considered the effect of the type of lead contamination (detrital, authigenic or both (Vassilev et al., 2012)) on lignocellulosic biomass pyrolysis. To this aim, three different doping procedures were considered to mimic the different contamination types, as discussed in detail in the following paragraphs.

4.1.1 Effect of lead chemical speciation

In order to elucidate the influence of lead chemical speciation on the pyrolysis process, the plain poplar biomass was doped via wet impregnation (Mayer et al., 2012) using lead acetate tri-hydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$) and lead nitrate ($\text{Pb}(\text{NO}_3)_2$). The doping solutions were prepared, dissolving

the salt (0.18 g of lead acetate or 0.16 g of lead nitrate) in 2 L of distilled water; 100 g of plain biomass were then added to the solution, stirred for 1 hour and kept in oven at 80 °C until the complete evaporation of the water. In the following, the plain biomass, the lead acetate doped biomass and the lead nitrate doped biomass are identified as P, P+PbAc and P+PbN, respectively. Both feedstocks have a theoretical Pb concentration of 900-100 ppm.

As can be seen in the following paragraphs, P+PbAc biomass resulted in a higher ash content than P and P+PbN, probably because of a different batch of poplar, harvested in a different area. To assess whether the presence of other inorganic elements can affect pyrolysis process and the characteristics of pyrolysis products, the wet impregnation procedure with lead acetate was repeated on a different batch of poplar that had the same ash content as P and P+PbN, producing a further pyrolysis feedstock identified as P+PbAc_II.

4.1.2 Effect of type of contamination

For the second set of pyrolysis tests, the plain poplar was demineralized by washing with distilled water: 100 g of biomass were soaked in 2 L of distilled water and continuously stirred for roughly 70 hours at room temperature. The biomass was then filtered, rinsed with 2 L of distilled water and kept in oven at 80 °C until completely dry.

The obtained demineralized biomass, that will be referred to as P_w, was doped following the three procedures described below using lead acetate tri-hydrate ($\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$) as doping salt:

- Dry mixing, (Mayer et al., 2012) that simulates the detrital contamination in which the metals are deposited on the external layers of the biomass: 0.025 g of salt were directly mixed with 16 g of demineralized biomass. This procedure was applied to small quantities of biomass to ensure a better homogenization of the salt on the biomass. The produced feedstock is referred to as P_w+PbAc_dm and has a theoretical Pb concentration of 800-900 mg/kg.
- Ion exchange (Mayer et al., 2012), that simulates the authigenic contamination in which the metals are tied to the chemical structure of the biomass: 0.24 g of salt were dissolved in 2L of distilled water; 100 g of demineralized biomass were then added to the solution and stirred continuously for 100 hours at room temperature. After 100 hours the biomass was filtered, rinsed with 2 L of distilled water and immersed in 2 L of distilled water; after 72 hours of continuous stirring at room temperature the biomass was filtered again and dried in oven at 80 °C. The produced feedstock is referred to as P_w+PbAc_ie and has a theoretical Pb concentration of 900-1000 mg/kg.
- Wet impregnation (Mayer et al., 2012), that simulates both detrital and authigenic contamination; the doping procedure is described in the previous paragraph. The produced

feedstock is referred to as P_w+PbAc_wi and has a theoretical Pb concentration of 800-900 mg/kg.

A sample of P_w+PbAc_wi was treated with the same washing procedure described for ion exchange and was then analyzed to determine the resulting Pb concentration. From the comparison with the unwashed sample, it resulted that 75 % of the original Pb content was still present in the biomass, as it is probably chemically bound to the biomass structure (authigenic contamination). The remaining 25 % of Pb that was removed by washing was just deposited on the biomass surface (detrital contamination).

This information was used to calculate the amount of salt needed for the ion exchange procedure.

Table 6 summarizes all the doped feedstocks that have been tested during the experimental work.

Table 6 List of the doped feedstocks tested during the experimental work

Feedstock name	Starting biomass	Pb salt	Doping method	Expected Pb contamination (mg/kg)
P+PbN	Untreated poplar wood from phytoremediation (P)	(Pb(NO ₃) ₂)	Wet impregnation	1000
P+PbAc		Pb(CH ₃ COO) ₂	Wet impregnation	1000
P+PbAc_II		Pb(CH ₃ COO) ₂	Wet impregnation	850
P_w+PbAc_dm	Demineralized poplar wood from phytoremediation (P_w)	Pb(CH ₃ COO) ₂	Dry mixing	850
P_w+PbAc_ie		Pb(CH ₃ COO) ₂	Ion exchange	1000
P_w+PbAc_wi		Pb(CH ₃ COO) ₂	Wet impregnation	850

4.2 Feedstocks characterization

All the eight considered feedstocks have been characterized with several analytical techniques to investigate their composition, inorganic content and decomposition behavior.

4.2.1 Proximate analysis

The proximate analysis returns the biomass composition in terms of moisture, volatile, fixed carbon and ash weight percentages. It is conducted using a TGA 701 analyzer from LECO, following the standard ASTM D5142 method (which was developed for coals and carbons but is commonly used also for biomass samples). The obtained results are reported on dry basis in Table 7.

Table 7 Proximate analysis of the feedstock used in the experimental work

Feedstock name	Moisture Weight (%)	Volatile	Weight % - Dry basis	
			Ash	Fixed Carbon
P	7.57 (±0.06)	81.80 (±0.85)	1.45 (±0.21)	16.75 (±0.64)
P+PbN	4.38 (±0.32)	81.33 (±0.18)	1.55 (±0.08)	17.12 (±0.14)
P+PbAc	6.54 (±1.01)	78.79 (±0.73)	3.26 (±0.36)	17.95 (±0.46)
P+PbAc_II	3.19 (±0.30)	80.87 (±0.67)	1.51 (±0.35)	17.62 (±0.69)
P_w	4.87 (±3.58)	82.87 (±0.19)	0.77 (±0.06)	16.36 (±0.14)
P_w+PbAc_dm	8.02 (±0.31)	84.46 (±0.32)	0.40 (±0.28)	15.13 (±0.07)
P_w+PbAc_ie	7.01 (±0.04)	85.33 (±0.30)	0.23 (±0.08)	14.43 (±0.31)
P_w+PbAc_wi	3.75 (±0.24)	83.75 (±1.06)	0.63 (±0.10)	15.62 (±0.99)

Looking at the first set of feedstocks, there is no appreciable effect of the doping procedure on the biomass composition. P, P+PbN and P+PbAc_II retain similar compositions: the main phase is the volatile phase, which accounts for more than 80 % of the total weight on a dry basis, while the ash content is quite low even for a woody biomass (Vassilev et al., 2010), resulting in about 1.5 %. P+PbAc, as stated before, has a higher ash content that results in a slight decrease in its volatile content, but this is not an effect of the doping procedure.

From the results regarding second set of feedstocks it is clear that the demineralization procedure was effective: P_w retains about half the amount of ash originally contained in P (0.7 % against 1.5 %). The three different doping procedures employed do not modify substantially the composition of the feedstocks. Only the ion exchange procedure slightly reduces the ash content since part of the inorganics are further dissolved in the aqueous solution and leached out during filtration.

4.2.2 Elemental analysis

The elemental analysis returns the biomass composition in terms of carbon (C), hydrogen (H) and nitrogen (N) weight percentage; oxygen (O) weight percentage is obtained by difference. It is conducted using a CHN628 analyzer from LECO, using ethylenediaminetetraacetic acid (EDTA) as calibration standard. The obtained results are reported on dry, ash free basis in Table 8.

Table 8 Elemental analysis of the feedstock used in the experimental work

Feedstock name	C	H	N	O (a)
	Wt. % - Dry ash free basis			
P	46.87 (±1.41)	6.20 (±0.11)	0.29 (±0.21)	46.64 (±1.94)
P+PbN	47.95 (±0.38)	6.17 (±0.27)	0.24 (±0.18)	45.65 (±0.91)
P+PbAc	48.94 (±1.45)	6.36 (±0.20)	1.02 (±0.02)	43.68 (±2.03)
P+PbAc_II	48.66 (±0.18)	6.19 (±0.03)	0.54 (±0.07)	44.60 (±0.64)
P_w	48.34 (±0.45)	6.13 (±0.14)	0.34 (±0.05)	45.19 (±0.69)
P_w+PbAc_dm	48.16 (±0.45)	6.11 (±0.14)	0.34 (±0.05)	45.39 (±0.91)
P_w+PbAc_ie	49.17 (±0.30)	6.18 (±0.12)	0.35 (±0.07)	44.31 (±0.57)
P_w+PbAc_wi	48.31 (±0.67)	6.18 (±0.11)	0.55 (±0.46)	44.96 (±1.34)
(a) Obtained by difference				

The elemental composition of the feedstocks does not vary with the addition of different lead salts, as can be seen looking at the results for P, P+PbN, P+PbAc and P+PbAc_II.

4.2.3 Inorganic content characterization

To analyze the composition of the inorganic phase of the biomass, the organic phase of the sample is dissolved via microwave-assisted acid digestion according to US-EPA 3051 method. The digested samples are then analyzed using an inductively coupled plasma mass spectrometry (ICP-MS) model 7500CE from Agilent. The obtained results, expressed in terms of weight concentrations, are reported in Table 9.

Table 9 Concentration of the main inorganic species of the feedstock used in the experimental work

Feedstock name	Mg	P	K	Ca	Fe	Zn	Pb
	(mg/kg)						
P	408.4 (±29.6)	512.3 (±11.5)	1648.5 (±98.3)	1737.8 (±276.1)	52.3 (±8.7)	18.7 (±1.8)	9.0 (±1.2)
P+PbN	506.4 (±28.4)	512.0 (±124.3)	1734.0 (±356.4)	2741.8 (±284.6)	76.3 (±27.4)	25.5 (±3.5)	889.5 (±105.3)
P+PbAc	1453.0 n.a.	1458.0 n.a.	5066.0 n.a.	5496.0 n.a.	1074.0 n.a.	99.2 n.a.	995.6 n.a.
P+PbAc_II	509.8 (±116.1)	556.2 (±39.8)	2155.0 (±420.0)	4487.8 (±1506.4)	41.4 (±58.5)	29.9 (±1.3)	766.6 (±11.2)
P_w	215.8 (±15.3)	77.7 (±21.0)	240.0 (±116.7)	1991.3 (±391.7)	0.0 (±0.0)	13.2 (±1.5)	9.0 (±2.2)
P_w+PbAc_dm	408.4 (±15.3)	512.3 (±21.0)	1648.5 (±116.7)	1737.8 (±391.7)	52.3 (±0.0)	18.7 (±1.5)	878.2 (±22.0)
P_w+PbAc_ie	315.0 (±40.3)	43.1 (±8.8)	77.6 (±9.8)	2522.8 (±269.3)	37.8 (±18.7)	19.2 (±3.2)	1147.0 (±117.4)
P_w+PbAc_wi	291.6 n.a.	63.3 n.a.	288.3 n.a.	2023.0 n.a.	0.0 n.a.	38.6 n.a.	787.0 n.a.

To understand the results obtained from ICP-MS it must be considered that, while this technique is capable of identifying really small amounts of inorganics, its accuracy is not high: a maximum error of 20% has to be considered for all the species. As elemental analysis, ICP-MS was not carried out for the dry-mixed feedstock P_w+PbAc_dm, as its doping procedure does not interact with the biomass structure.

As anticipated, P+PbAc feedstock must be carefully considered, since it shows an increase in every inorganic element considered with respect to both P and the other treated feedstocks P+PbN and P+PbAc_II, which confirm that this phenomenon is not due to the impregnation procedure, or to the specific lead salt used; the observed differences can be attributed to the use of a different poplar batch. Mg, P, K and Ca, that are the main naturally occurring inorganics in lignocellulosic biomass, are three times higher for P+PbAc than for the other feedstocks; moreover, P+PbAc also shows a Fe content of 1000 mg/kg, while the same element is present in negligible quantities in the other feedstocks.

The Pb content in all the treated feedstock matches the desired concentrations, confirming that the doping procedures were successful. Moreover, looking at the two sets of feedstocks separately, it is clear that no other inorganic was added to the base biomass except for lead; the only exception is P+PbAc_II, which has a higher content of Ca and K with respect to P.

The demineralization procedure for the production of the second set of feedstocks was also successful: in fact, the content of Mg is halved in P_w with respect to P, while P and K contents are

reduced to 15 % of the initial content. On the other hand, Ca content was not affected by the demineralization.

4.2.4 Thermogravimetric analysis

The thermal decomposition of all the feedstocks is evaluated using a thermogravimetric analyzer Pyris STA 6000 from Perkin-Elmer. The samples are heated in inert atmosphere under a fixed N₂ flux of 80 mL/min, reaching 900 °C/min with a heating rate of 10 °C/min. For each analyzed feedstock, the weight loss curve and the differential thermogravimetry curve (DTG), which represents the decomposition rate of the sample, are calculated.

4.3 Slow pyrolysis experimental setup

The majority of pyrolysis test was performed under slow pyrolysis conditions. There are two main reasons for this choice: firstly, slow pyrolysis conditions allow to reduce the occurrence of inorganics mechanically driven transfer mechanisms, such as aerosol formation and char particle elutriation, giving the opportunity to focus on the chemical effects of heavy metals presence. Moreover, the results obtained from the experimental campaign will be also used as basis for the individuation of the optimal operational conditions of the realized screw reactor, which is meant to work in slow/intermediate pyrolysis conditions.

The slow pyrolysis system employed in the present work is constituted mainly by two parts, the pyrolysis reactor and the exiting line that can be arranged both for bio-oil collection or permanent gas analysis. Many features of the system, from the inert gas feeding system to the heating elements, are controlled by a dedicated software developed in Labview, coupled with a Data Acquisition System from National Instruments.

4.3.1 Pyrolysis reactor

The reactor consists of a jacketed prismatic reaction chamber (L=0.24 m, W=0.04 m, H=0.052 m) (Ragucci et al., 2013); the carrier gas flows into the jacket and then it is reversed towards the pyrolysis chamber, passing through a ceramic flow straightener before entering in the chamber. The inert gas used in this work is N₂ which is supplied through a digital mass flow controller to maintain a constant flux for the whole pyrolysis test. The N₂ flow used for the pyrolysis tests presented in this work is 3 NL/min.

Inside the reaction chamber there are 5 trays that are the sample holders; the biomass is loaded on the trays and fed to the reactor at ambient temperature, and the produced char can be recovered once the

reactor cools off completely after each test. Both the reactor and the trays are made of FeCrAlloy, a metallic alloy with high temperature resistance.

During the pyrolysis process, the temperature inside the reactor is monitored using three N-type thermocouples positioned as shown in Figure 7; based on the measurements of these thermocouples, the heating rate is calculated.

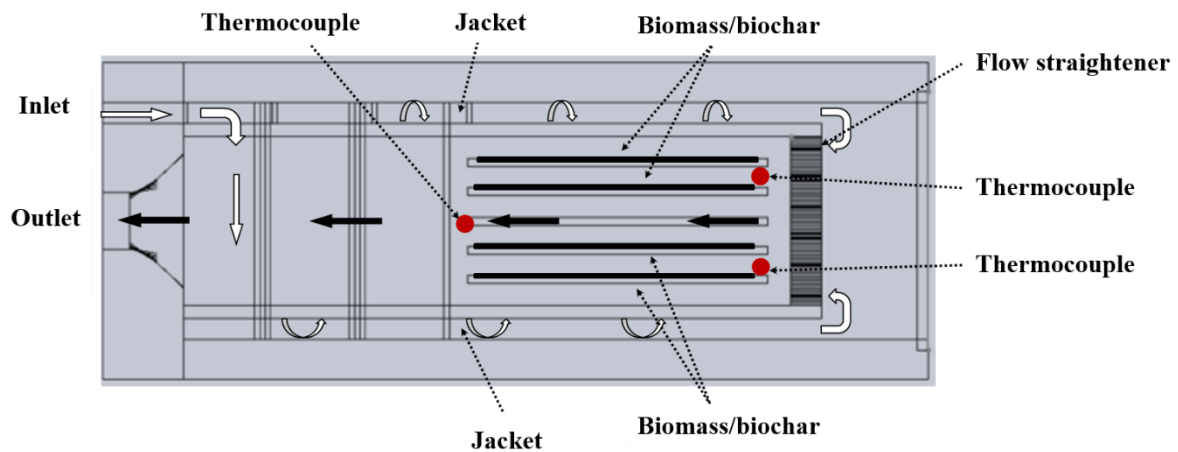


Figure 7 Longitudinal section of the reactor used in the experimental work

The reactor is surrounded by 4 ceramic heating panels for a total input power of 1.8 kW. In the gap between the reactor and the two heating panels on the sides, there are two air-compressed nozzles (Figure 8); the air flow is used during the pyrolysis tests to improve the heating transfer between the heating elements and the reactor, and at the end of the test to help the system cooling. Two more thermocouples are placed on the surface of the heating panels to monitor their temperature, which is used as a control parameter to prevent any damage that could be caused by overheating.

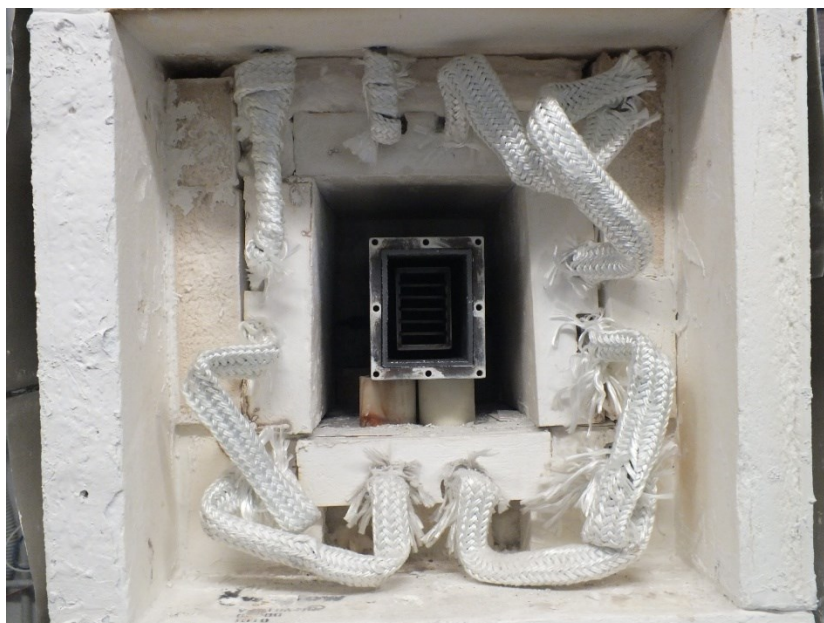


Figure 8 Frontal view of the reactor used in the experimental work

4.3.2 Condensation/gas discharge section

The pyrolysis gas and condensable vapor phase exit the reactor carried by the N_2 flow and are directed to a first cooling stage that consists of a double pipe heat exchanger that uses distilled water from a chiller as cooling fluid. After this exchanger, the line changes according to the purpose of the pyrolysis test.

- For bio-oil collection: after the first heat exchanger, kept at 35 °C, the gas and vapors pass through a double condensation stage in liquid nitrogen, composed of two collection flasks immersed in 10 cm of liquid nitrogen. This setup can trap a good part of the condensable vapor phase produced during the pyrolysis. The amount of collected bio-oil for the conducted pyrolysis tests was between 54 % and 65 % of the theoretical calculated bio-oil yield. After the double condensation stage the gas flow is discharged directly.
- For pyrolysis gas analysis: after the first heat exchanger, the gas and vapors pass through a glass condenser that is also water cooled; both stages are kept at 22 °C. After the condenser, which is meant to remove part of the condensable compounds, the gas flow passes 2 filters for the remotion of further condensable compounds, and a silica gel trap, that removes the remaining moisture from the gas. After the filters there is a sampling port for gas analysis connected either directly to a μ -GC system for online gas analysis or to a manual sampling system to fill sampling gas bags for subsequent offline analysis.

When collecting bio-oil, the low temperature induced by the liquid nitrogen causes the solidification of CO₂ in the trap, thus affecting the results of the gas analysis. When both the bio-oil collection and the gas analysis are reported, they refer to separate tests.

4.3.3 Experimental campaign and reactor performance

The feedstocks presented in Section 4.1 were pyrolyzed under slow pyrolysis conditions at three different pyrolysis temperatures: 465, 600 and 800 °C.

The lowest considered temperature, 465 °C, is a possible pyrolysis temperature for of intermediate and fast pyrolysis and, moreover, it is reported to be the threshold temperature below which Pb is mostly retained in the char (He, et al., 2019a) (Grottola et al., 2019). Regarding the two other considered temperatures, 600 °C represents the upper limit of the appropriate intermediate and fast pyrolysis temperature, while 800 °C is a typical operational temperature for flash pyrolysis and could lead to the production of char with high specific surface area.

The specific pyrolysis tests, and the derived pyrolysis products, will be indicated from now on with the name of the feedstock followed by the pyrolysis temperature. For each test the reactor was fed with a quantity of biomass between 6 g (1.5 g per tray using only 4 trays) and 15 g (3 g per tray using all the 5 trays) depending on the amount of char needed for off-line characterization. As can be seen in Table 10, the amount of feedstock didn't influence the char yield when varying from 6 to 10 g. The observed differences result within the standard deviation of the measurements, thus are not significant.

Table 10 Char yields variation for different amounts of feedstocks.

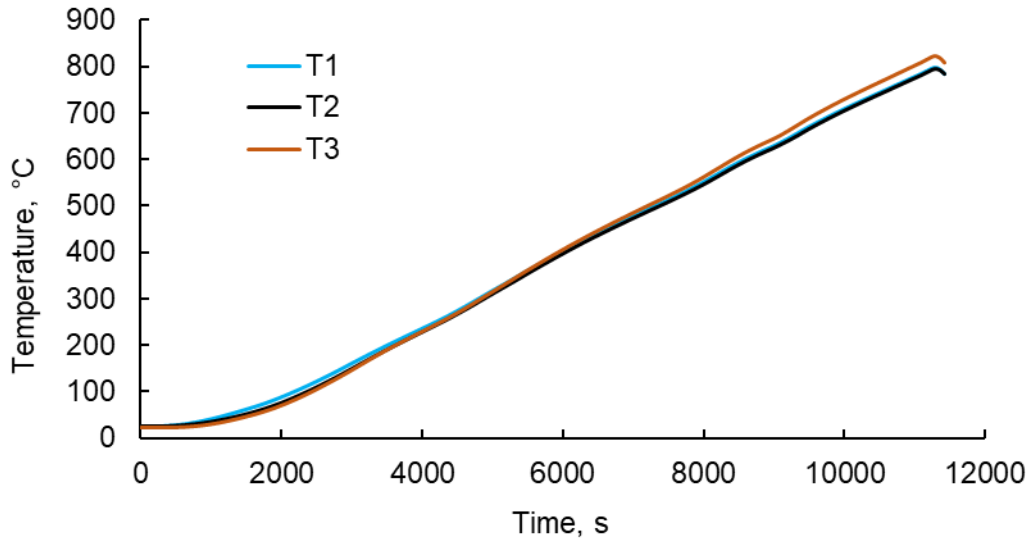
Temperature (°C)	P		P+PbN		P+PbAc	
	6 g	10 g	6 g	10 g	6 g	10 g
465	25.5	24.9	24.2	23.8	29.2	29.0
600	22.5	22.0	22.0	21.2	26.4	25.9
800	20.7	20.9	20.3	20.1	23.7	23.8

An overview of the experimental campaign that was carried out is reported in Table 11.

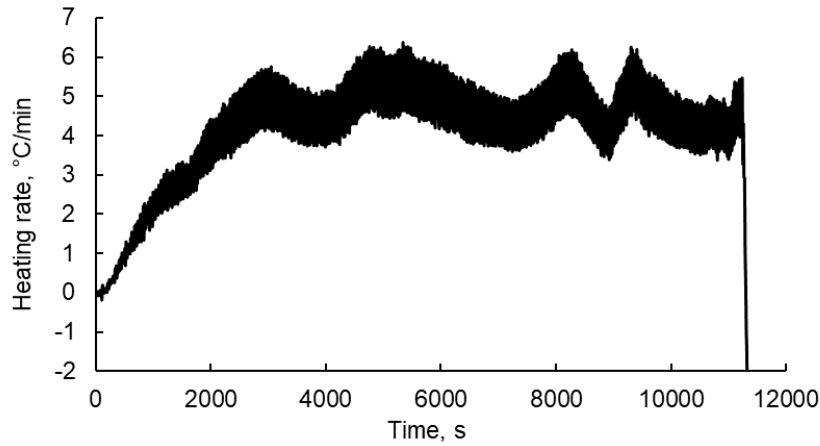
Table 11 Overview of the experimental design

Feedstock name	Temperature (°C)		
	465	600	800
P	L	L	L/G
P+PbN	L	L	L/G
P+PbAc	L	L	L/G
P+PbAc_II	L	L	G
P_w	L	L	G
P_w+PbAc_dm	L	L	G
P_w+PbAc_ie	L	L	G
P_w+PbAc_wi	L	L	G
L = bio-oil collection			
G = gas analysis			

The operational parameters other than pyrolysis temperature are kept constant for the whole experimental campaign and are as follows: mean heating rate = 5 °C/min; N₂ flow rate = 3 NL/min; pressure = 1 atm. The main advantage of this pyrolysis system is the high temperature uniformity that can be achieved in the reactor chamber alongside good control of the heating rate. The temperature profile of a typical pyrolysis test at 800 °C and the corresponding heating rate are reported in Figure 9.



a)



b)

Figure 9 (a) Temperature profile along the test run time measured in different position of the reactor, (T1, T2; T3); (b) heating rate during the test run based on T2 measurement.

As can be seen, the temperatures registered by the 3 thermocouples inside the reactor are almost equal to each other for the whole duration of the pyrolysis test. The maximum difference between two of these temperatures is about 20 °C and is registered at high temperatures. The homogeneous distribution of the temperature is observed for all the conducted tests, regardless of pyrolysis temperature or feedstock type.

As for the heating rate, it increases slowly until it reaches a quasi-stable regime at 3000 s, corresponding to a temperature of about 120 °C, which is still low for the onset of pyrolysis reactions. From this point on the heating rate remains stable at around 5 °C/min, oscillating between 4 and 6 °C/min. However, in the literature there isn't any evidence of significant changes in the pyrolysis mechanisms in this range of heating rate (Xiao et al., 2020).

4.4 Pyrolysis products characterization

In the following paragraphs, the analytical techniques employed for the characterization of the pyrolysis products are summarized and briefly described.

4.4.1 Char

Char yield is obtained by weighting each tray sample holder with the loaded biomass and with the resulting char. All the produced char are characterized via several analytical techniques described in the following sub-sections:

- Elemental analysis for the determination of char composition in terms of weight percentages of C, H and N. The details of the analysis are reported in Section 4.2.2.
- ICP-MS for inorganic content determination, as described in Section 4.2.3; the results were used to calculate the Pb recovery in char as reported in Equation 1.

$$Pb\ recovery = \frac{Pb\ content\ in\ char\ [\frac{mg}{kg}]}{Pb\ content\ in\ biomass\ [\frac{mg}{kg}]} \cdot yield^{char} \quad (1)$$

- The ash content of the produced chars was determined by incineration in a muffle furnace at 700 °C for 2 hours.
- Porosimetry analysis to determine the specific surface of produced chars.; the details of the analysis will be discussed in the following paragraph.
- BCR sequential extraction to gain insight of the possible speciation of Pb and other metals retained in the char.
- XRD analysis to investigate the physical structure of inorganic compounds.

4.4.1.1 Porosimetry – BET specific surface

Porosimetric analysis can give much information on the physical structure of chars, in terms of pore volume, pore size distribution and specific surface. In the present work, the only property investigated is the specific surface, which is calculated following the Brunauer-Emmett-Teller (BET) model.

BET specific surface was determined using a Autosorb iQ (Quantachrome) porosimeter, which consists of a degassing station and an analysis station. Degassing is a necessary treatment to ensure a correct measurement of the specific surface area: by heating the sample under vacuum, degassing ensures that there is no moisture or volatile species trapped inside the porous structure of the char that would hinder the nitrogen adsorption necessary for the analysis phase. For all the analyzed chars, the degassing temperature was set at 200 °C and held for 3 hours. The samples were kept under vacuum until the analysis step.

During the analysis phase the sample cells are soaked in liquid nitrogen at 77.35 K and the adsorption

isotherm curve of the sample is calculated. The adsorption isotherm curve represents the relationship between the volume of gaseous N₂ adsorbed by the sample and the partial pressure of the same gas in the measurement cell.

The BET specific surface is calculated from a selected range of partial pressures of the adsorption isotherm following the Equation 2.

$$\frac{1}{w\left(\left(\frac{P_0}{P}\right)-1\right)} = \frac{1}{w_m C} + \frac{C-1}{w_m C} \left(\frac{P}{P_0}\right) \quad (2)$$

Where P/P_0 is the relative pressure and W is the weight of gas adsorbed corresponding to that pressure. W_m is the weight of adsorbate constituting a monolayer of surface coverage, and C is the BET C constant, which is related to the energy of adsorption in the first adsorbed layer.

4.4.1.2 BCR sequential extraction

The BCR sequential extraction is an analytical procedure developed for heavy metals speciation analysis in soils and sediments (Ure et al., 1993) but that is commonly applied also to char and biomasses (Gong et al., 2018). This technique consists of three extractions carried out with different reagent solutions that extract specific chemical forms of metals, classifying them into four fractions depending on their mobility. In the present work, the three steps procedure reported below (Rauret et al., 2000) has been followed and applied to most of the feedstocks and chars. All the centrifugations were carried out at 2300 rcf for 30 minutes and each recovered supernatant was then analyzed with ICP-MS.

1. 40 mL of a solution of acetic acid (0.11 mol/L) are added to 1 g of dried sample, and then shaken on a magnetic stirrer for 16 hours for the extraction. After 16 hours, the solid residue of the sample is separated from the extract by centrifugation and the supernatant is collected for analysis. The metals contained in the first extract are classified as exchangeable and soluble fraction (F1).

The solid residue is then washed with distilled water, recovered and taken for the next step.

2. 40 mL of a solution of hydroxylamine hydrochloride (0.5 mol/L) acidified with nitric acid are added to the solid residue from step 1 and shaken on a magnetic stirrer for 16 hours for the extraction. After 16 hours, the solid residue is separated from the extract by centrifugation and the supernatant is collected for analysis. The metals contained in the second extract are classified as reducible fraction (F2).

The solid residue is then washed with distilled water, recovered and taken for the next step.

3. 10 mL of hydrogen peroxide (8.8 mol/L) are added to the solid residue from step 2 and let to digest for 1 hour at room temperature; then the digestion is continued for 1 hour at 85 °C in a water bath. A further aliquot of 10 mL of hydrogen peroxide is added, and the digestion is continued for another hour at 85 °C. After the digestion, without discarding any liquid, a solution of ammonium acetate (1 mol/L) is added and shaken on a magnetic stirrer for 16 hours for the extraction. After 16 hours, the solid residue is separated from the extract by centrifugation and the supernatant is collected for analysis. The metals contained in the third extract are classified as oxidizable fraction (F3).
4. The last fraction of metals that were not previously extracted is called residual fraction (F4). The residual fraction can be determined by direct analysis of the solid residue of step 3 or, as in the present work, calculated by difference, if the metal content of the starting sample is known.

4.4.1.3 XRD analysis

X-ray diffraction (XRD) was used to characterize the crystalline phases present in the feedstocks and biochars samples.

Before the analysis, the samples were grinded to a fine powder and compressed in the sample holder, forming a disk few millimeters thick and with 1 cm diameter. The biomass samples were dried at 105 °C overnight to improve their grindability, while the biochar samples did not require any additional treatment.

A Bruker D8 advance XRD instrument with a Cu anode was used at 40 mA and 40 kV with a NaI detector, which analyzed at 6 s/step from 10 to 65° in 0.025°/step increments. The raw data were evaluated with the software TOPAS 3.0 Rietveld.

4.4.2 Gas

Pyrolysis gas analysis was carried out either online with a micro gas chromatography system (μ -GC) or offline with a gas chromatography system (GC), according to instrumental availability. The gas analysis was carried out only for the pyrolysis tests at 800 °C since it comprises also the gas evolution of lower temperature tests. Both the gas analysis systems were calibrated using specific gas mixtures containing known concentrations of different gas species.

In order to compare the obtained results regardless of the employed analysis method, the results considered are only in the temperature ranges 310-490 °C and 600-700 °C. These temperatures are characterized by the maximum gas production, and in particular by high CO and CO₂ production in the low temperature range and by H₂ and CH₄ production in the high temperature range.

The gas yield can be calculated only for the feedstocks whose gas analysis was conducted with μ -GC.

4.4.2.1 μ -GC analyses

The online pyrolysis gas analysis was conducted with an Agilent 3000 Quad μ -GC that registered the volumetric composition of the pyrolysis gas. The instrument is equipped with two chromatographic columns:

- A Molsieve 5A column, which is operated at 110 °C with argon as gas carrier and separates the lighter gas species: H₂, O₂, N₂, CH₄ and CO.
- A PLOT U column equipped with a PLOT Q precolumn, which is operated at 80 °C with helium as gas carrier and separates the heavier gas species: CO₂, C₂H₄, C₂H₆ and C₂H₂.

After each column there is a TCD detector, which calculates the concentration of the species that exit the column.

During the pyrolysis tests, the μ -GC analyzes a gas sample every 147 s (corresponding to a temperature increase of about 10 °C) with an analysis time of 120 s. The first analysis starts when the reactor has a temperature of about 120 °C, and for each pyrolysis test a total of 70-80 analyses were conducted.

The results obtained from the μ -GC analysis can be manipulated to obtain the single gas species yields and the total gas yield. The value of the N₂ flow is used to convert the volumetric composition of the gas phase in volumetric release rate curves of the gas species. By integrating the gas release rate, it is possible to calculate the produced gas volume for each gas species and the mass by applying the ideal gas law.

4.4.3 Bio-oil

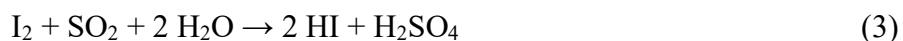
Bio-oil yield can be calculated by difference only when the gas yield is available. In the other cases, an estimation of the bio-oil yield can be obtained by weighting the collected bio-oil. However, not all the bio-oil is successfully condensed in the cold traps: part of it can condense in a previous section of the outlet line or the pyrolysis system, sticking to the tube walls, and part of it can be entrained in the gas phase and not condense at all. Because of this, the collected bio-oil usually gives a strong underestimation of the actual bio-oil yield.

Bio-oil characterization can be quite difficult given its complex chemical composition. The analytical techniques employed in the present work are listed in the following.

4.4.3.1 Water content – KF titration

The water content of the bio-oils was determined by using a Mettler Toledo V20 Karl Fischer volumetric titrator.

The elementary reaction responsible for water quantification in the Karl Fischer titration is the oxidation of sulfur dioxide (SO₂) with iodine (I₂), according to the reaction reported in the Equation 3, in which one mole of I₂ is consumed for each mole of H₂O.



Iodine is added to the solution until it is present in excess, marking the end point of the titration, which can be detected generally by potentiometry. In particular, a solution of two component reagents containing methanol and iodine (Titrant 5) from Aquastar Merck was used as titrant.

The reaction is run in an alcohol solution (usually methanol) containing a base capable of neutralizing the sulfuric acid produced by the reaction and creating a buffer solution that stabilizes the pH at optimal values (between 5 and 7). A commonly used base is imidazole. In fact, a solution of two component reagents containing methanol and imidazole of Aquastar Merck was adopted as solvent.

The process consists of two steps: the reaction of methanol with sulfur dioxide to give a monomethyl sulfite and the subsequent oxidation of the formed sulfite by iodine.

The quantity of bio-oil used for the Karl Fisher analysis depended on its water content; in fact, the quantity of sample used must be such that the milligrams of water present are between 5 and 10 mg so that the error is minimal. More specifically, an amount of bio-oil between approximately 8 and 20 mg were used for each analysis.

4.4.3.2 HPLC analysis – Levoglucosan content

High-performance liquid chromatography (HPLC) is used to determine the weight percentage of levoglucosan in the produced bio-oils. The samples are analyzed with an Agilent 1200 Infinity Series HPLC system, equipped with a TSK-GEL G3000PW_{XL} column, which works with water as mobile phase. The column is followed by a DAD detector and an RID detector; only the latter is involved in levoglucosan detection. Each produced bio-oil from slow pyrolysis tests was analyzed at least in triplicate; for each analysis, 30 µL of bio-oil were injected in the system through an injection loop of 9 µL. The run time of each analysis was 65 minutes, in which the column was kept at 25 °C and the RID detector at 35 °C. The mobile phase flow in the column was set at 0.5 mL/min. The calibration curve for the quantification of levoglucosan was obtained by analyzing three solutions of levoglucosan at 2, 4 and 6 wt. %.

4.4.3.3 GC-MS analysis

The Gas chromatography–mass spectrometry (GC–MS) is a powerful analytical technique that is capable of identifying hundreds of bio-oil components. The samples are analyzed with an Agilent 7890A gas chromatography system (GC) coupled with a mass spectrometer MS 5975C-VLMSD. The GC is equipped with a 624 capillary column, which works with helium as gas carrier. The bio-oil samples are highly diluted in acetone (10 % bio-oil and 90 % acetone) before the injection in the GC-MS that occurs through an autosampler. 1 μ L of sample was injected for each analysis, whose run time was about 118 minutes. The column was heated according to the following temperature program: 4 minutes at 45 °C, heating up to 235 °C with a heating rate of 3 °C/min and 50 minutes at 235 °C. The sample was injected in “split mode” and carried by a flux of helium of 1.8 mL/min. The detector was set to scan a range of m/Z between 35 and 350; the lower limit was set to detect small species like acetic acid while avoiding causing too much baseline noise.

The results obtained from GC-MS analysis give qualitative information on bio-oil composition. In the present work, only the most abundant compounds will be considered, such as acetic acid, acetol, furfural, phenol, guaiacol, 5-hydroxymethylfurfural and syringol.

4.5 Data reproducibility

To assess the reproducibility of the obtained results, most of the tests of the first set of pyrolysis experiments were carried out in duplicate or triplicate. The repetitions of each test resulted in maximum 1 wt. % yield variation, with the observed differences within the standard deviation of the measurements; this was also highlighted in Table 10.

Moreover, the products obtained from duplicate experiments were characterized to confirm the consistency of the products characteristics measurements. The results obtained from char elemental analysis and ICP-MS, gas analysis and bio-oil characterization are all in agreement: the differences registered in samples produced from duplicate experiments are comparable to the differences obtained from multiple analysis of the same sample (ranging from less than 2 % for chromatographic techniques to a maximum of 20 % for ICP-MS analysis). These results ensure that the data presented in the present work are highly reproducible.

5 Results and discussion

In the present chapter, the results obtained during the experimental campaigns will be discussed focusing on the effects of Pb speciation and contamination type.

Firstly, the effects of Pb on the biomass pyrolysis mechanisms are evaluated by considering the variations of pyrolysis products yields and properties.

Then, Pb displacement is considered, investigating also Pb chemical transformation and final speciation.

Lastly, the data obtained from the startup and preliminary test run of the screw reactor are reported to evaluate the reactor performances.

5.1 Pb effect on pyrolysis mechanisms

5.1.1 TGA analysis

All the feedstocks, except for P_w+PbAc_dm, were subjected to thermogravimetric analysis to evaluate their decomposition behavior. Figure 10 reports the results of the first set of feedstocks.

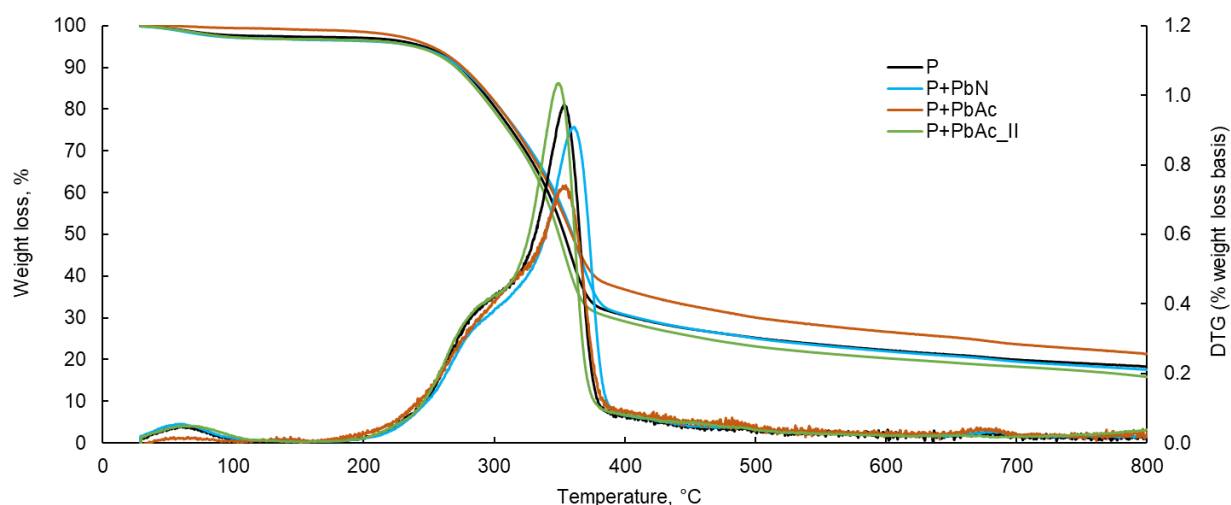


Figure 10 Weight loss and differential thermogravimetric curves (DTG) of plain poplar and samples doped with different Pb salts

The differences between P+PbAc and P must be attributed to its higher ash content, which causes an increase solid residue for temperature above 400 °C and a slower decomposition rate in the most reactive temperature range (350-400 °C). It is well known that AAEMs anticipate the decomposition of cellulose and catalyse reaction pathways leading to gas and lighter volatile products (Giudicianni et al., 2021). Neither P+PbN or P+PbAc_II have relevantly different weight loss curve from P. However, there are some mild effects on the maximum decomposition rate, that results shifted toward

a lower temperature for P+PbAc_II and toward higher temperatures for P+PbN, indicating an effect of the Pb speciation (i.e. of the counteranion) on the decomposition of the biomass. The use of different salts in wet impregnation induces the presence in the aqueous medium of both cations and anions, and the acid-base properties of the anions have to be considered due to their possible effect on the biomass structure and thus on the pyrolytic biomass behavior. These effects were already observed for the inherent AAEMs present in the lignocellulosic biomasses (Giudicianni et al., 2021). For example, NO_3^- expresses a higher catalytic activity than HPO_3^{2-} (Patwardhan et al., 2010). Acetate is compared to carbonate anion, but nothing can be said about their relative effect because the observed higher activity of carbonate corresponds to a higher concentration of the salt on a molar basis (Zhao et al., 2017).

The results of the second set of feedstocks are reported in Figure X, along with the plain biomass P for comparison. P_w+PbAc_dm was not analyzed by Tg analysis since, given the very low amount of material used in this kind of analysis it is not possible to obtain homogeneous samples through dry mixing at so low weight scale.

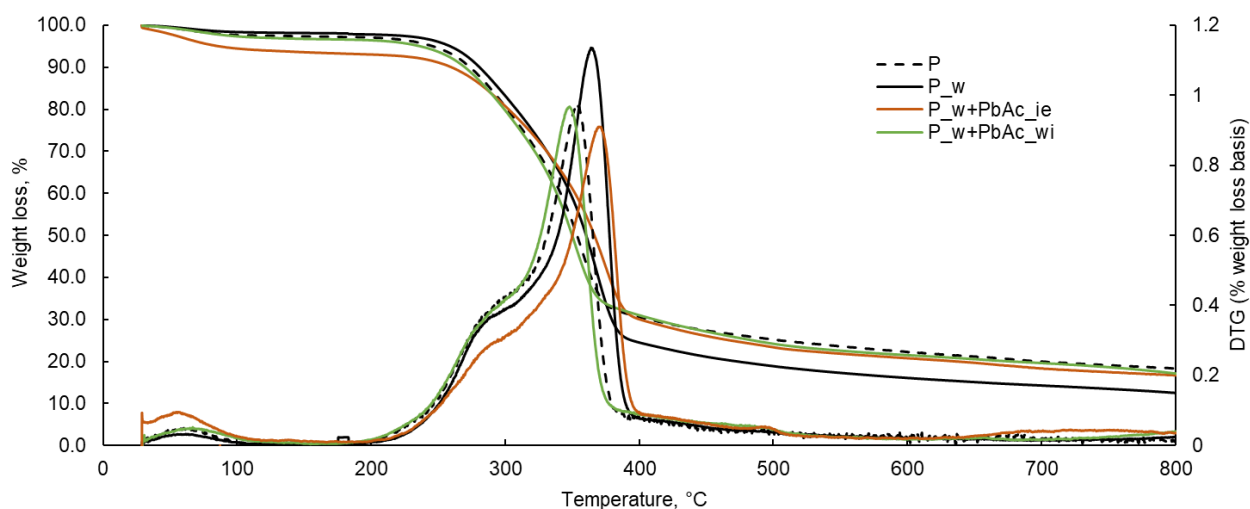


Figure 11 Weight loss and differential thermogravimetric curves (DTG) of plain and demineralized poplar and samples doped with different procedures.

Looking at the difference between P and P_w, it is clear that the demineralization procedure results in a higher decomposition rate and a lower solid residue. This is a confirmation that the observed behavior of P+PbAc is due to its inorganic concentration and is not attributable to the presence of Pb.

The different doping methods influence the decomposition behavior of the biomass: for both P_w+PbAc_ie and P_w+PbAc_wi the residual weight is higher than for P_w, reaching the values obtained for P. As for the decomposition rate, the two doping methods produce opposite effects: wet

impregnation causes a slight reduction of the temperature at which P_w+PbAc_wi reaches the maximum decomposition rate. On the other hand, ion exchange results in an increase of around 20 °C of the maximum decomposition temperature; in general, P_w+PbAc has a lower reactivity between 270 and 370 °C.

A similar small variation in the maximum decomposition temperature was observed by (Mayer et al., 2012) considering demineralized willow wood doped with lead nitrate via ion exchange and wet impregnation. The consistency of the qualitative effect of the doping method (regardless of the considered Pb salt) is a confirmation of the influence of the contamination type on biomass decomposition mechanisms.

5.1.2 Products yield

Char yields were obtained gravimetrically after each pyrolysis test. As reported in Figure 12, the char yield decreases for each sample as the pyrolysis temperature increases, ranging from 29-24 wt. % at 465 °C to 24-20 wt. % at 800 °C. The results are in agreement with the DTG curves showed in Figure 10, which are almost flat in this temperature region denoting that most of the volatiles have been already released at temperature lower than 465 °C.

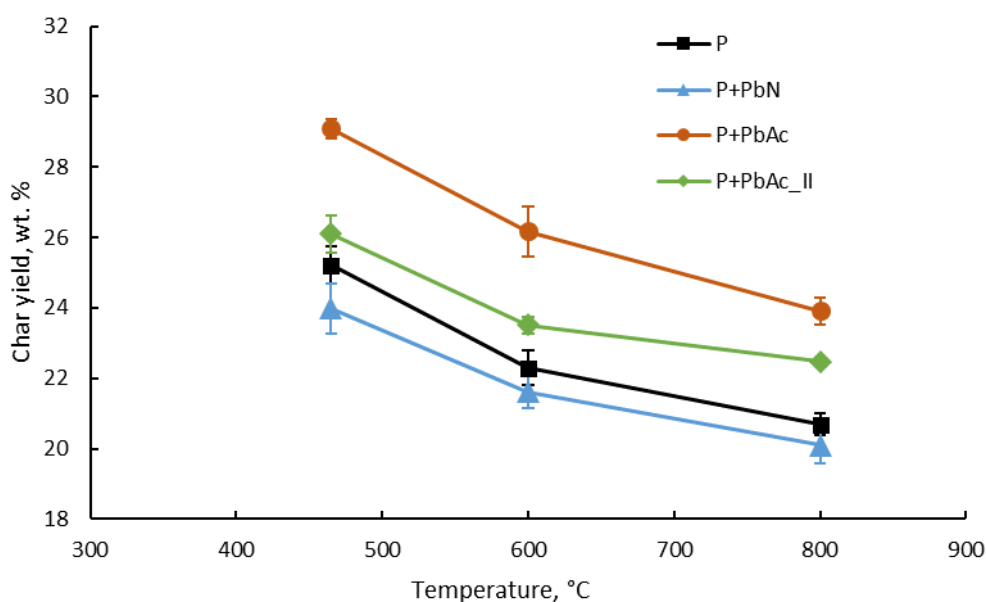


Figure 12 Char yields at different temperatures of plain poplar and samples doped with different Pb salts

For each considered pyrolysis temperature, P+PbN and P result in comparable char yields, while P+PbAc give a considerably (around 4 wt. %) higher char yield. The behavior of P+PbAc is partially due to their higher inorganics content (see Table 9); anyway, P+PbAc_II still results in a slightly

higher char yield than P, confirming that the presence of lead acetate can increase char yield, especially at 800 °C. The results are consistent with the TG curves obtained for the same samples.

As reported in Figure 13, the char yield decreases for each sample as the pyrolysis temperature increases, ranging from 21-22 wt. % at 465 °C to 17-19 wt. % at 800 °C.

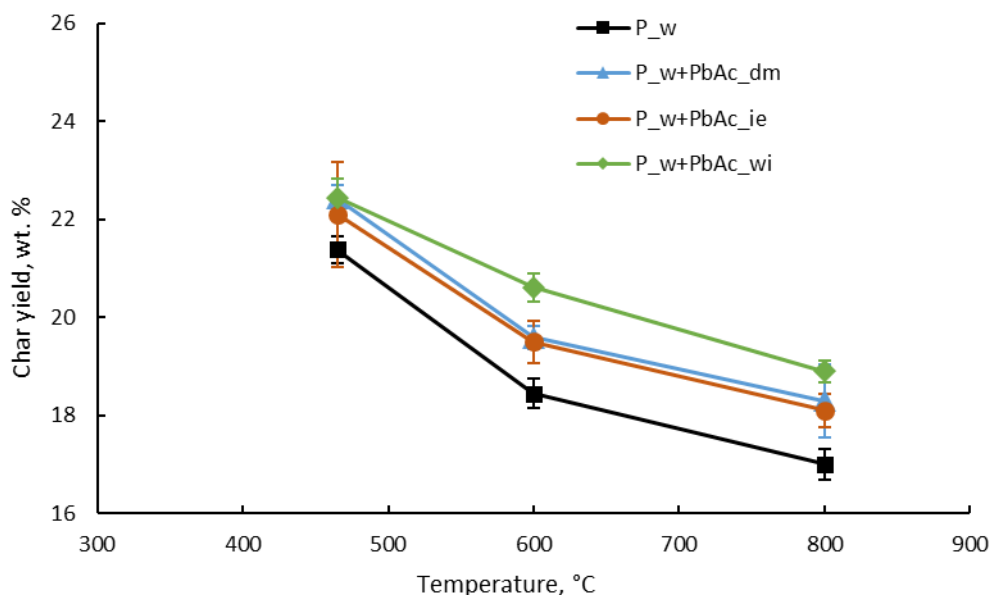


Figure 13 Char yields at different temperatures of demineralized poplar and samples doped with different procedures

For each considered pyrolysis temperature, the plain demineralized poplar has the lowest yield in agreement with the results obtained from TG analysis. At 465 °C the differences in char yield among the samples doped with different procedure are negligible, and their yield is similar to that of demineralized poplar. As the pyrolysis temperature rises, all the doped samples return a slightly higher char yield than the demineralized poplar with P_w+PbAc_wi returning the highest values.

In Figure 14, the yields of permanent gases generated during the pyrolysis process are reported.

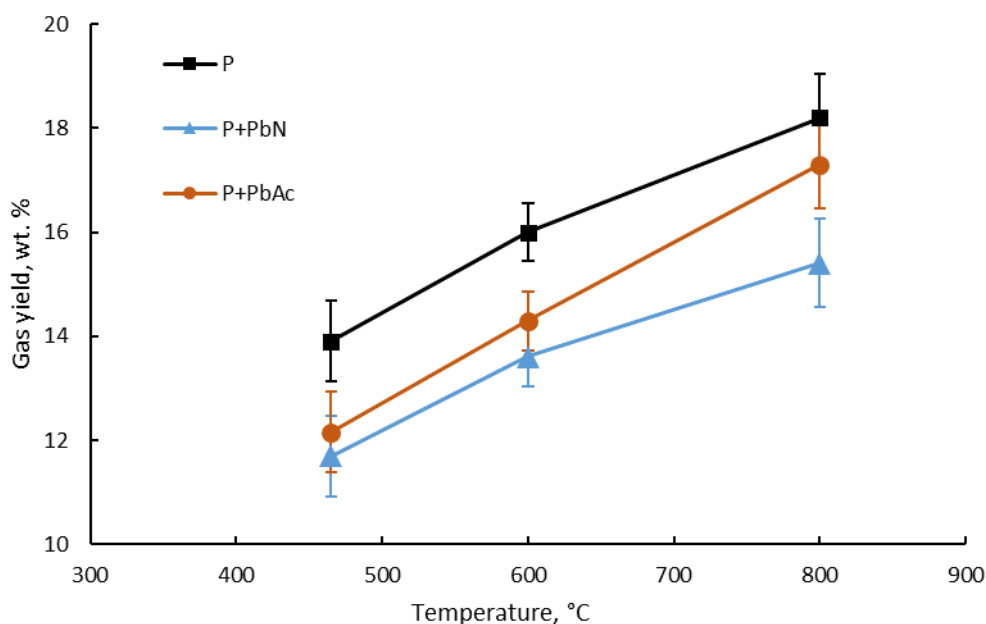


Figure 14 Gas yields at different temperatures of plain poplar and samples doped with different Pb salts

For all the considered biomasses the yields of permanent gases are higher as the pyrolysis temperature increases. For each pyrolysis temperature, the plain poplar has the highest gas yield. At low and moderate pyrolysis temperatures the two doped biomass have comparable gas yield, both lower than that observed for the plain poplar. This result was not expected for P+PbAc since it contains higher amount of alkali and earth-alkali metals (AAEMs) which are recognized to favor the decomposition pathways leading to the production of low molecular condensable species and permanent gases. It seems that AAEMs and Pb induce two opposing effects on the gas yield. On the other hand, at 800 °C the poplar doped with lead acetate shows a gas yield more similar to the plain biomass.

In Figure 15 is reported the condensable vapor phase (or bio-oil) yield, which is obtained by difference considering both char and permanent gas yields.

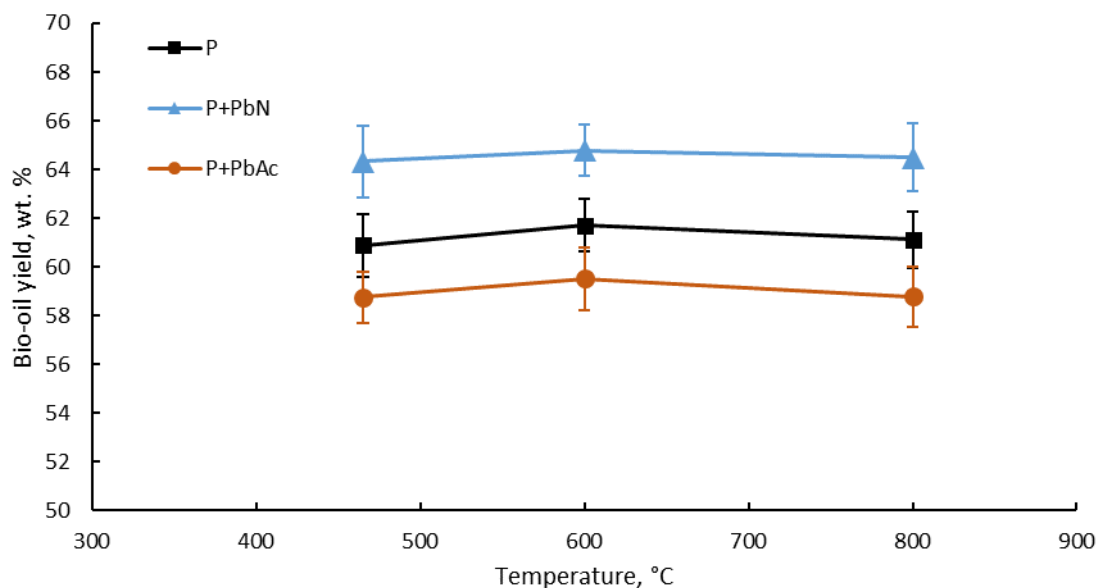


Figure 15 Bio-oil yields at different temperatures of plain poplar and samples doped with different Pb salts

Bio-oil yields are almost independent from pyrolysis temperatures, while there is a clear effect of the employed biomass. Lead nitrate doped poplar has the highest bio-oil yield (about 65 wt. %) while the lead acetate doped poplar and plain poplar have comparable bio-oil yield. Given the higher content of AAEMs in the P+PbAc sample, a lower liquid yield would have been expected. This result confirms that AAEMs and Pb induce contrasting effects on the biomass devolatilization mechanism.

The observed variation in pyrolysis products yields seems to be confirmed from literature data. The impregnation of water hyacinth with high quantity of Pb (2-10 wt. %) (Jiu et al., 2015) resulted in only a slight decrease of char yield when compared with the untreated biomass, while bio-oil and gas yield showed higher variations. In particular, Pb addition causes a decrease in gas yield and an almost corresponding increase in bio-oil yield in the whole considered temperature range (275-550 °C), as observed also in the present study.

Similar results were obtained for Pb nitrate impregnated *Arundo donax* and *Broussonetia papyrifera* (Han et al., 2018) pyrolyzed at 450 °C. The introduction of Pb caused an increase in bio-oil yield at the expenses of gas and char yields for *Arundo donax*. However, for *Broussonetia papyrifera* both the bio-oil and gas yields showed an increase with respect to the untreated biomass. The entity of the observed variation was different for the two employed biomasses; it is not clear if the reported differences are to be attributed to the influence of the biomass composition or of the Pb content.

From the available data, reported in Table 12, it seems that the observed variations in pyrolysis products yield are caused by Pb presence; moreover, the extent of yields variation seem to be related to Pb concentration.

Table 12 Literature data reporting the effect of Pb on pyrolysis products yields under different pyrolysis conditions

Feedstock	Feedstock Pb contamination, mg/kg	Pyrolysis temperature, °C	Char yield variation, wt %	Bio-oil yield variation, wt %	Gas yield variation, wt %	Reference
Poplar wood	1000	465	-1.0	+2.0	-2.0	This work
Arundo donax	3200	450	-0.6	+2.0	-2.0	(Han et al., 2018)
Broussonetia papyrifera	6600	450	-3.0	+2.5	+0.8	(Han et al., 2018)
Water hyacinth	60000	450	-5.0	+20	-15.0	(Jiu et al., 2015)

5.1.3 Char properties

5.1.3.1 Elemental composition

In Tables 13 and 14 the char composition is reported in terms of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) weight percentage; O content is obtained by difference. In the same tables is also reported the ash content.

Table 13 Elemental analysis of char produced at different temperatures from plain poplar and samples doped with different Pb salts

Sample	C	H	N	O (a)	Ash
	wt. % - Dry ash free basis			wt. % - Dry basis	
Char at 465 °C					
P	81.82	3.28	0.74	14.17	5.70
	(±0.71)	(±0.05)	(±0.21)	(±0.96)	
P+PbN	79.67	3.54	0.81	15.97	6.40
	(±0.63)	(±0.04)	(±0.08)	(±0.75)	
P+PbAc	78.12	3.26	1.66	16.96	11.15
	(±0.30)	(±0.08)	(±0.09)	(±0.48)	
Char at 600 °C					
P	89.57	2.42	0.98	7.02	6.43
	(±1.35)	(±0.03)	(±0.05)	(±1.43)	
P+PbN	86.16	2.41	1.03	10.39	7.03
	(±1.82)	(±0.13)	(±0.18)	(±2.13)	
P+PbAc	83.87	2.33	1.82	11.99	12.33
	(±0.89)	(±0.02)	(±0.02)	(±0.93)	
Char at 800 °C					
P	92.87	0.86	0.98	5.29	7.09
	(±0.73)	(±0.06)	(±0.10)	(±0.90)	
P+PbN	86.88	1.16	0.90	11.05	7.62
	(±0.78)	(±0.49)	(±0.26)	(±1.52)	
P+PbAc	84.09	0.64	1.25	14.02	13.74
	(±0.44)	(±0.15)	(±0.08)	(±0.67)	
(a) Obtained by difference					

A common trend observed for all the first set of feedstocks is that as pyrolysis temperature increases, C content of the produced char increases while H content decrease, whereas N content has a maximum at 600 °C for lead acetate doped poplar and an increasing trend for the other chars. O content of the plain poplar decreases with the temperature, while the opposite behavior is observed for both the doped samples. All the doped chars show a lower C content and a higher O content with respect to the plain biomass; chars from lead acetate poplar have the highest N content in the whole temperature range.

Concerning the N content, literature evidence shows that there is not a clear trend of N content with the temperature for lignocellulosic biomass, whereas a decreasing trend was observed for N-rich feedstock such as sewage sludges (Weber & Quicker, 2018). The higher content observed in presence of lead acetate can be ascribed to the higher content of inorganics of this sample as confirmed by the results obtained with demineralized poplar and the corresponding lead acetate doped sample (see Table 14) showing comparable N contents in the whole temperature range. This result is also

supported by literature findings showing the inhibition of N-containing species release in presence of AAEMs (Xiong et al., 2023). However, each inorganic element can have a different contribution on N-containing species production and release, both in the liquid and gas phases, depending also on its speciation (Liu et al., 2017).

C and O contents deserves specific attention given the unexpected increasing trend with the temperature observed for both the lead doped samples. To investigate this aspect the differences of C, H and O content of chars in response to temperature change and the presence of Pb have been represented as O/C and H/C molar ratios in the Van Krevelen diagram shown in Figure 16. As expected from the elemental analysis, H/C and O/C decreases with the temperature for plain poplar chars whereas for the doped samples H/C and O/C have opposite trends with temperature. More specifically, O/C increases with the temperature, more remarkably in presence of lead acetate.

The C and O contents of biomass typically range between 50 and 40 wt. % on a dry ash free basis, whereas the H content varies between 5 and 7 wt. % (Weber & Quicker, 2018). The most significant changes during char production occur in the temperature range 200-400 °C, where C and O contents are in the range of 70-80 and 10-30 wt. %, respectively. The chars produced from all the poplar samples at 465 °C are the result of the cleavage of the glycosidic linkages between the sugars of cellulose and of dehydration and depolymerization reactions (removal carbonyl, carboxyl and hydroxyl groups) and their C, O and H contents meet the typical values observed for other biomasses, resulting in a decrease of both O/C and H/C ratios with respect to the initial feedstock. Pb seems to affect the poplar decomposition pathways even in the lower temperature range. Analyzing the Figure 18 where the release rate of CO₂ and CO is reported along the pyrolysis temperature, Pb seems to depress the production of CO and CO₂, species characterized by a O/C ratio higher than most of the other condensable species, leaving a char with higher O and lower C content compared to the char from plain poplar. The effect of Pb is even more remarkable in the case of the P+PbAc sample, as it is still visible despite the high presence of inorganics that should act in the opposite direction.

As temperature increases carboxyl, carbonyl, and methoxyl groups are released up to the complete falling off at temperatures in the range of 600 °C–700 °C. At temperatures higher than about 700 °C, charring reactions occur, determining the growth of graphene layers and the removal of heteroatoms, thus increasing the char aromaticity. At these temperatures, typically, chars may reach C and O contents of higher than 95% and lower than 5% respectively, whereas the H content decreases to less than 2%(Weber & Quicker, 2018). Once again, also at higher temperature, Pb seems to affect the pyrolytic mechanisms. In fact, whereas the chars obtained from plain poplar at 600 and 800 °C resemble the typical composition observed for other lignocellulosic biomasses, the chars obtained

with doped poplar have higher O and lower C contents thus resulting in higher O/C ratios. This result is in agreement with literature findings related to other metal acetates (Ni, Zn, Cu and Co) acetates (Koppolu et al., 2003). However, the presence of a peak in the CO₂ and CO releasing rate curves at about 650 °C of the lead acetate doped samples is not consistent with the higher O/C ratio of the corresponding char at 800 °C. Other reasons must be invoked to justify this result. One possible contribution to this may be the lower concentration (and yield) of water in the bio-oil obtained at 600 and 800 °C from both doped samples reported in Tables 17 and 18. However, the possibility of high-temperature formation of organometallic compounds leading to devolatilization of Pb and C should not be ruled out. This hypothesis will find confirmation, as will be seen in the next section, in the results obtained from the analysis of Pb content in char at increasing pyrolysis temperature.

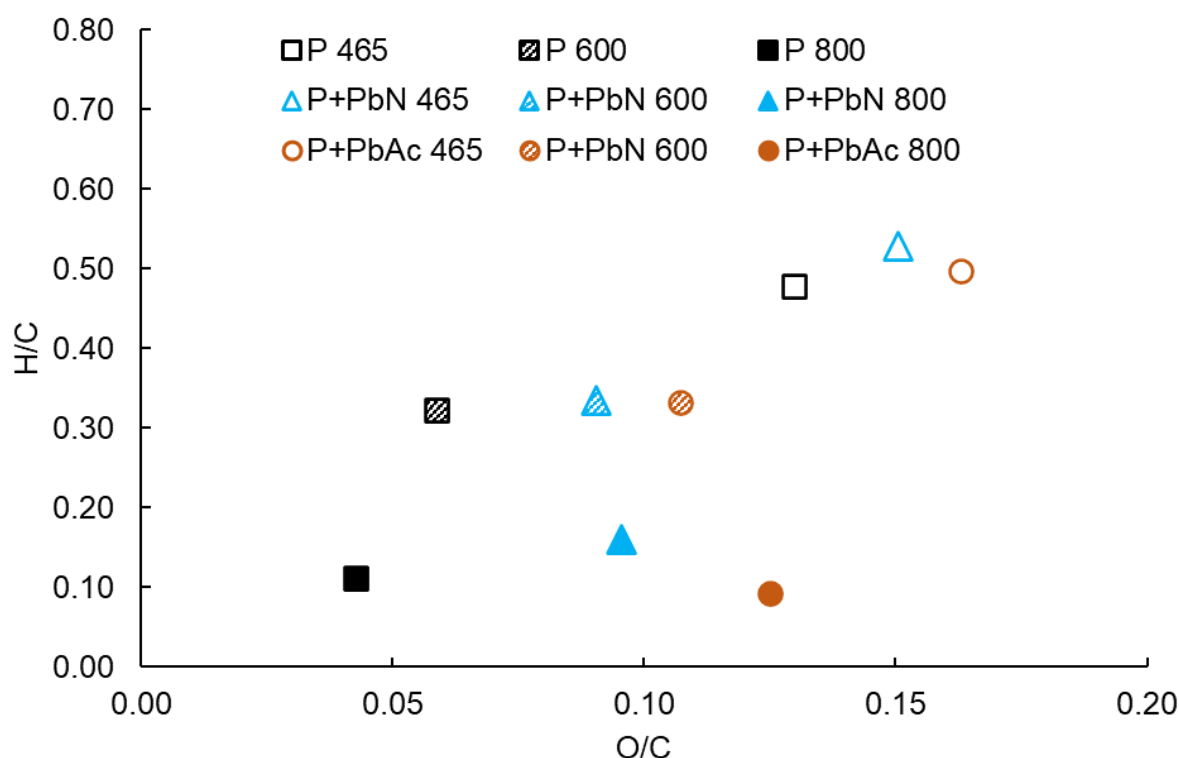


Figure 16 H/C and O/C ratios of char produced at different temperatures from plain poplar and samples doped with different Pb salts

Considering the second set of feedstocks, the only general trend that can be identified regards H concentration, which decreases with the increase of pyrolysis temperature for all the produced char. The different simulated contamination type results to affect greatly the composition of doped chars at the considered temperatures. P_{w+PbAc} follows the same trends observed for the control biomass, P_w: the C concentration of the derived char increases while O content decreases with

temperature in the whole considered range. On the contrary, when passing from 600 to 800 °C, the composition of char produced from P_w+PbAc_dm does not change significantly, whereas the char produced from P_w+PbAc_wi exhibits a decrease in C content and an increase in O content. This confirms that the Pb contamination type can affect the char production mechanisms during pyrolysis of contaminated biomass.

The release rates of CO₂ and CO along the temperature of all these samples are currently being analyzed to elucidate the reason underpinning the unexpected behavior of P_w+PbAc_dm and P_w+PbAc_wi. Regarding the latter it is likely that the explanation given in that case of P+PbAc II can also be transferred to this case, whose only difference from the former is a lower inorganic content. However, even though the trend of C and O contents at increasing temperatures of P_w+PbAc_wi and P+PbAc II are consistent, the comparison with the corresponding plain biomass produces opposite results. More specifically, P+PbAc II chars were characterized by lower C content and higher O content with respect to P, whereas P_w+PbAc_wi chars have higher C content and lower O content with respect to P_w, thus unrevealing a different effect of Pb depending on the presence of the other inorganics.

Table 14 Elemental analysis of char produced at different temperatures from demineralized poplar and samples doped with different procedures

Sample	C	H	N	O (a)	Ash
	Wt. % - Dry ash free basis			Wt. % - Dry basis	
Char at 465 °C					
P_w	81.09	3.87	0.84	14.21	3.6
	(±0.31)	(±0.19)	(±0.12)	(±0.62)	
P_w+PbAc_dm	81.02	4.24	0.93	13.82	1.8
	(±2.98)	(±0.40)	(±0.06)	(±3.44)	
P_w+PbAc_ie	71.67	3.22	0.84	24.27	1.0
	(±4.38)	(±0.17)	(±0.45)	(±5.00)	
P_w+PbAc_wi	85.72	4.76	0.73	8.78	2.8
	(±3.17)	(±0.37)	(±0.08)	(±3.62)	
Char at 600 °C					
P_w	86.14	2.69	0.90	10.27	4.2
	(±4.78)	(±0.12)	(±0.14)	(±5.04)	
P_w+PbAc_dm	85.85	2.91	0.96	10.29	2.1
	(±3.15)	(±0.48)	(±0.12)	(±3.75)	
P_w+PbAc_ie	88.39	3.08	0.67	7.87	1.2
	(±2.94)	(±0.33)	(±0.06)	(±3.33)	
P_w+PbAc_wi	93.40	3.71	0.73	2.15	3.1
	(±6.42)	(±1.14)	(±0.01)	(±7.57)	
Char at 800 °C					
P_w+PbAc_dm	86.09	1.17	0.75	11.98	1.9
	(±2.73)	(±0.13)	(±0.06)	(±2.92)	
P_w+PbAc_ie	94.90	2.23	0.61	2.26	1.3
	(±7.64)	(±0.81)	(±0.06)	(±8.51)	
P_w+PbAc_wi	87.92	1.32	0.80	9.96	3.3
	(±2.35)	(±0.27)	(±0.09)	(±2.71)	
(a) Obtained by difference					

The observed differences in the elemental composition are reported also in Figure 17. It emerges that the doped chars are characterized by higher H/C values than the control biomass for all the considered temperatures and that the char produced after wet impregnation doping of poplar have lower O/C ratios than those obtained from poplar not doped and doped through dry mixing procedure.

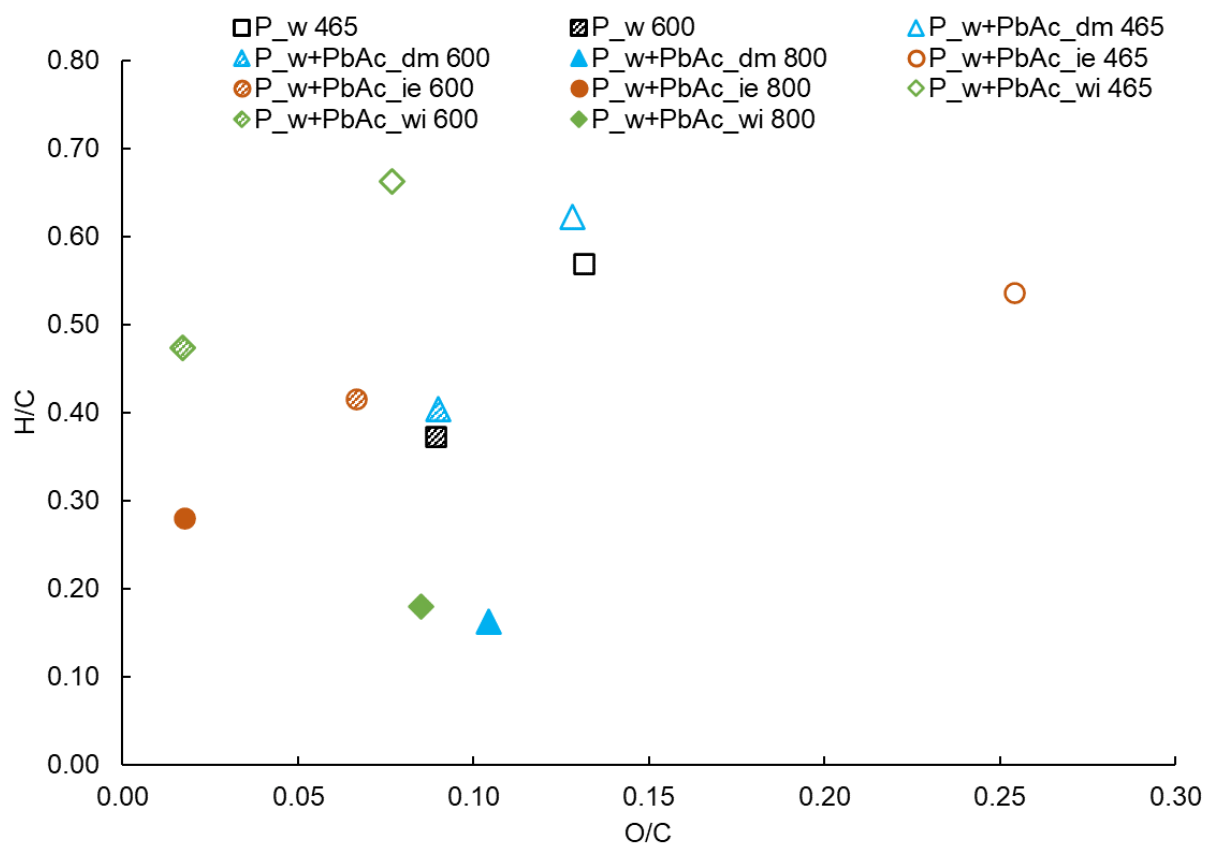


Figure 17 H/C and O/C ratios of char produced at different temperatures from demineralized poplar and samples doped with different procedures

When passing from 600 to 800 °C the effect of dry mixing and wet impregnation is evident from the increase of the O/C ratio, that is not present for ion exchange doping. This effect could be caused by the presence of detrital Pb contamination, that is simulated by both dry mixing and (partially) by wet impregnation. A further confirmation of this hypothesis is that the same O/C increase occurs for P+PbAc (Figure 16), which is doped via wet impregnation, too.

5.1.3.2 Porosimetry

The structure of the chars and specifically their porosity was compared through the measurement of their BET surface (Table 15).

Table 15 BET specific surface of char produced at different temperatures from plain poplar and samples doped with different Pb salts

Char sample	BET surface, m²/g
Char at 465 °C	
P	10
P+PbN	17
P+PbAc	8
P+PbAc_II	8
Char at 600 °C	
P	369
P+PbN	292
P+PbAc	11
P+PbAc_II	370
Char at 800 °C	
P	205
P+PbN	10
P+PbAc	27
P+PbAc_II	6

Except for P+PbAc all the chars have a non-monotonous trend with the temperature. The maximum BET was observed at 600 °C due to the devolatilization of most of the volatile fraction. At higher temperature BET decreased due to several factors: polymerization reactions of the volatiles still entrapped in the solid matrix may form secondary char whose structure and chemical composition, much more similar to that of carbon coke, can partially occlude the pores; moreover, the thin walls between micropores can collapse to form larger pores resulting in an increase in porous volume and a decrease in specific surface area. Concerning the effect of the different lead salts it is clear that their presence greatly affects the porosity of the chars, mainly at 600 and 800 °C, whereas at 465 °C the observed differences are within the experimental error. At 600 °C lead nitrate has a detrimental effect on the BET surface, whereas the effect observed in the sample doped with lead acetate is mainly due to the higher content of the other inorganics (Fe and Ca) as confirmed by the comparable BET surface values of P and Pb+Ac_II. Differently, at 800 °C both the lead salts have a negative effect on the char porosity and in this case only a slight positive effect of the other inorganics in the char derived from P+PbAc sample has been detected since the BET value of P+PbAc is only slightly higher than P+PbAc_II derived sample. The negative effect of the lead salts cannot be ascribed to the occurrence of melting and sintering phenomena of the salts, because at this temperature, as will be presented in Figure 22, most of the lead has been devolatilized. It is more likely that by increasing the temperature from 600 to 800 °C Pb affects positively the extent of polymerization reactions, as some authors have

observed for AAEMs species (Nowakowski & Jones, 2008). However, (Han et al., 2018) did not observe any strong interaction of Pb with the biomass components, resulting in a qualitatively similar porosity development of the doped and untreated biomasses based on SEM observations. The heavy metals were found uniformly distributed into the pore structure of the chars. However, SEM analysis is not able to detect differences at nano-scale, which is the dimension scale of the micro and mesopores.

From the data reported in Table 16, it appears that contamination type has a lesser effect on char porosity and BET specific surface development than Pb chemical speciation. In general, the demineralization pre-treatment causes an increase of porosity development in this set of feedstocks (Giudicianni et al., 2021), though the non-monotonous trend with temperature is confirmed and the maximum BET is still obtained at 600 °C.

Table 16 BET specific surface of char produced at different temperatures from demineralized poplar and samples doped with different procedures

Char sample	BET surface, m ² /g
Char at 465 °C	
P_w	18
P_w+PbAc_dm	4
P_w+PbAc_ie	18
P_w+PbAc_wi	11
Char at 600 °C	
P_w	424
P_w+PbAc_dm	410
P_w+PbAc_ie	429
P_w+PbAc_wi	398
Char at 800 °C	
P_w	346
P_w+PbAc_dm	341
P_w+PbAc_ie	321
P_w+PbAc_wi	307

For the char produced at 465 °C, the observed differences are within the experimental error and the BET specific surface values are quite low since the main porosity development occurs at higher temperatures. The negligible effect of lead acetate on BET specific surface at 600 °C is confirmed since the values obtained for P_w and doped chars are quite similar. At both 600 and 800 °C the different doping methods do not cause great variations of BET surface. In this case, also at 800 °C the BET surface values obtained for doped char are still comparable to the ones registered for P_w.

This suggests that the negative effect on porosity development observed for the first set of samples at 800 °C could be due interactions between Pb and the naturally occurrent inorganics.

5.1.4 Gas composition

The analysis of the gas produced during pyrolysis provides more information on the possible effect of the Pb on the biomass decomposition mechanisms. In Figure 18 and Figure 19 the release rate of the main gaseous species is showed as function of the pyrolysis temperature, whereas in Tables 17 e 18 the yields of the single gaseous species and the composition of the gas phase are reported.

To better understand any effects of Pb, it is necessary to briefly describe what are the main decomposition mechanisms a biomass undergoes when subjected to pyrolysis. At low temperatures, the holocellulosic fraction of biomass, through a glycosidic cracking mechanism, reduces its degree of polymerization producing oligosaccharides with predominantly carbonyl and carboxylic and partly methoxylic functional groups. Cracking ($280\text{ °C} < T < 400\text{ °C}$) of the carbonyl and carboxyl groups and subsequent reforming results in the release of CO₂, CO, while cracking of the methoxyl groups is responsible for the formation of CH₄. From the cracking reactions, condensable compounds (sugars, acids, alcohols, furans) are formed in addition to permanent gases. The glycosidic cracking mechanism competes with the transglycosylation mechanism (Shafizadeh & Chin, 1977); (Shafizadeh, 1983), which produces essentially sugars (levoglucosan). For $T > 500\text{ °C}$ the condensable compounds released during the primary degradation of holocellulose undergo further degradation (secondary cracking) involving the formation of secondary char and the release of CO, CO₂, CH₄, H₂. The degradation of the ligninic fraction at low temperature ($T < 600\text{ °C}$) produces limited amounts of aromatic condensables (phenols, guaiacols, and syringols) and gases (CO₂, CO, and CH₄), while the release of gases (CO₂, CO and CH₄, H₂) at $T > 600\text{ °C}$ is substantial (greater than that observed for holocellulose) and is mainly due to charring reactions (Yang et al., 2007).

The release of the gaseous species seems to be affected by the presence of Pb. More specifically, at low temperature Pb inhibits the production of CO and CO₂ also in presence of higher inorganics content (as it is the case of P+PbAc sample) which, on the contrary, should promote their release. However, even though up to 465 °C CO and CO₂ yields are reduced by the presence of Pb for both the doped samples, in case of doping with Pb nitrate their concentrations are comparable to those obtained for the plain poplar. On the contrary in the case of Pb acetate the concentration of CO is higher at the expense of CO₂. It is unclear if this result is due to the different speciation of Pb or if it should be attributed to the higher inorganics content of the doped sample. The analysis of the gas evolved from P+PbAc II will clarify this aspect.

Also CH₄ production is affected by Pb in form of nitrate even at low temperature and is responsible of the higher concentration of the corresponding gas up to 465 °C. Also in this case, the analysis of the gas evolved from P+PbAc II will indicate if this is the result of the effect of inorganics or of a different speciation of Pb.

At higher temperature two main results are worth to be noted: (i) the CO and CO₂ release rate curves of the sample doped with Pb acetate show two peaks at about 485 °C and 650 °C; (ii) H₂ release is enhanced in case of Pb doping. Unfortunately, at this stage it is not yet possible to clarify whether these differences are due to Pb speciation or to the higher inorganic content of the acetate doped sample. However, it is worth noting that the two peaks are not due to acetate decomposition since thermogravimetric analysis of the isolated salt shows that it decomposes completely at 360 °C.

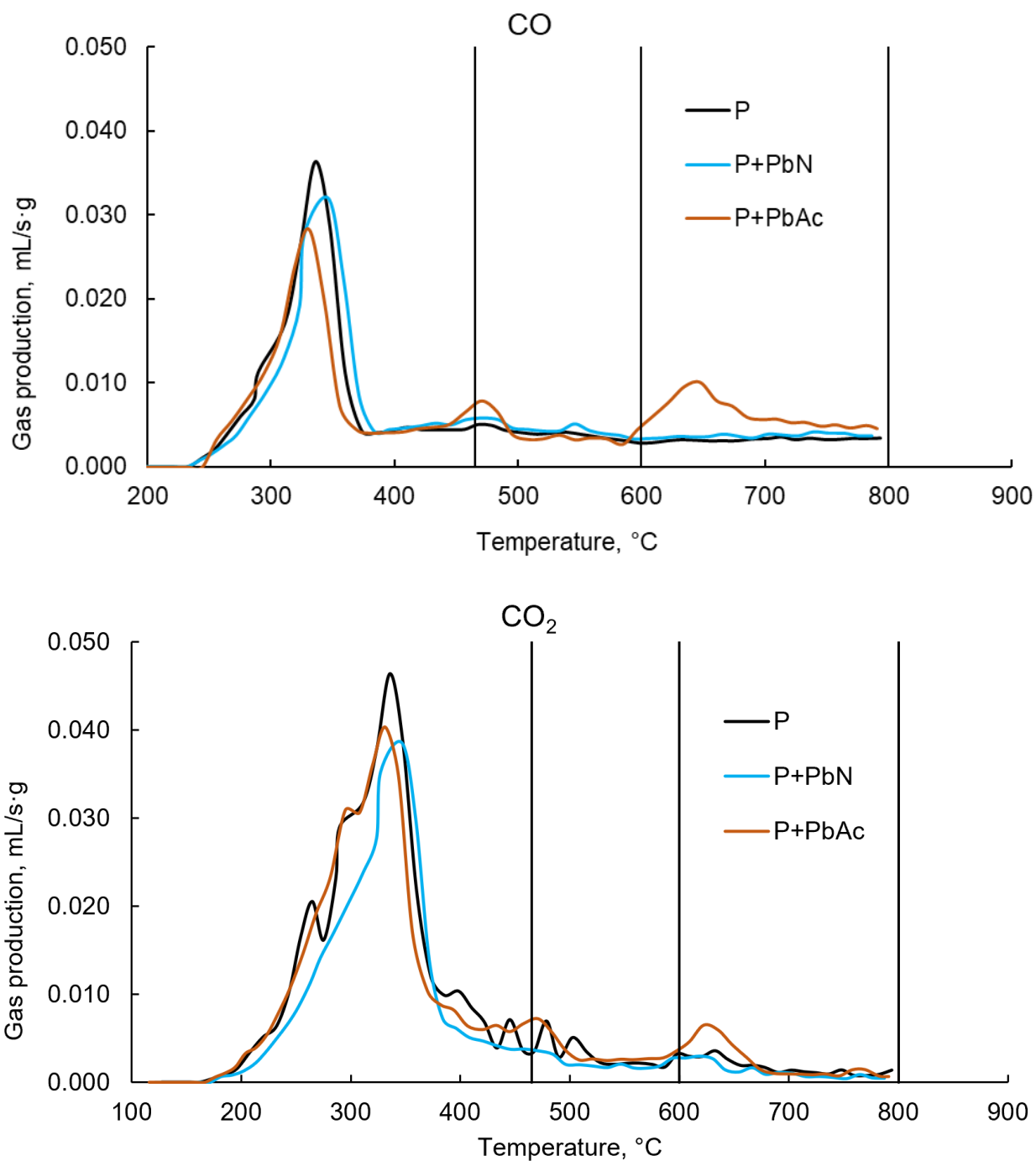
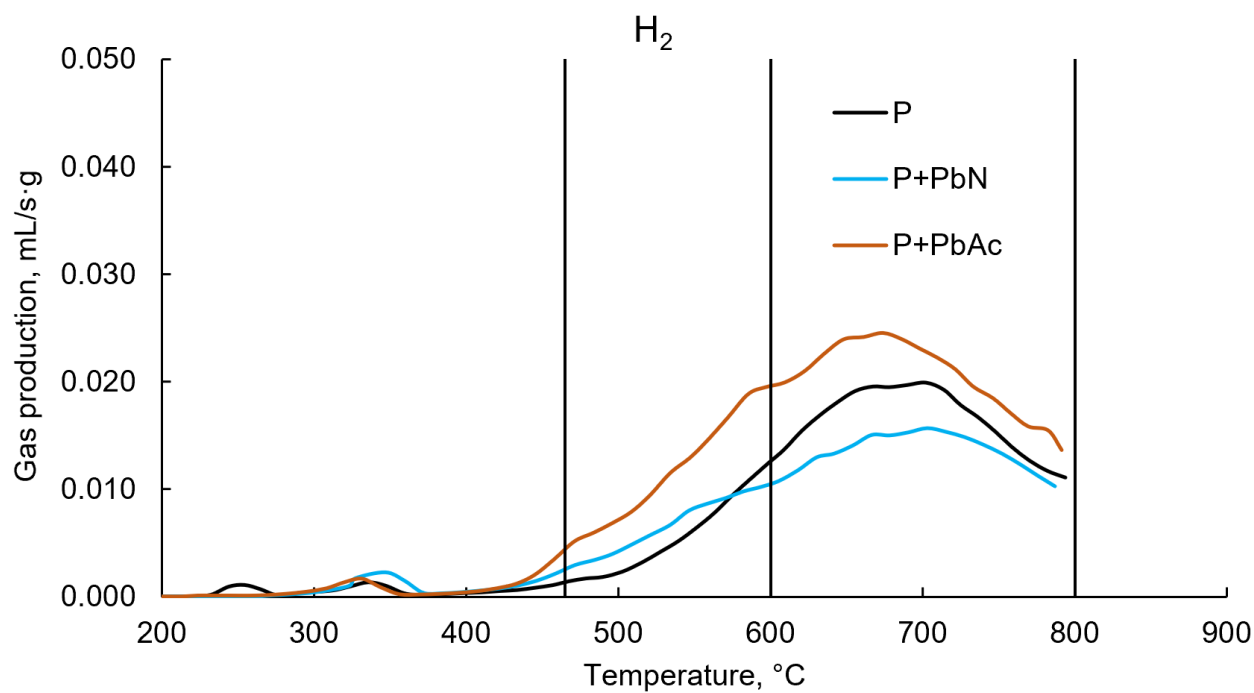
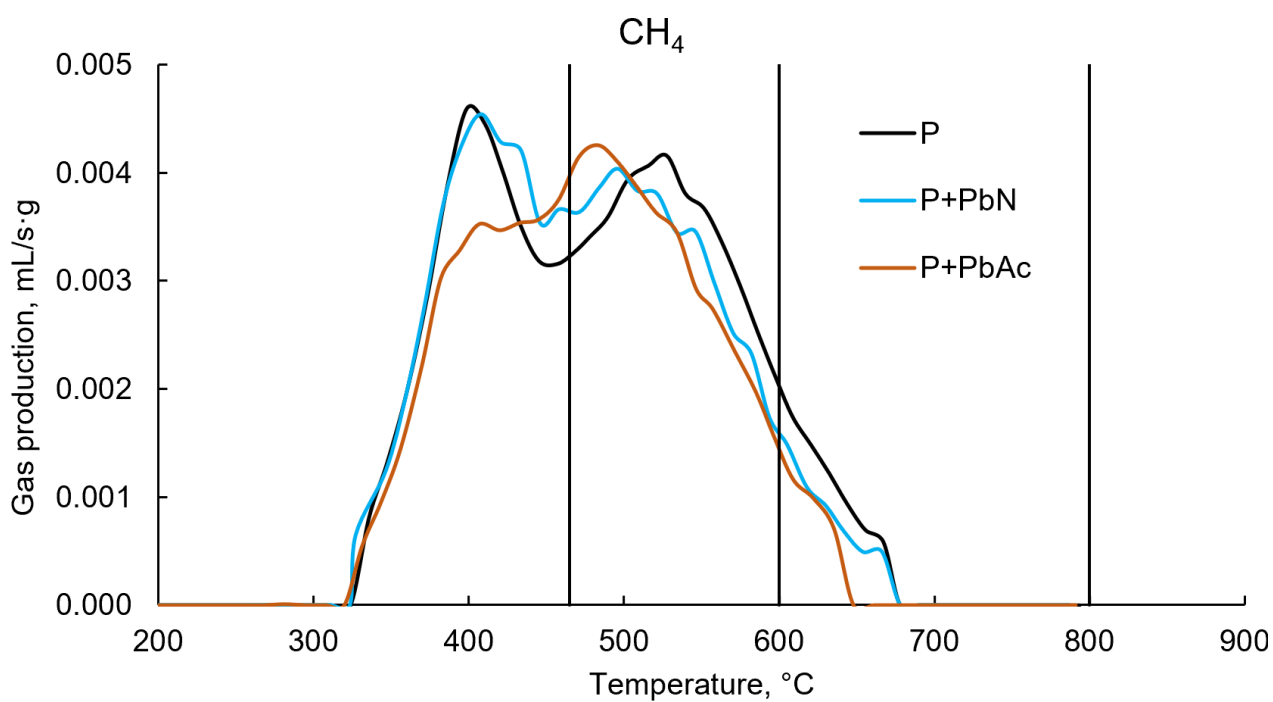


Figure 18 CO and CO₂ release rate during pyrolysis of plain poplar and samples doped with different Pb salts



a)



b)

Figure 19 H_2 and CH_4 release rate during pyrolysis of plain poplar and samples doped with different Pb salts

Table 17 Gas species yields (wt. %) for plain poplar and samples doped with different Pb salts

Sample	H ₂	CH ₄	CO	CO ₂
% wt.				
465 °C				
P	0.02	0.35	3.32	10.21
P+PbAc	0.02	0.31	2.83	8.99
P+PbN	0.02	0.37	3.19	8.11
600 °C				
P	0.09	0.73	4.08	11.14
P+PbAc	0.17	0.65	3.58	9.88
P+PbN	0.12	0.71	3.97	8.76
800 °C				
P	0.44	0.81	5.05	11.93
P+PbAc	0.59	0.69	5.25	10.78
P+PbN	0.37	0.75	4.99	9.25

Table 18 Gas species composition (wt. %) for plain poplar and samples doped with different Pb salts

Sample	H ₂	CH ₄	CO	CO ₂
% wt.				
465 °C				
P	0.14	2.52	23.88	73.45
P+PbAc	0.16	2.55	23.29	73.99
P+PbN	0.17	3.17	27.29	69.38
600 °C				
P	0.56	4.55	25.44	69.45
P+PbAc	1.19	4.55	25.07	69.19
P+PbN	0.88	5.24	29.28	64.60
800 °C				
P	2.41	4.44	27.70	65.44
P+PbAc	3.38	3.99	30.35	62.28
P+PbN	2.41	4.88	32.49	60.22

5.1.5 Bio-oil composition

The water content of bio-oil is a fundamental characteristic as it influences many physical properties such as density and viscosity. Figure 20 shows the water content of the bio-oils of the first set of feedstocks. As reported in the previous section the production of water is mainly due to the low temperature removal of hydroxyl groups and its yield only slightly increases with the temperature in the examined temperature range, however its concentration in the bio-oil can have a different trend depending on the relative production of water and organic species.

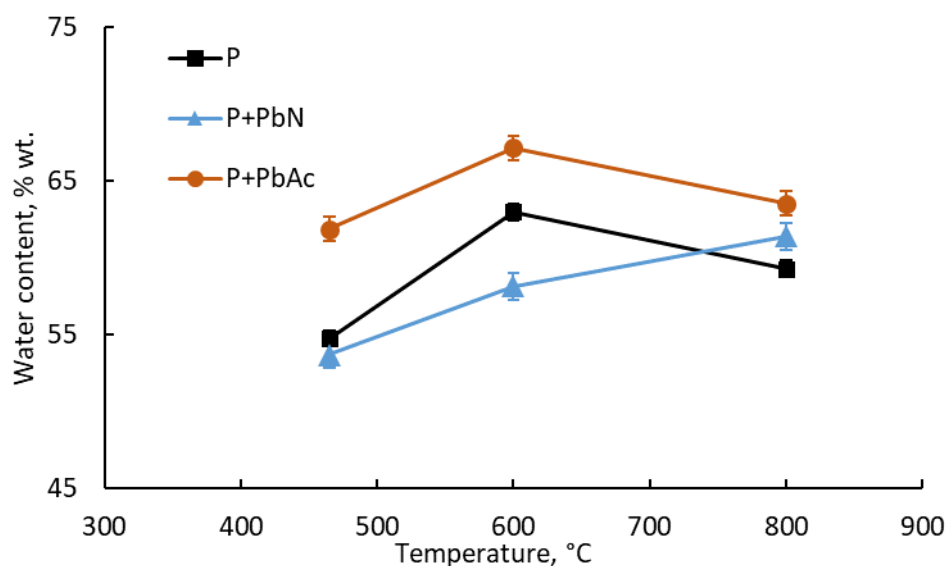


Figure 20 Water content of bio-oils produced at different temperatures from plain poplar and samples doped with different Pb salts

According to the results reported in Figure 20, the water content of the bio-oils produced from P and P+PbAc follows a non-monotonous trend with the pyrolysis temperature, with a maximum at 600 °C, whereas the water content of P+PbN increases, being lower than those of bio-oil from plain poplar at temperature lower than 800 °C. The higher percentages of water reported for P+PbAc are due to the effect of the elevated inorganic concentration of the feedstock. In fact, the water content of P+PbAc_II (not reported in Figure 20) bio-oil is lower than that in P (61 wt. % and 63 wt. % respectively).

Table 19 reports the water content of the bio-oils produced from the second set of feedstocks. In general, the water content of bio-oil from the demineralized sample results lower than those obtained for plain poplar confirming that AAEMs that promotes dehydration reactions during pyrolysis (Fahmi et al., 2018).

Table 19 Water content of bio-oils produced at different temperatures from demineralized poplar and samples doped with different procedures

Bio-oil sample	Water content, wt. %
Bio-oil at 465 °C	
P_w	48.71 (±1.18)
P_w+PbAc_dm	51.63 (±0.33)
P_w+PbAc_ie	42.44 (±0.40)
P_w+PbAc_wi	48.66 (±1.93)
Bio-oil at 600 °C	
P_w	55.40 (±3.71)
P_w+PbAc_dm	50.97 (±0.42)
P_w+PbAc_ie	40.10 (±0.80)
P_w+PbAc_wi	48.66 (±0.68)

The bio-oils produced from P_w show a relevant increase in water content between 465 and 600 °C, passing from 49 to 55.5 %, whereas all the three doped feedstocks, instead, result in a slight decrease in bio-oil water content in the same temperature range. At 465 °C only the sample doped through the ion exchange procedure produces a bio-oil with a water content significantly lower than the other samples. At 600 °C, all the doped samples produce bio-oils with lower water content with respect to the demineralized not doped sample. Again, the lowest value is recorded for the sample doped through ion exchange, thus pointing out that authigenic contamination affects the water content more than the detrital one.

Figure 21 shows the levoglucosan concentration for the bio-oils obtained from the first set of feedstocks.

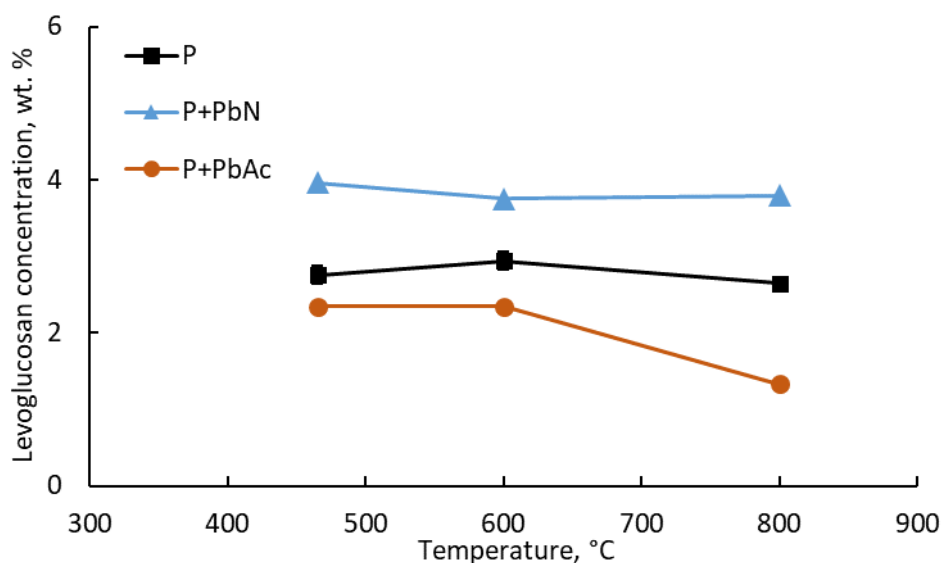


Figure 21 Levoglucosan content of bio-oils produced at different temperatures from plain poplar and samples doped with different Pb salts

The three feedstocks have similar trends with pyrolysis temperature, and do not show any major variation in levoglucosan concentration as temperature increases, except for the case of Pb acetate doped sample which shows a decrease in the levoglucosan yield at 800 °C. Apparently the two lead salts have opposite effect on the levoglucosan percentage, however, the preliminary result obtained for P+PbAc_II (not reported in Figure 21) at 600 °C (4.4 wt. %) follows the same trend as those obtained with P+PbN. The higher concentrations of levoglucosan obtained for P+PbN and P+PbAc_II are consistent with the lower production of CO and CO₂ that is, typically, associated to the cellulose decomposition mechanism leading to the production of lighter species such as aldehydes at the expense of levoglucosan. The decrease in levoglucosan content observed for P+PbAc is caused by its higher ash content, and in particular by the interaction of AAEMs with the decomposition mechanism of cellulose (Giudicianni et al., 2021).

This interaction explains also the higher levoglucosan concentration observed for all the bio-oils produced from demineralized samples, as reported in Table 20. For instance, the levoglucosan content of the demineralized sample passes from roughly 3 % for P to 5.6 % for P_w

Table 20 Levoglucosan content of bio-oils produced at different temperatures from demineralized poplar and samples doped with different procedures

Bio-oil sample	Levoglucosan concentration, wt. %
Bio-oil at 465 °C	
P_w	5.64 (±0.19)
P_w+PbAc_dm	7.20 (±0.11)
P_w+PbAc_ie	9.77 (±0.15)
P_w+PbAc_wi	7.40 (±0.35)
Bio-oil at 600 °C	
P_w	5.59 (±0.23)
P_w+PbAc_dm	7.82 (±0.01)
P_w+PbAc_ie	10.64 (±0.15)
P_w+PbAc_wi	5.99 (±0.24)

All the doping methods result in a higher levoglucosan concentration in the bio-oil with respect to P_w for both the considered temperatures. P_w+PbAc_ie shows the greatest concentration values, which is about 5 % more than P_w, while P_w+PbAc_dm results in about 2 % increase. These results denote a clear influence of the doping method, and consequently of the Pb contamination type, on bio-oil levoglucosan content; in particular, authigenic contamination seems to be more relevant than detrital in the determination of levoglucosan concentration.

Table 21 and Table 22 show the composition of the bio-oils obtained from the two sets of feedstocks. Given the complexity of the bio-oil composition, only seven of the most abundant compounds are reported. The percentages reported represent the ratio between the area of the peak registered for the specific compound and the total area of the bio-oil chromatogram.

Table 21 Composition of bio-oils produced at different temperatures from plain poplar and samples doped with different Pb salts

Peak area [%]							
Compound	Acetic acid	Acetol	Furfural	Phenol	Guaiacol	5-Hydroxymethyl furfural	Syringol
RT [min]	9.3	10.9	20.3	32.1	34.8	45.3	48.1
PM [g/mol]	60.05	74.08	96.09	94.11	124.14	126.11	154.16
Bio-oil at 465 °C							
P	30.0 (±0.83)	8.3 (±0.35)	3.3 (±0.13)	3.9 (±0.05)	0.4 (±0.01)	0.7 (±0.16)	2.2 (±0.09)
P+PbN	17.6 (±0.48)	6.0 (±0.25)	2.0 (±0.08)	4.0 (±0.05)	1.9 (±0.06)	1.3 (±0.28)	2.7 (±0.11)
P+PbAc	30.2 (±0.83)	8.9 (±0.37)	2.7 (±0.11)	3.1 (±0.04)	2.0 (±0.06)	0.8 (±0.17)	2.3 (±0.09)
P+PbAc_II	25.8 (±0.71)	6.5 (±0.27)	2.9 (±0.12)	3.3 (±0.04)	1.5 (±0.04)	0.5 (±0.12)	2.4 (±0.09)
Bio-oil at 600 °C							
P	32.1 (±0.88)	9.0 (±0.37)	3.4 (±0.13)	4.6 (±0.06)	1.8 (±0.05)	0.6 (±0.14)	1.9 (±0.08)
P+PbN	27.2 (±0.75)	8.3 (±0.35)	3.3 (±0.13)	4.2 (±0.06)	1.7 (±0.05)	0.9 (±0.20)	1.9 (±0.08)
P+PbAc	33.7 (±0.93)	9.5 (±0.39)	2.6 (±0.10)	3.5 (±0.05)	1.9 (±0.06)	0.6 (±0.13)	2.1 (±0.08)
P+PbAc_II	23.9 (±0.66)	6.8 (±0.28)	2.6 (±0.10)	5.2 (±0.07)	1.8 (±0.05)	0.4 (±0.09)	2.9 (±0.12)
Bio-oil at 800 °C							
P	30.2 (±0.83)	9.0 (±0.38)	3.3 (±0.13)	4.8 (±0.06)	1.9 (±0.06)	0.7 (±0.15)	2.1 (±0.08)
P+PbN	29.4 (±0.81)	8.8 (±0.37)	3.5 (±0.14)	4.8 (±0.06)	1.8 (±0.05)	0.8 (±0.18)	1.8 (±0.07)
P+PbAc	34.6 (±0.95)	9.9 (±0.41)	3.1 (±0.12)	3.7 (±0.05)	2.2 (±0.07)	0.6 (±0.13)	2.1 (±0.08)

Table 22 Composition of bio-oils produced at different temperatures from demineralized poplar and samples doped with different procedures

Peak area [%]							
Compound	Acetic acid	Acetol	Furfural	Phenol	Guaiacol	5-Hydroxymethyl furfural	Syringol
RT [min]	9.3	10.9	20.3	32.1	34.8	45.3	48.1
PM [g/mol]	60.05	74.08	96.09	94.11	124.14	126.11	154.16
Bio-oil at 465 °C							
P_w	25.6 (±0.70)	5.8 (±0.24)	4.1 (±0.16)	2.6 (±0.03)	1.2 (±0.03)	1.9 (±0.43)	1.9 (±0.07)
P_w+PbAc_dm	21.4 (±0.59)	5.5 (±0.23)	3.8 (±0.15)	3.6 (±0.05)	1.6 (±0.05)	2.0 (±0.45)	2.3 (±0.09)
P_w+PbAc_ie	19.3 (±0.53)	3.8 (±0.16)	3.6 (±0.14)	3.2 (±0.04)	1.2 (±0.04)	2.2 (±0.49)	2.0 (±0.08)
P_w+PbAc_wi	21.2 (±0.58)	5.9 (±0.24)	3.4 (±0.13)	3.8 (±0.05)	1.5 (±0.04)	1.8 (±0.40)	2.4 (±0.09)
Bio-oil at 600 °C							
P_w	26.8 (±0.74)	6.0 (±0.25)	4.4 (±0.17)	3.2 (±0.04)	1.3 (±0.04)	1.8 (±0.40)	1.9 (±0.07)
P_w+PbAc_dm	21.0 (±0.58)	5.4 (±0.22)	3.7 (±0.15)	3.7 (±0.05)	1.5 (±0.04)	2.2 (±0.49)	2.3 (±0.09)
P_w+PbAc_ie	15.9 (±0.44)	3.9 (±0.16)	3.0 (±0.12)	3.0 (±0.04)	1.3 (±0.04)	2.3 (±0.51)	1.9 (±0.08)
P_w+PbAc_wi	20.7 (±0.57)	5.7 (±0.24)	3.3 (±0.13)	3.7 (±0.05)	1.5 (±0.04)	1.5 (±0.33)	2.3 (±0.09)
Bio-oil at 800 °C							
P_w	21.1 (±0.58)	4.8 (±0.20)	3.7 (±0.15)	2.4 (±0.03)	1.1 (±0.03)	1.7 (±0.37)	1.7 (±0.07)

Looking at the results of P (Table 21) and P_w (Table 22) it is possible to identify the effect of the inherent inorganics that are removed during the demineralization procedure, mostly AAEMs. The presence of AAEMs favours the production of acetic acid, acetol and phenol, showing also a minor effect on guaiacol concentration at high temperatures (600 and 800 °C). On the other hand, the concentration of furfural and hydroxymethylfurfural are higher in the bio-oils obtained from P_w, indicating a detrimental effect of AAEMs on their production. These results are confirmed by (Gargiulo et al., 2015), in which the addition of Na and K to the biomass (*Arundo donax*) caused a great reduction in furfural and hydroxymethylfurfural and an increase in acetic acid concentrations. (Patwardhan et al., 2010) attribute furfural and hydroxymethylfurfural reduction to the interaction of Na ions with the cellulose and hemicellulose structure, promoting ring opening reactions. These effects must be considered in the analysis of all the other results.

Regarding the first set of feedstocks, it is clear that the composition of the bio-oil produced from P+PbAc is heavily influenced by its higher inorganic content (Table 9), as confirmed also by the results of P+PbAc_II. However, with this in mind, it is possible to identify the effects of the two salts on some of the considered compounds by comparing the results of the doped biomass with P. Both lead nitrate and lead acetate cause a reduction in the acetic acid concentration at 465 and 600 °C. On other compounds, the two salts have smaller effects that can vary with the temperature; for example, the presence of lead acetate causes a reduction of furfural concentration, while the presence of PbN does not affect it. It must be noted that the results for P+PbN 465, although showing unexpected concentrations value of the considered compounds, are statistically significant.

As for the second set of feedstocks, the detrimental effect of lead acetate on the concentration of acetic acid and furfural is confirmed for all the contamination types by the comparison of doped feedstocks with P_w. The ion exchange procedure seems to affect the bio-oil composition differently than the other considered doping procedures; however, the observed differences are due to the lower concentration of AAEMs in P_w+PbAc_ie caused by the doping procedure itself (Table 9). This is clear both for the acetic acid and acetol: for the first one, the detrimental effects of the lead acetate and of the lower AAEMs content add up, causing a greater reduction in acetic acid concentration in P_w+PbAc_ie than in the other doped feedstocks; for the second one, the presence of lead acetate does not affect acetol concentration and its observed decrease in P_w+PbAc_ie is exclusively due to the lower AAEMs content.

In general, it results that Pb speciation clearly affect bio-oil composition regardless of the considered pyrolysis temperature; on the other hand, Pb contamination type seems to have a lighter effect on bio-oil composition. However, from the observed results it appears that the effects of AAEMs on bio-oil composition are prevalent on Pb effects, probably also because of their different concentrations in the biomass.

5.2 Pb displacement and speciation

5.2.1 Inorganic content

Table 23 and Table 24 report the concentration of Pb and other six relevant inorganic elements (Mg, P, K, Ca, Fe and Zn) for the two series of samples. The results could be useful to assess if possible interactions between Pb and other inorganics should be considered in the study of the Pb behavior during pyrolysis.

Table 23 Concentration of the main inorganic species in the char produced at different temperatures from plain poplar and samples doped with different Pb salts

Sample	Mg	P	K	Ca	Fe	Zn	Pb
mg/kg							
Char at 465 °C							
P	1499.5 (±156.3)	1878.8 (±173.6)	7244.8 (±1692.5)	6780.5 (±539.5)	30.6 (±43.3)	45.4 (±23.5)	36.5 (±0.9)
P+PbN	1402.8 (±35.0)	1565.5 (±334.5)	5987.5 (±396.7)	7440.5 (±1675.1)	93.0 (±131.5)	60.8 (±6.2)	2893.0 (±90.5)
P+PbAc	3669.0 (±575.6)	3684.3 (±28.6)	14252.5 (±661.1)	24089.0 (±9926.4)	2876.5 (±389.6)	234.4 (±47.7)	2874.0 (±79.2)
Char at 600 °C							
P	1461.5 (±68.6)	2063.0 (±463.9)	7101.3 (±1261.8)	6835.3 (±2851.5)	35.3 (±49.9)	55.0 (±2.0)	28.4 (±5.7)
P+PbN	2506.3 (±388.6)	3984.5 (±2134.8)	18207.5 (±6657.4)	7591.5 (±2001.8)	138.7 (±37.9)	84.1 (±17.5)	3349.5 (±341.5)
P+PbAc	3342.0 (±116.0)	3558.8 (±264.1)	14960.0 (±1569.8)	15685.0 (±2029.4)	2454.5 (±334.5)	210.1 (±17.7)	2446.0 (±346.5)
P+PbAc_II	2226.5 n.a	2105.5 n.a	10092.0 n.a	11486.0 n.a	309.0 n.a	89.2 n.a	2285.0 n.a
Char at 800 °C							
P	2525.7 (±429.2)	3358.3 (±392.9)	11886.7 (±1898.1)	7971.3 (±2396.1)	188.8 (±118.7)	6.7 (±6.1)	1.2 (±0.3)
P+PbN	2375.0 (±247.6)	2982.8 (±483.8)	12986.7 (±3034.5)	8224.8 (±1184.8)	219.2 (±14.4)	1.2 (±1.1)	367.9 (±105.0)
P+PbAc	3965.0 (±468.1)	4450.8 (±270.5)	15895.0 (±388.9)	17340.0 (±1032.4)	3373.5 (±447.6)	45.5 (±64.3)	53.6 (±1.3)
P+PbAc_II	1756.0 n.a	1722.5 n.a	8018.5 n.a	10675.2 n.a	256.4 n.a	3.8 n.a	33.5 n.a

The concentration of most of the considered inorganic elements is higher in all the char produced at 465 and 600 °C with respect to the corresponding biomass. This occurs because most of the inorganic compounds that are present in the biomass are thermally stable up to 600 °C and are retained in the char, as confirmed by the total ash content reported in Table 13. At the same time, the organic fraction of the biomass decomposes and devolatilizes, causing the reduction of the solid fraction weight and the subsequent increase of inorganics concentration.

At 800 °C AAEMs (Mg, K and Ca), P and Fe still result in high concentrations, comparable to that registered at 600 °C or even higher, thus indicating the thermal stability of such elements at high temperatures. On the other hand, Zn and Pb concentrations in all the chars produced at 800 °C result way lower than in the corresponding low temperature chars and biomass, revealing a strong devolatilization of these metals between 600 and 800 °C. More specifically, Pb concentration both in

the plain and lead acetate doped poplar decreases even at temperature higher than 465 °C. This result is qualitatively consistent with other literature evidence (He, et al., 2019a), even though quantitative differences can be observed due to the different type of biomasses. Overall, it is possible to conclude that at temperature lower than 600 °C the simultaneous presence of Pb and other inorganics should be considered as possible factor affecting Pb devolatilization. In order to clarify this aspect, it is possible to compare the results obtained for P+PbAc and P_w+PbAc chars (see Table 24) differing only for the inorganics content higher in the first set of chars. When inorganics content is reduced through the demineralization procedure Pb seems to be more thermally stable, since its concentration increased in the chars produced up to 600 °C. This result is in contrast with (He et al., 2021) who shows a consistent increase in Pb concentration in char produced from the co-pyrolysis on MgCO₃ and contaminated *Avicennia marina*, alongside a general stabilization of heavy metals. The same authors report a similar effect after the addition of FeCl and Fe(NO₃)₃ (He et al., 2020): the Pb concentration increased in char produced at 300, 500 and 700 °C for both the considered ferric salts when compared to the control samples. However, the observed stabilization effects of Mg and Fe could depend on the peculiar chemical speciation considered, which could be different from the inherent speciation in biomass.

Table 24 Concentration of the main inorganic species in the char produced at different temperatures from demineralized poplar and samples doped with different procedures

Sample	Mg	P	K	Ca	Fe	Zn	Pb
mg/kg							
Char at 465 °C							
P_w+PbAc_dm	1630.0	375.1	2279.0	11940.0	163.5	94.2	2170.0
P_w+PbAc_ie	1133.5	151.8	262.9	8299.2	130.6	67.6	4002.0
P_w+PbAc_wi	1473.0	273.5	1289.5	9435.8	150.3	81.1	3090.0
Char at 600 °C							
P_w+PbAc_dm	1141.5	390.2	2116.0	11250.0	180.7	49.8	1715.0
P_w+PbAc_ie	1759.0	220.9	587.9	13904.0	202.6	50.5	4506.0
P_w+PbAc_wi	1676.0	324.1	1864.5	10866.0	142.9	51.8	3643.0
Char at 800 °C							
P_w+PbAc_dm	227.1	178.7	1836.5	8324.8	141.2	16.2	1233.0
P_w+PbAc_ie	1869.0	237.6	707.2	14408.0	217.0	4.0	218.6
P_w+PbAc_wi	1573.0	314.8	1827.5	11236.0	151.9	6.8	74.5

The observations reported above can be overall extended to the second set of feedstocks, with some differences caused by the doping procedure. For example, the lower K content obtained for all the considered temperatures for P_w+PbAc_ie is a consequence of the washing phase of the ion exchange doping method, as revealed by the biomass analysis reported in Table 9. In general, in contrast to the remarkable increase of inorganics with the temperature observed in the first set of chars obtained from not demineralized poplar, in the second set of chars the inorganics concentration exhibits lower variability with the pyrolysis temperature, indicating that the inorganics still retained in the poplar after demineralization are present in a less thermally stable chemical form. This is even more evident in case of dry mixing doped chars where the inorganics concentration decreases at 800 °C. The behavior of Pb is dependent on the type of contamination (detrital or authigenic). In P_w+PbAc_wi and P_w+PbAc_wi chars Pb concentration increases up to 600 °C indicating a more thermal stability with respect to the Pb in the P_w+PbAc_dm chars which decreases in the whole temperature range. It is likely that P in authigenic contamination is more prone to interact with the biomass than Pb in detrital form and these interactions reduce its volatility.

Pb behavior will be discussed in detail in the following.

5.2.2 Pb recovery

The Pb displacement among pyrolysis products was mainly monitored considering the quantity of Pb retained in the produced biochar. The remaining amount of Pb has been transferred to other pyrolysis

products, i.e. bio-oil or gas phase, depending by its affinity with the two products. The amount of Pb retained in the biochar must be related to the initial Pb amount present in the biomass and is therefore expressed as Pb recovery following the Equation 1.

Looking at Figure 22, it is possible to observe that Pb recovery decreases as pyrolysis temperature increases, especially when passing from 600 to 800 °C.

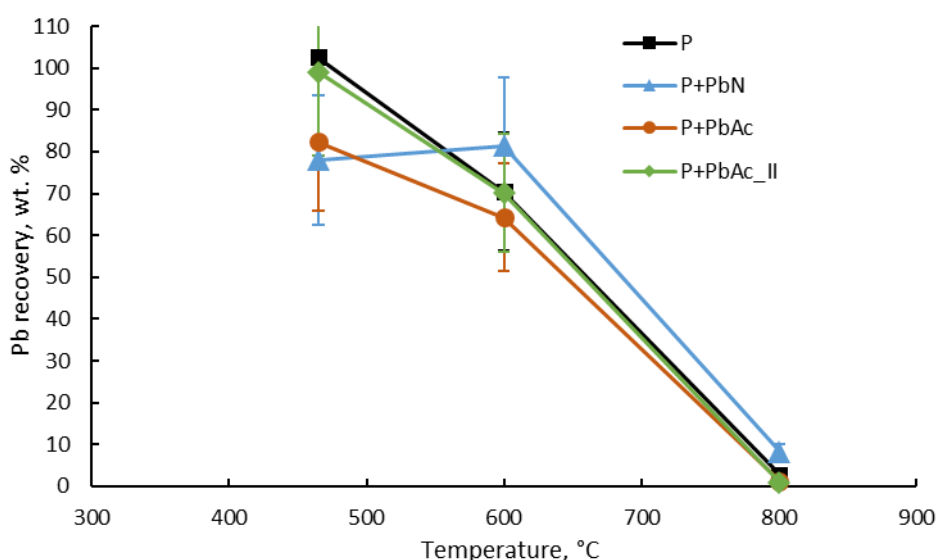


Figure 22 Pb recover in the char produced at different temperatures from plain poplar and samples doped with different Pb salts

The untreated biomass P has a Pb retention of 100 % at 465 °C, which decreases to 70 % at 600 °C; at 800 °C almost all the initial Pb is released from the biochar, with a recovery of only 3%. The biochar produced from the doped feedstocks P+PbN and P+PbAc exhibit a similar behavior. The differences observed at low temperature are within the experimental error. These results are in agreement with the findings of (He, et al., 2019a), that reported the same Pb devolatilization trend with temperature: the Pb recovery shows a slight decrease when passing from 400 to 600 °C (from 80 % to 74 %), while at 800 °C the Pb recovery drops at around 1 %.

On the other hand, the observed trends are in disagreement with the thermal decomposition behavior of the pure lead salts.

In fact, as can be observed in Figure 23, Pb nitrate starts decomposing at about 360 °C. Its decomposition proceeds slowly up to about 600 °C leaving a solid residue of about 60 wt. %.

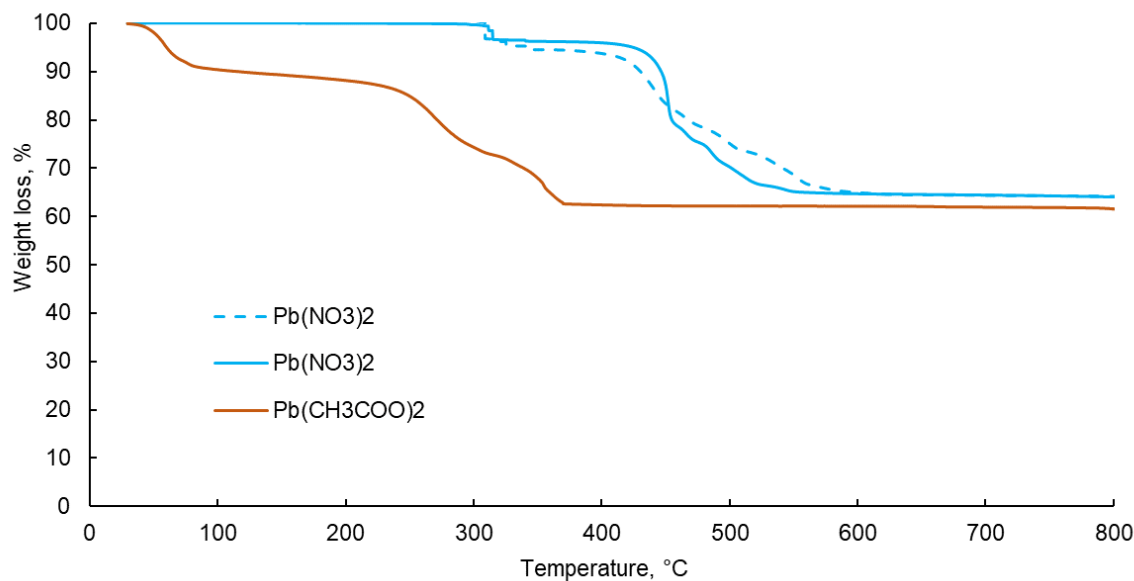


Figure 23 Weight loss of $\text{Pb}(\text{NO}_3)_2$ and $\text{Pb}(\text{CH}_3\text{COO})_2$

The discrepancies reported for the two repetitions of Pb nitrate analysis are probably caused by the interaction of the lead salt with the crucible of the thermogravimetric analyzer, which is made of alumina. Pb acetate starts to decompose at about 260 °C and its decomposition results complete at 370 °C leaving a solid residue of about 60 wt. % consisting in PbO (Martínez-Casado et al., 2016). Metals oxides are very thermally stable chemical species (Perry & Green, 2008), for example PbO has a volatilization temperature of 1470 °C. For both the considered salts, the totality of Pb is found in the solid residue after decomposition in a form that is thermally stable. This is in complete disagreement with the obtained recovery values, allowing to postulate that the volatilization of Pb and the consequent reduction of Pb recovery at 800 °C is to be attributed to interactions between Pb with other biomass components to form more volatile species. This interaction results being independent from the initial Pb chemical form.

Looking at the second set of pyrolysis tests (Figure 24), it looks like the type of contamination affects Pb recovery more than Pb initial speciation. The samples treated with ion exchange and wet impregnation (P_w+PbAc_ie and P_w+PbAc_wi) have a similar trend with temperature: Pb recovery is quite high and almost constant between 465 and 600 °C, equal to around 80 % for P_w+PbAc_ie and around 90% for P_w+PbAc_wi. At 800 °C the Pb recovery drops to almost 0 % for both the feedstocks, as already observed for the first set of pyrolysis tests. On the other hand, the samples doped with dry mixing (P_w+PbAc_dm) exhibit a totally different behavior: their Pb recovery is quite low at 465 °C, amounting to 55 %, and then decreases slightly as temperature increases, reaching 40

% at 600 °C and 25 % at 800 °C. The lower Pb recovery obtained at 465 °C could be due to the formation of more volatile Pb compounds during the pyrolysis of sample prepared through dry mixing, when compared to the other doping procedures. The further Pb volatilization at 600 and 800 °C could derive from the interaction of the lead acetate degradation product, PbO, and the biochar given that direct volatilization of PbO occurs at much higher temperatures. The results obtained for P_w+PbAc_dm is in disagreement with the behavior of Pb at high pyrolysis temperatures observed by (He, et al., 2019a), that reported a Pb recovery of 1 % at 800 °C for the pyrolysis of contaminated *Avicennia marina*. However, the considered biomass was naturally contaminated and was washed to remove any soil and dust, excluding the occurrence of detrital contamination. This confirms that the observed behavior of P_w+PbAc_dm is due to the detrital contamination type, simulated via dry mixing.

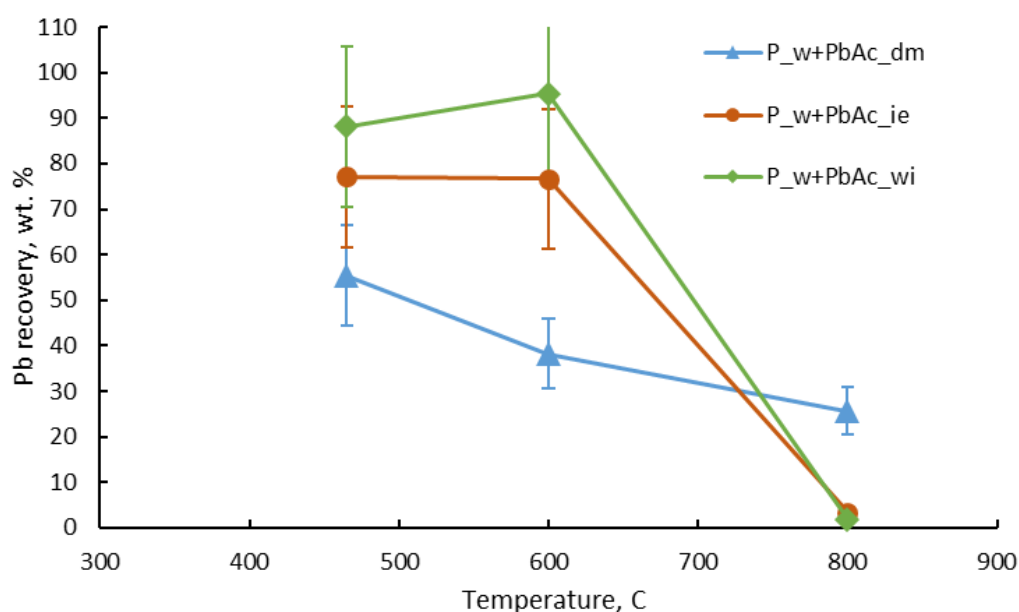


Figure 24 Pb recover in the char produced at different temperatures from demineralized poplar and samples doped with different procedures

5.2.3 BCR sequential extraction

It is worth noting that 100% of Pb in the doped feedstocks is in F1 fraction given the contamination procedure, whereas 62% of Pb in P and P_w is in F1 as obtained from results of BCR extraction (not reported).

Figure 25 represents the F1 fraction of the analyzed biochar of the first set of pyrolysis tests. It results that the biochar produced at 600 °C contains a bigger mobile fraction than the ones produced at 465 °C. The biochar produced at 800 °C shows the lowest F1 content, indicating that an increase in pyrolysis temperature results in a better immobilization of the metals retained in the biochar (Huang et al., 2018). The increase of Pb in the F1 fraction when passing from 465 to 600 °C remains unclear, as there are no available literature data that shows a similar behavior.

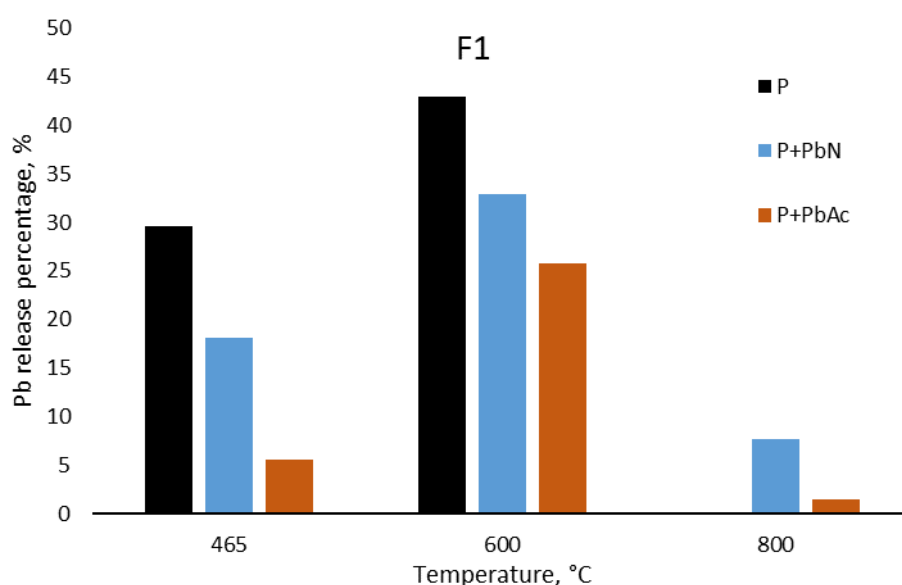


Figure 25 Pb release in F1 fraction for the char produced at different temperatures from plain poplar and samples doped with different Pb salts

Regardless of the temperature, a robust trend with the feedstock type is observed: F1 fraction is always the highest for P and the lowest for P+PbAc, suggesting an effect of the Pb chemical speciation on the stability of the Pb retained in the biochar. In particular, the naturally occurring Pb, that is found in P, results to be the most mobile, while the Pb present in the lead acetate doped feedstock is always the least mobile. The sample P 800 does not show any retained Pb in the char, and is therefore absent from Figure 25.

Figure 26 reports the complete characterization of Pb for some selected biochar that are characterized by higher Pb content. The results of the fractions F2, F3 and F4 related to biochars with low Pb concentrations, as P biochar and high temperature P+PbAc biochar, resulted unreliable due to the very low amount of initial Pb in the char.

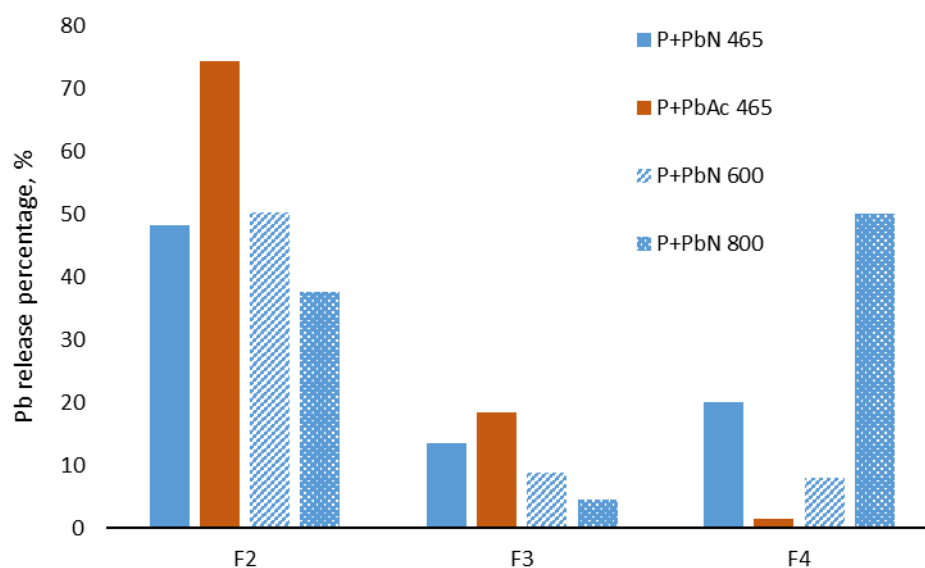


Figure 26 Pb release in F2, F3 and F4 fractions for a selected group of char produced from the first set of feedstocks

The F2 reducible fraction results to be the most abundant for all the considered biochar except for P+PbN 800: in this case the majority of lead is in the F4 fraction thus confirming that high pyrolysis temperatures contribute to the formation of stable metal compounds. As anticipated, the available literature data regarding the speciation of heavy metals, and in particular Pb, in contaminated biomass and char are scarce and they don't agree with each other. For example (Gong et al., 2018) found that the Pb contained in ramie stems was already for the most part in F3 fraction in the biomass, and that the pyrolysis process did not affect this fraction while causing the complete transformation of the most mobile fractions (F1 and F2) in F4 fraction already at low temperature (400 °C). On the contrary, (Huang et al., 2018) observed that at low temperature (350 °C) there was around the same amount of Pb in F2 and F3 fractions of chars obtained from *Brassica juncea*; as pyrolysis temperature increased, the Pb present in F1-F3 fractions was transformed almost entirely in F4 fraction. In both cases, the Pb distribution is different from what observed in the present work for all the analyzed samples. However, it must be noted that *Brassica juncea* and ramie are hyperaccumulator biomasses and consequently they differ greatly from the considered poplar biomass, either doped or untreated, in terms of Pb content and initial chemical speciation. The prevalence of F1 exchangeable fraction and F2 reducible fraction in the produced doped char could be due to the employed wet impregnation doping procedure; unfortunately, to the best of my knowledge, BCR sequential extraction has never been applied to a heavy metal enriched biomass and consequently this affirmation is difficult to support. The only trend that is in common with literature data is the increase of Pb in F4 fraction at high temperature (800 °C), that could derive from the advanced graphitization state of the high temperature char. In fact, (J. Zhang et al., 2020) reported as possible causes of the increase in F4

fraction the formation of metal-C complex and the occurrence of π -bonds between metal cations and aromatic carbon.

The abundance of Pb in F2 fraction could be tied to the high O content observed in the doped char, as reported in Table 13. In fact, (Chen et al., 2008) identified the F3 oxidizable fraction as “potentially instable” and observed that an environment with high oxidizing potential, as can be an oxygen rich char, can promote the transformation of F3 fraction in F1 and F2 fractions. Moreover, PbO results to be the main decomposition products of the considered lead salts, so it is possible that the Pb retained in the char is found in this chemical form that falls under the F2 reducible fraction.

Figure 27 represents the F1 fraction of the analyzed char. The sample P_w 800 does not show any retained Pb in the char and is therefore absent from Figure 27.

The chars produced at 465 °C have the lowest Pb content in the soluble and exchangeable fraction, while Pb content in F1 reaches the maximum at 600 °C (except for P_w+PbAc_wi) as already observed for the first set of feedstocks. The fact that the char produced at 600 °C contains a bigger soluble and exchangeable fraction than the ones produced at 465 °C is against literature findings that indicate that an increase in pyrolysis temperature results in a better immobilization of the metals retained in the char (Huang et al., 2018). However, (Huang et al., 2018) consider an herbaceous biomass naturally contaminated from phytoremediation procedure. It can be postulated that biomasses with different composition can have different interactions with Pb.

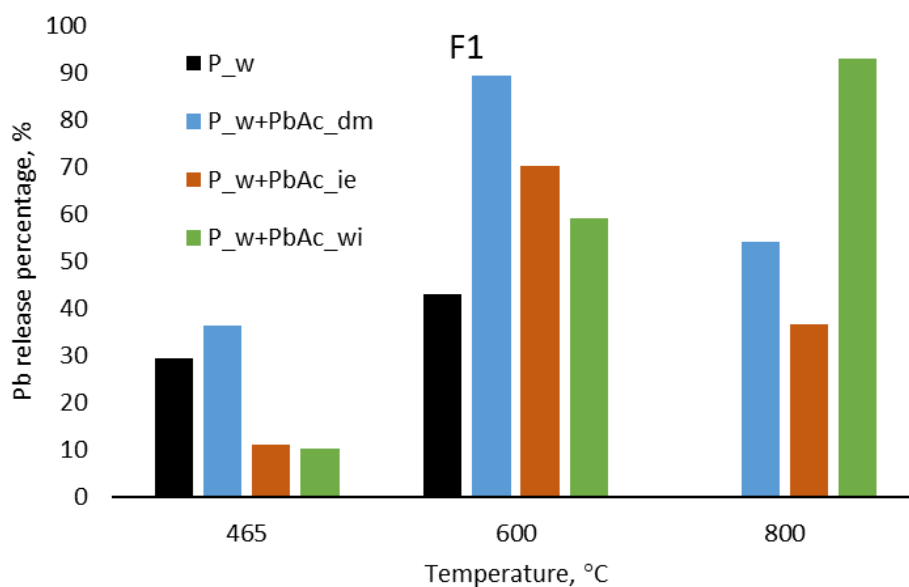


Figure 27 Pb release in F1 fraction for the char produced at different temperatures from demineralized poplar and samples doped with different procedures

Regardless of the temperature, an influence of the contamination type is observed: F1 fraction is always higher for P_w+PbAc_dm than for P_w+PbAc_ie, suggesting that the Pb originated from detrital contamination is retained in the char in a more mobile form than Pb from authigenic contamination.

Figure 28 reports the complete characterization of Pb for some selected biochar; the excluded results resulted unreliable.

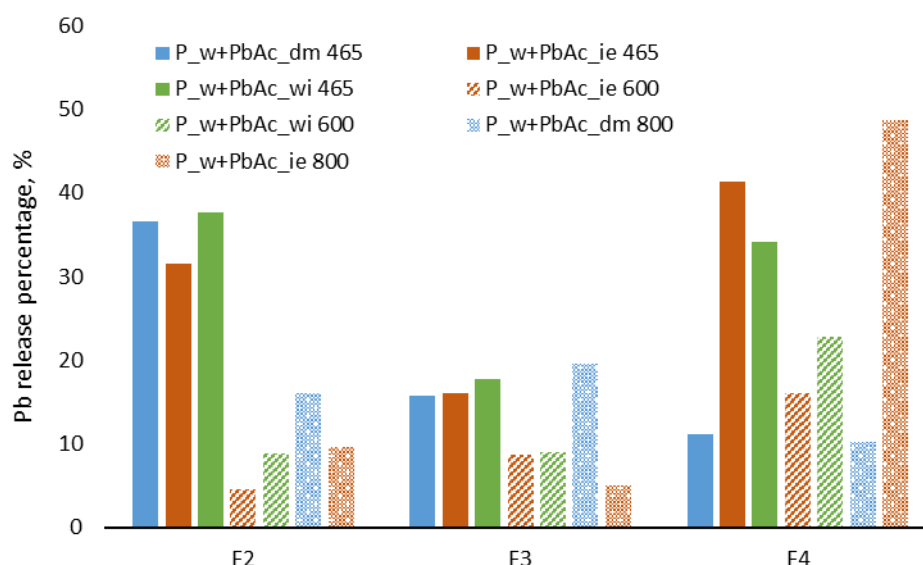


Figure 28 Pb release in F2, F3 and F4 fractions for a selected group of char produced from the second set of feedstocks

Looking at the char produced at 465 °C, the different doping procedure cause a similar distribution of Pb in F2 and F3 fractions; however, P_w+PbAc_dm shows a considerably lower concentration of Pb in the F4 residual fraction, indicating the presence of more mobile Pb species. P_w+PbAc_dm retains the same low concentration of Pb in F4 fraction at 800°C; on the other hand, P_w+PbAc_ie 800 shows an increase of Pb presence in the F4 fraction. This confirms that detrital contamination results in more mobile Pb species than authigenic contamination.

Both wet impregnation and ion exchange doped samples results in lower Pb concentration in the F4 fraction at 600 °C than at 465 °C, corresponding to the increase of Pb in the F1 fraction. A similar result was observed also for the first set of feedstocks; however, the reason behind this behavior remains unclear.

5.2.4 XRD analysis

XRD analysis for Pb detection in vegetal derived materials can be tricky for a number of reasons. For example, the organic fraction of the sample causes background noise during XRD scan, and this can interfere with the detection of the usually low concentration of Pb. Moreover, XRD can analyze only crystalline materials; consequently, if Pb occurs in amorphous form it won't be detected. Nevertheless, the analysis of the produced feedstocks and chars lead to some interesting results; all the XRD patterns are reported in Figures from 29 to 35.

It is possible to follow the evolution of Ca mineralogical phase in the whole considered temperature range. In the feedstocks (Figure 29), Ca is always present as Whewellite ($\text{Ca}(\text{C}_2\text{O}_4) \cdot (\text{H}_2\text{O})$); other

inorganic elements cannot be detected either because of their amorphous form or their low concentration compared to the high organic content of the biomass. During the pyrolysis process, the Whewellite decomposes forming calcium carbonate (CaCO_3), which is found as Calcite in all the samples at 465 °C (Figure 30 and 33). As pyrolysis temperature increases, Calcite starts to mutate into Vaterite, which is another polymorph of CaCO_3 . At 600 °C (Figure 31 and 34) the Calcite peaks are more pronounced than Vaterite peaks, meaning that Calcite presence is more abundant than Vaterite. When passing to 800 °C (Figure 32 and 35) the Calcite peaks amplitude decreases, indicating that higher temperatures promote the rearrangement of CaCO_3 into Vaterite.

The evolution of Pb is more difficult to trace since it is present in low concentrations. As for the feedstocks, no crystalline Pb is observed since the considered doping methods involve the dissolution of Pb salts in water, and, probably, Pb is retained in the biomass in other forms than crystalline $\text{Pb}(\text{CH}_3\text{COO})_2$ or $(\text{Pb}(\text{NO}_3)_2)$. This is not true for the dry mixing procedure; however, P_w+PbAc_dm feedstock was not analyzed as it would have been simply resulted in the presence of unmodified $\text{Pb}(\text{CH}_3\text{COO})_2$.

Among the char produced at 465 °C, only P_w+PbAc_dm shows the presence of PbO, as lead oxide is the main solid decomposition products of lead acetate, which is totally decomposed at 370 °C (Martínez-Casado et al., 2016). The fact that in the other char at the same temperature there is no trace of PbO can confirm that during wet impregnation and ion exchange the Pb speciation can change with respect to the employed salt.

As pyrolysis temperature increase to 600 °C, PbO is detected in all the produced char, giving an insight on Pb chemical transformations during pyrolysis. However, when temperature further increases at 800 °C, the only sample in which PbO is still detected is P+PbN, suggesting that Pb initial speciation still plays a role in Pb chemistry. The absence of PbO in the high temperature char that have a high Pb concentration, such as P_w+PbAc_dm, could be due to possible reaction between the lead oxide and the biomass components, that transform Pb in a more stable amorph phase.

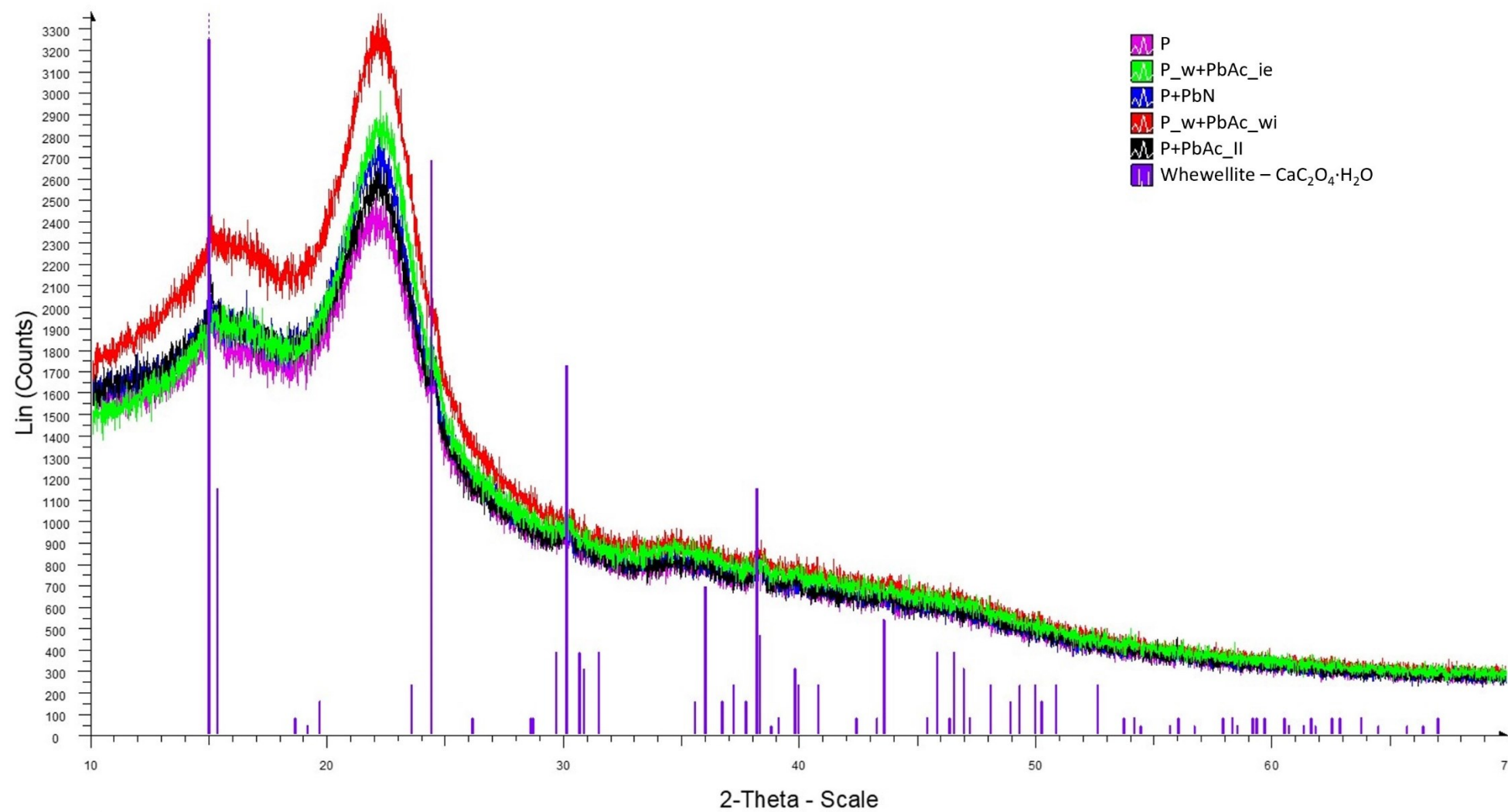


Figure 29 XRD spectra of the feedstocks

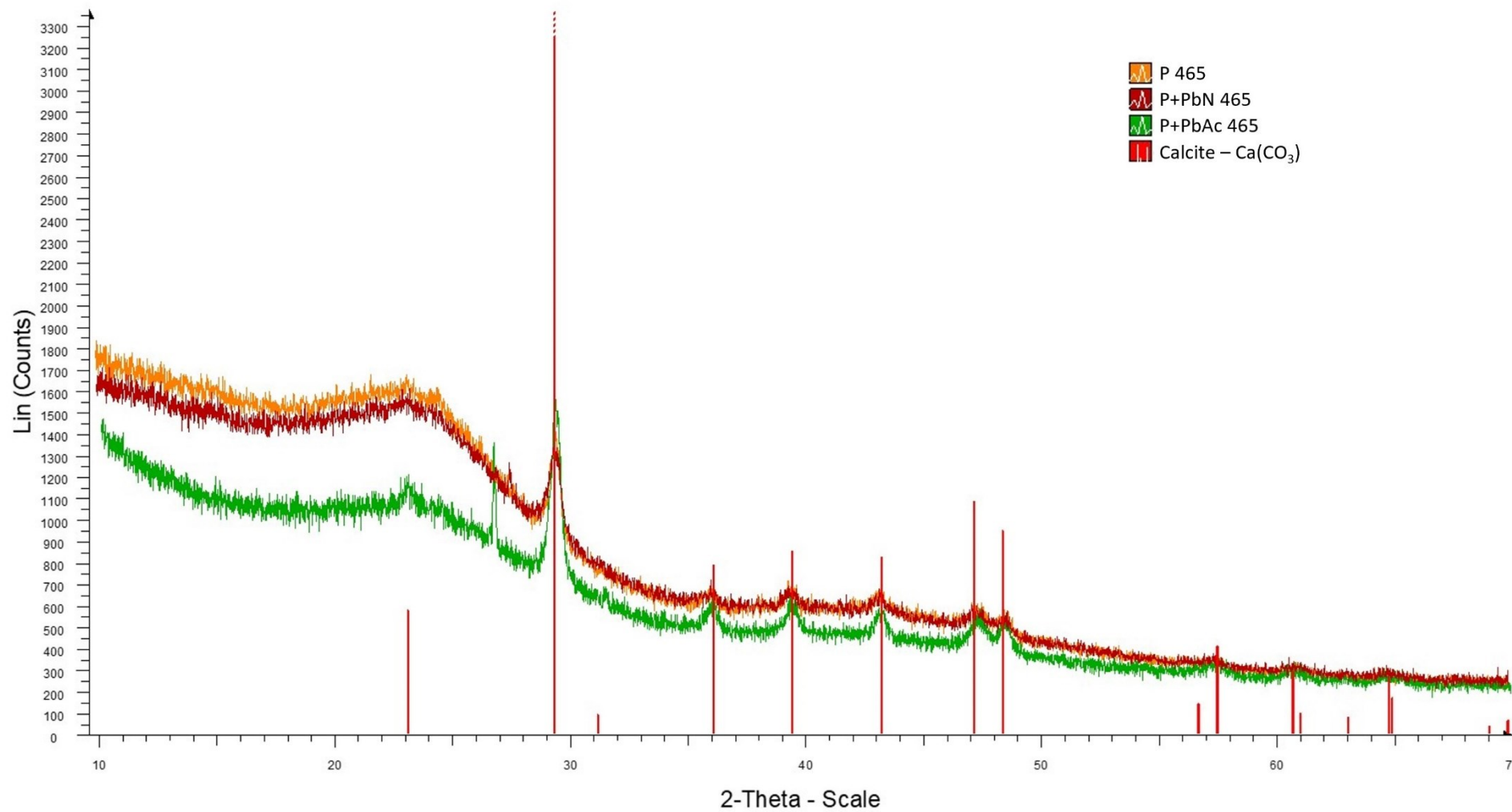


Figure 30 XRD spectra of the char produced at 465 °C from samples doped with different Pb salts

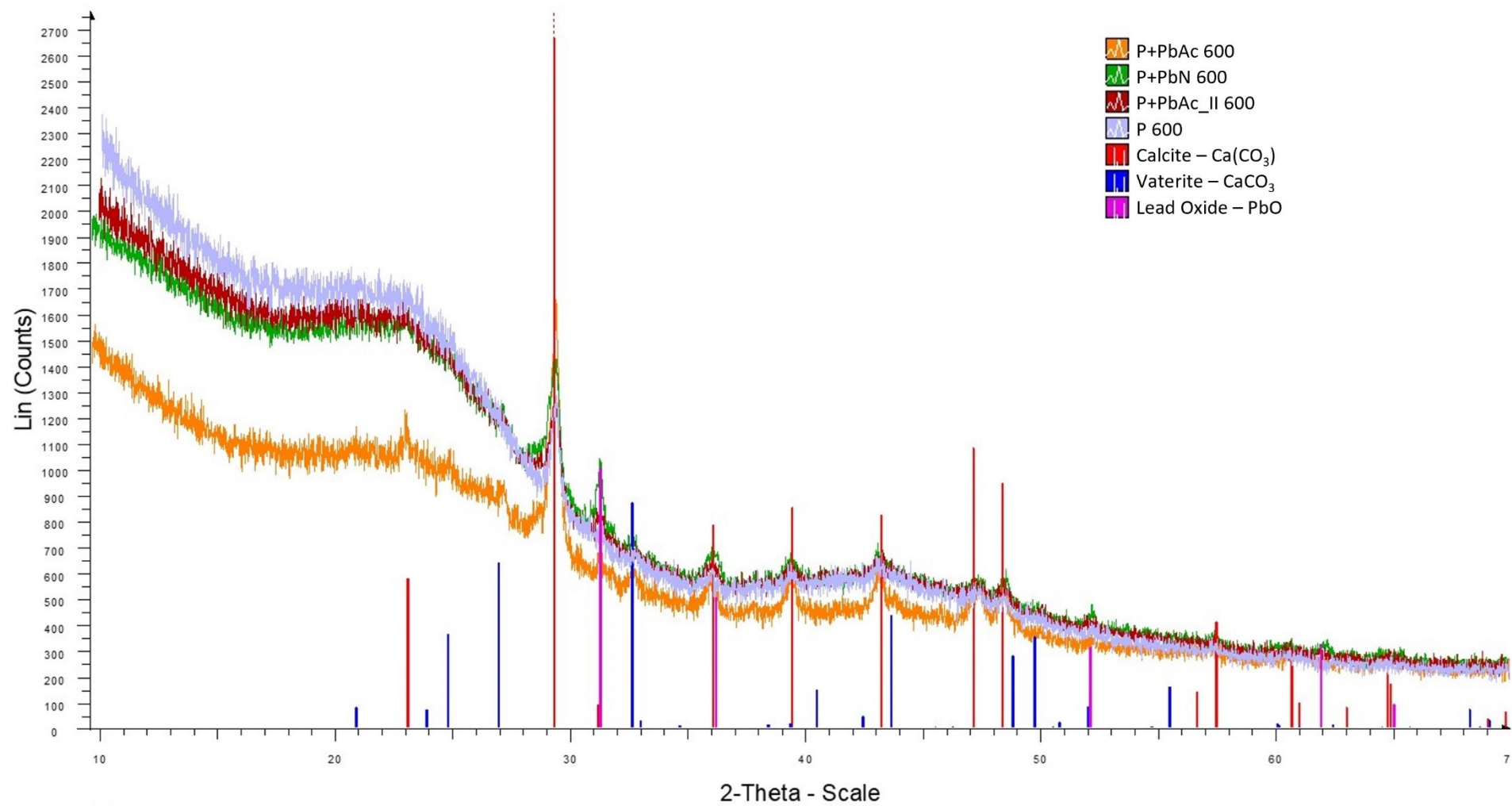


Figure 31 XRD spectra of the char produced at 600 °C from samples doped with different Pb salts

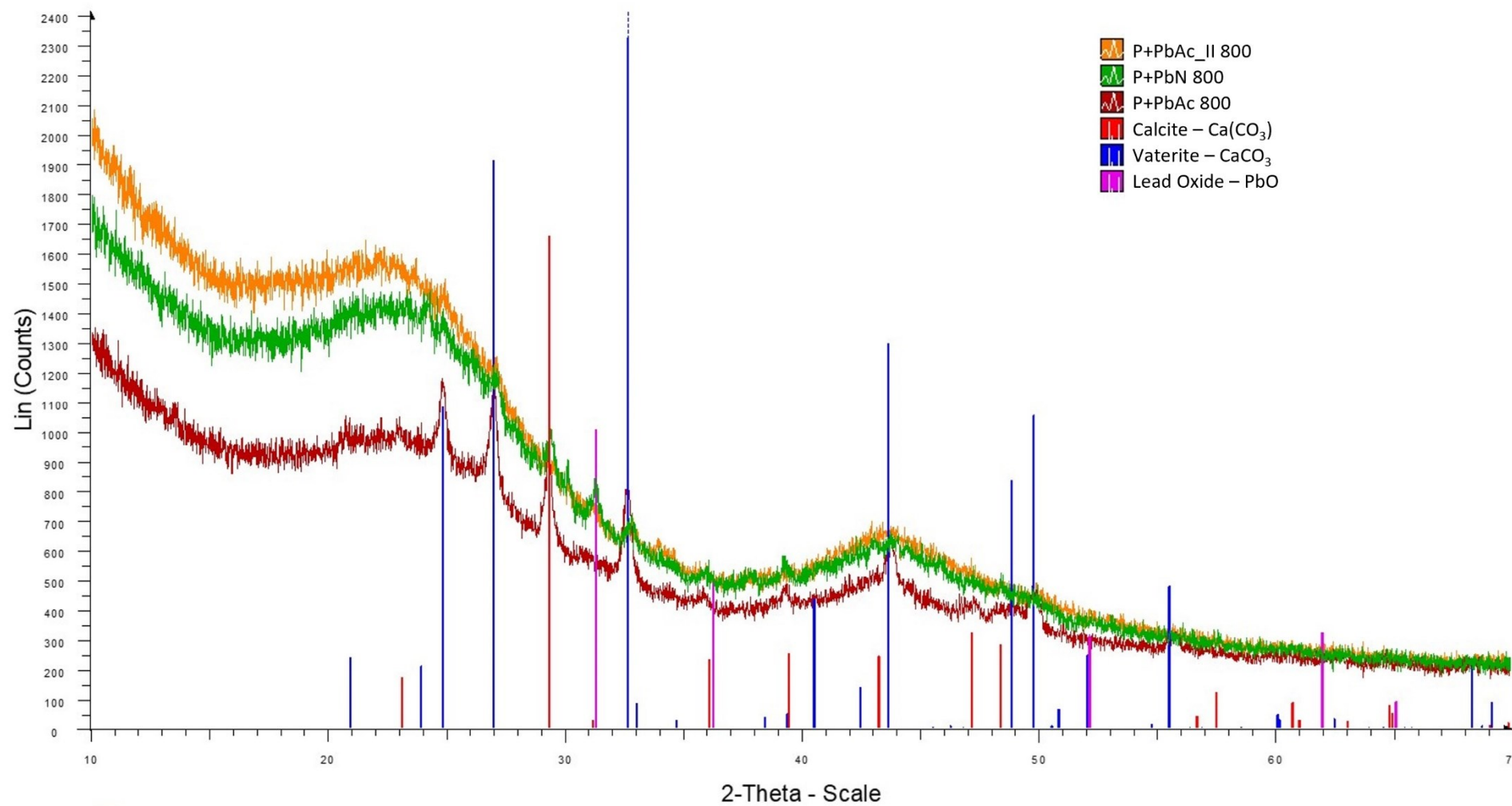


Figure 32 XRD spectra of the char produced at 800 °C from samples doped with different Pb salts

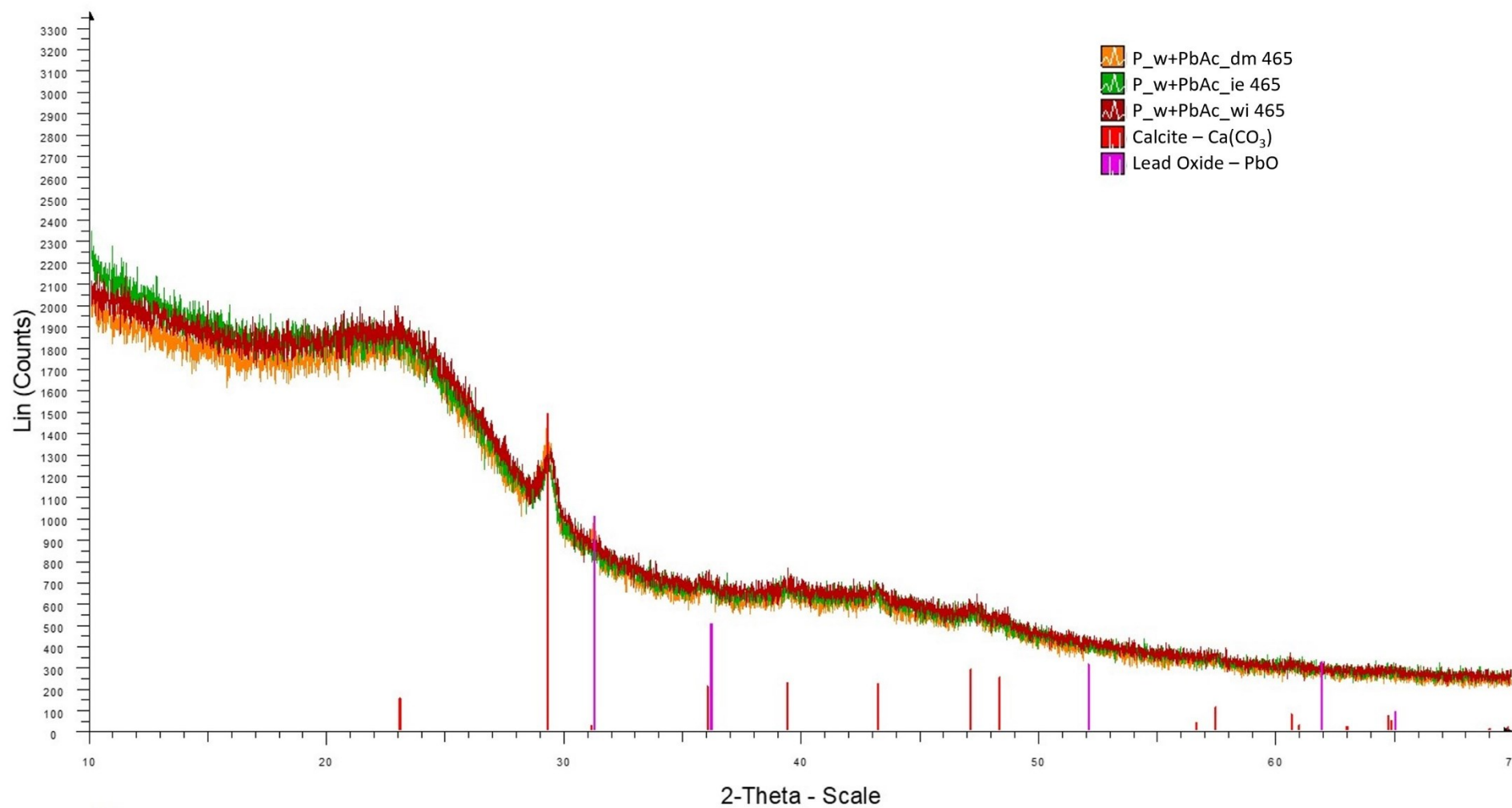


Figure 33 XRD spectra of the char produced at 465 °C from samples doped with different procedures

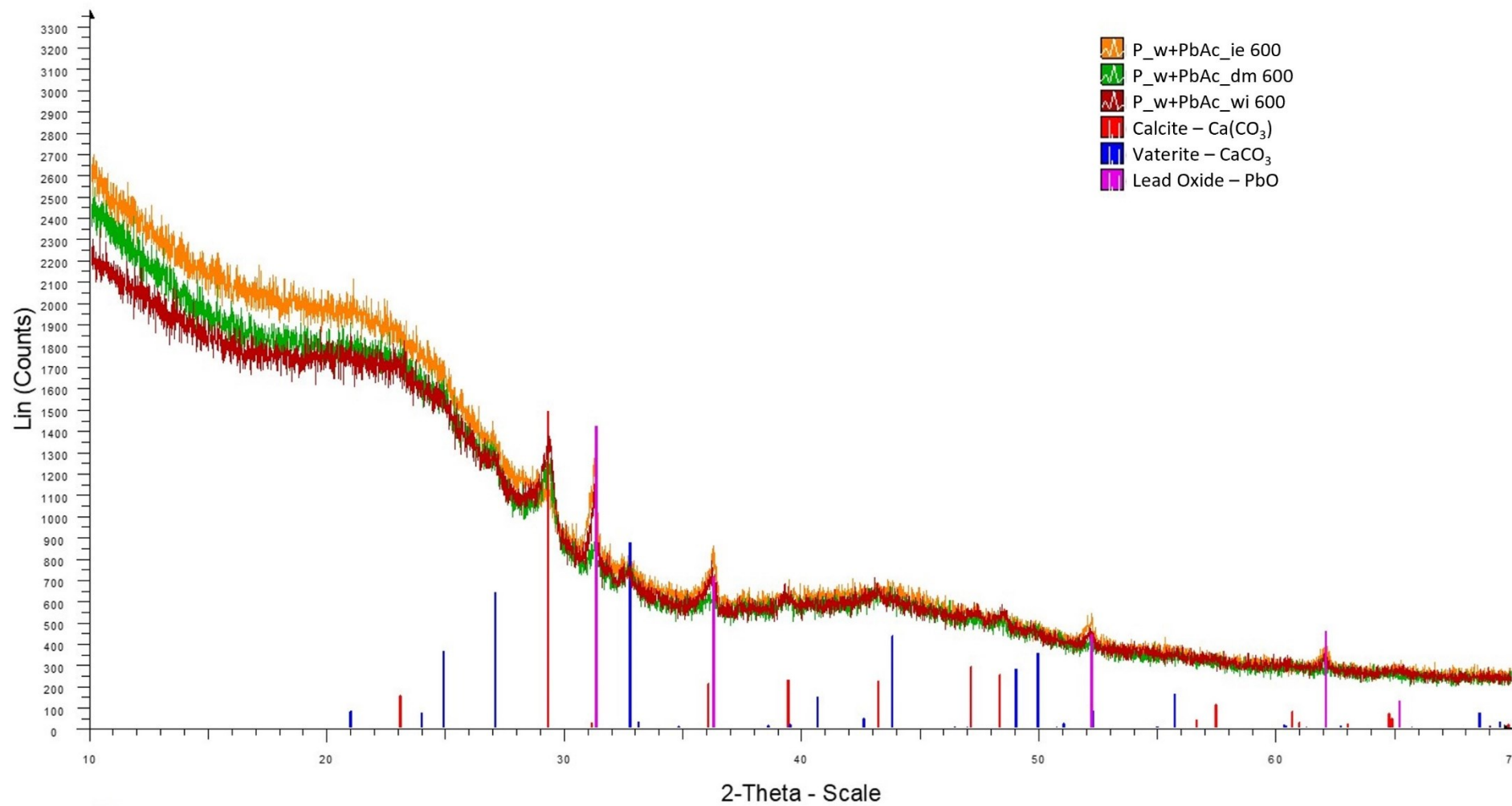


Figure 34 XRD spectra of the char produced at 600 °C from samples doped with different procedures

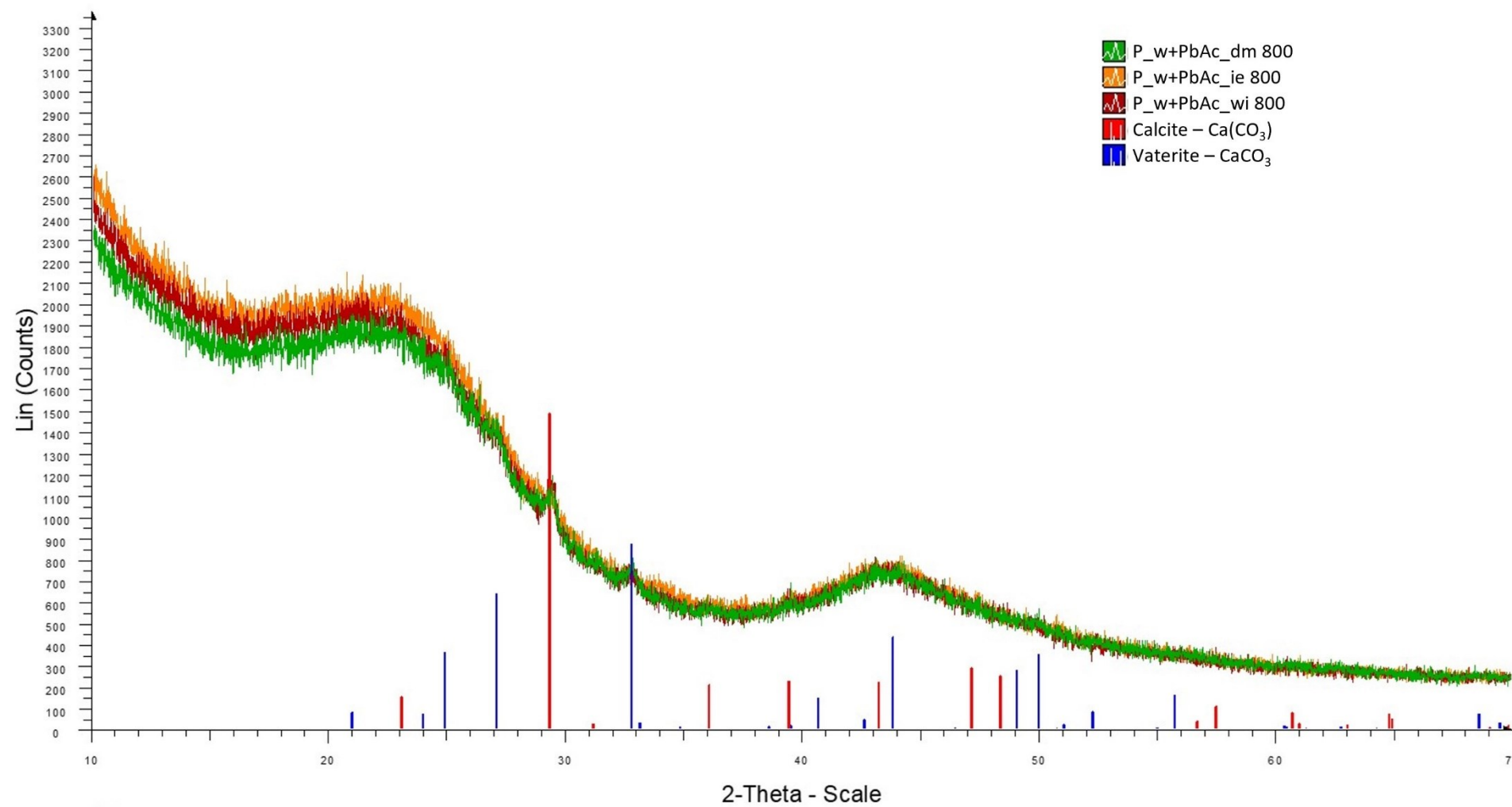


Figure 35 XRD spectra of the char produced at 800 °C from samples doped with different procedures

6 Continuous pyrolysis system realization

The results of the slow pyrolysis experimental campaign provide fundamental indications for the conceptualization, realization and optimization of a very robust pyrolysis continuous system aimed at both char and bio-oil production considering not only the yields of the desired product but also heavy metals content and stability.

In the following, the steps that led to the realization and testing of the intermediate pyrolysis system are discussed.

6.1 Choice of pyrolysis reactor configuration

When designing a pyrolysis system, it is important to take into account reactor flexibility in terms of pyrolysis temperature, vapor and solid residence time, feedstock size and carrier gas flow rate. These aspects are even more important if the minimization of transfer of heavy metals from the feedstock to the bio-oil should be achieved, other than the production of high bio-oil yields. Among the numerous pyrolysis reactor configurations, the screw reactor (or auger reactor), as shown in Table 25, has a great flexibility with regard to the operating conditions in which it can be used to carry out the pyrolysis of biomass.

Moreover, the auger reactor results in easier operation with respect to other configurations since they would have required a complex gas/solid separation train to limit the transfer of solid fines inside the condensation unit and finally into the bio-oil.

The auger reactor configuration guarantees an appropriate mixing efficiency of the biomass inside the reaction chamber and, therefore, homogeneity of heating.

More advantages of using an auger reactor are summarized as follows:

- Proven technology: the first report on the use of the screw reactor was described by Laucks in 1927. He found quite a few problems, arising from the temperature difference between the hot walls and the cold crankshaft, which caused tar deposit. Laucks suggested to transfer heat by providing a hollow crankshaft. From 1950 onward, numerous studies have been performed on biomass pyrolysis in screw reactors.
- Wide range of particle sizes that can be processed; anyway, particles that are too small may be subject to entrainment in the carrier gas stream, while particles that are too large may obstruct the reactor aperture and, depending on the auger pitch, not provide the mixing necessary for efficient heat transfer.

- Good control of residence time and temperature: the biomass feed rate, reactor size, and auger speed combine to determine the residence time in the reactor, which must ensure complete thermal degradation of the biomass but can be easily varied to achieve different pyrolysis product properties.
- Good mixing characteristics.

In contrast, the main disadvantages are:

- High cost of maintenance due to the presence of moving parts in the hot environment.
- Scalability is limited because the ratio of screw surface area to reactor volume decreases for larger reactors. Some sources mention that scaling up is reasonable up to 40 cm of the inner diameter of the reactor (Batidzirai et al., 2013).
- Tar condensation on the shaft for auger reactors heated only indirectly through the external wall.

6.2 Pyrolysis vapors cleaning and condensation

Even though it is possible to tune properly the operating variables of the pyrolysis reactor (feedstock size and moisture, temperature, carrier gas flow rate) for limiting both the water content and the transfer of heavy metals into the vapor phase, it is pivotal to design properly the cleaning of the vapor phase before its condensation and optimize the condensation train.

It is inevitable that a fine fraction of char will be elutriated and dragged by the vapor phase exiting the screw reactor. In order to remove this fraction different gas/solid separation systems can be considered, namely cyclones, hot filters and electrostatic precipitators. In Figure 36 the separation efficiency of these systems as function of the solid particle size is shown.

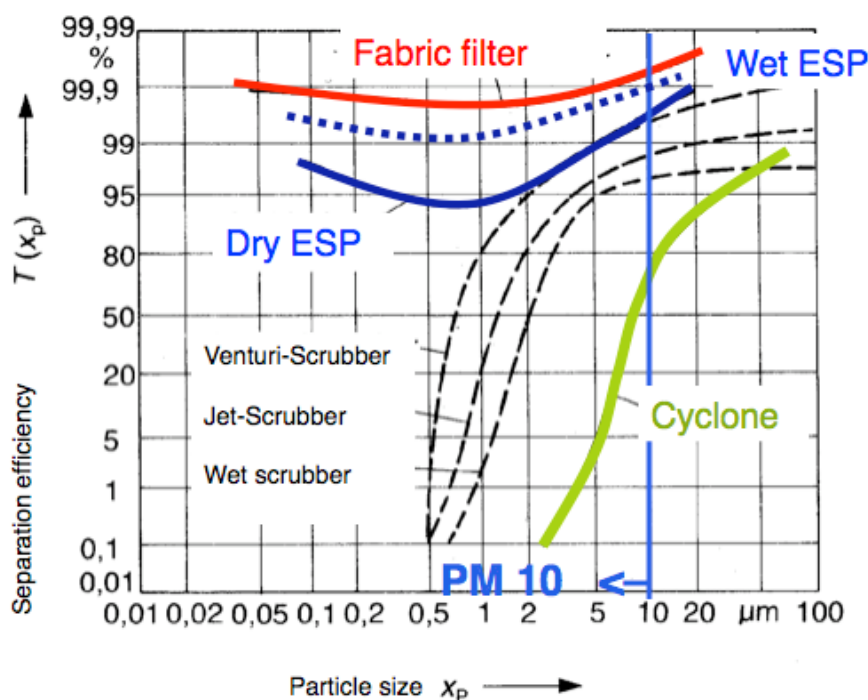


Figure 36 Separation efficiency of gas/solid separation systems as function of the solid particle size.

Based on the separation efficiency reported in Figure 36, usually a cyclone is included at the exit of the pyrolysis reactor before the condensation train. This gas/solid separation system will prevent the transfer of the bigger particles. Given the low efficiency of the cyclone for particles size $< 10 \mu\text{m}$, fabric filters and dry electrostatic precipitator (ESP) can be added and possible further off-line filtering treatment are under investigation as post-treatment step (Koutsonikolas et al., 2022).

Apart from solid particles treatment, the condensation section is a fundamental part of the pyrolysis system since the amount of collected bio-oil depends greatly on the condensation efficiency. An expedient that can give great advantages in bio-oil subsequent use is the design of a fractional condensation system, obtaining a separation between water, high molecular weight compounds and low molecular weight compounds in the same system that produce the bio-oil itself (Tumbalam Gooty et al., 2014). Two or more condensers working at different temperatures are needed to obtain a fractional condensation.

6.3 Conceptual desing of the pyrolysis plant

In this section, a brief description of the operating parameters that have been taken into account for the design of the screw reactor is provided. Literature experimental set-up have been used as starting reference and all the calculations have been made using (Brown & Heindel, 2009) as reference. If necessary, specific adaptations have been made to take into account the use of heavy metals contaminated biomass as feedstock.

Regarding the capacity of the plant, it was considered appropriate to keep the size of the system within the limit to process 2 kg/h of biomass. Large quantities of contaminated biomass are not always available and a smaller reactor allows to carry out, with a reduced amount of material, various tests to fine-tune the reactor optimization procedure. A literature review was carried out to identify the usual dimensions of auger reactors for a nominal feed rate lower than 10 kg/h; the main geometrical characteristics, operational conditions and performance in terms of products yields of the reactors are summarized in Table 25. Literature data report a reactor length not higher than about 170 cm and reactor internal diameter in the range 5-7.5 cm for reactors with a biomass capacity ranging between 1-2 kg/h. Based on the dimensions of commercially available auger and screw shaft an internal diameter of 6 cm was chosen and screw and reactor diameters have been used to calculate the effective (void) volume of the reactor. Then, considering that the optimal volume filling to allow proper mixing and transportation of the biomass is about 50% of the effective volume at the maximum capacity (2 kg/h), the rotational speed range of the screw has been defined so that allowing to vary the residence time of the biomass between 2 and 20 min. The bulk density of the biomass particle (in form of pellet) was assumed equal to 600 kg/m³. Finally, the maximum carrier gas flow rate was chosen considering two requirements: (i) minimize the extent of the secondary decomposition reactions of the primary volatiles evolving during biomass pyrolysis; (ii) minimize the elutriation of solid particles in the gas phase flow. To meet both the requirements, St number has been calculated to evaluate the elutriation of biomass/biochar fines produced during the reactor operation as function of the particle diameter at different gas flow rate and for each flow rate the gas residence time has been calculated considering the total flow (N₂+produced vapors) at different temperatures in the range 450-600 °C at the maximum reactor capacity. The operating temperature range was set considering the typical temperatures of maximization of bio-oil yields under similar conditions. Moreover, the results of the experimental campaign with Pb contaminated poplar were taken into account, indicating 600 °C as the maximum temperature for limiting the devolatilization of Pb under different forms.

For the calculation of the produced vapors in the desired temperature range many literature data have been collected considering both slow, intermediate and fast pyrolysis conditions (Giudicianni et al., 2021).

At the exiting end of the reactor, the produced biochar a dedicated container is placed to collect by gravity, while the gaseous phase, composed of permanent gases and pyrolysis vapors, is conveyed to the condensation section of the system.

In Table 28 and Table 29 the main reactor geometrical characteristics and the operational variability ranges are summarized, whereas in Figure 37 a sketch of the reactor is shown.

Table 25 Existing auger reactors characteristics

	(Papari et al., 2019)	(Hassan et al., 2009)	(Qi & Wright, 2020)	(Ren et al., 2016)	(Puy et al., 2011)	(Pittman et al., 2012)	(Ingram et al., 2008)				(Desai, 2016)		
Feed, kg/h	2	3	1	8.5	from 3.9 to 6.9	1.5, 2	1				0.1		
Feedstock type	Softwood sawdust	Loblolly pine (whole tree)	Cotton wood (whole tree)	Red oak	Panicum virgatum	scots pine, black pine	corn stalks untreated and acid treated pine wood pine bark oak wood				oak bark	Arundo donax	
Feedstock size, mm	2	1-3	1, 2	<2	20	0.5-5	2-4				< 0.425	0.425< size <0.850	0.850< size <1.0
Reactor diameter, cm	5.1	n.a.	6.35x3.81	10x10	n.a.	7.62	7.6				2.54		
Reactor length, cm	164	n.a.	55.9	250	n.a.	101.6	102				45.72		
Biomass residence time	n.a.	n.a.	n.a.	1.2	from 1.5 to 5 min	0.83	0.83				5.03 s		
Gas residence time, s	n.a.	n.a.	n.a.	n.a.	n.a.	2	2				n.a.		
Carrier gas rate, l/min	no gas	n.a.	n.a.	20	5	no gas	no gas				0.235		
Solid heat carrier	steel shots	no solid	sand	no solid	no solid	no	no				sand		
Operating temperature, °C	465	450	515	500	from 500 to 800	400	450				500		
Bio-oil yield, wt. %	52	53.7	60	52	see Table 26	see Table 27	48.7–55.2	42.8–44.2	49.6–56.3	43.8–49.8	51.6	51.9	50.1
Water content, wt. %	12	16.8	n.a.	42.3	see Table 26	see Table 27	16	19.8	22.5	22	n.a.	n.a.	n.a.
HHV, MJ/kg	13-14	24.7	n.a.	n.a.	see Table 26	see Table 27	21.9	18.3	18.7	19	n.a.	n.a.	n.a.

Table 26 Integration of Table 25 (Puy et al., 2011)

Reaction Temperature, °C	Solid residence time, min	Mass flow rate, kg/h	Liquid yield, wt%	Solid yield, wt%	Gas yield, wt%
800	5	3.9	36.6	19	44.4
700	5	3.9	37.2	21.3	41.6
600	5	3.9	45.1	23.7	31.2
550	5	3.9	51.4	25.7	22.7
500	5	3.9	56.5	26.4	19
500	3	3.9	57	26	18
500	2	3.9	53.2	28.7	16.7
500	1.5	3.9	45	41.5	15
500	5	4.8	56.4	27.8	22.5
500	5	6.9	58.7	25.8	24.7

Table 27 Integration of Table 25 (Pittman et al., 2012)

	corn stalks untreated 400 °C	corn stalks untreated 450 °C	corn stalks acid treated 400 °C	corn stalks acid treated 450 °C
Bio-oil yield, wt. %	35	35	51	46
Water content, wt. %	54.7	27.3	41.6	21
HHV, MJ/kg	7	21.4	8.85	17
HHV, MJ/kg	10.2	22.3	12	18.3

The possibility of the introduction of a solid heat carrier to improve biomass heating was evaluated. The system used by Papari et al. (2017) relies on the use of hot steel shots to heat the biomass, but the use of a solid heat carrier can cause undesired effects when working with heavy metals contaminated biomass. The introduction Dastyar et al., 2019 of solid materials in the reactor results in strong mechanical stress on biomass and biochar, causing a grinding effect that produces fine particles. Since one of the expected transfer mechanisms of heavy metals contaminants to bio-oil is the formation of aerosol and fines elutriation, the formation of small particles should be avoided. Moreover, the presence of solid heat carriers could cause catalytic effects on the pyrolysis process. Although in some cases these catalytic effects have been proven to be beneficial on the overall process by retaining part of the contaminants (Lievens et al., 2008), aiming to study the behavior of heavy metals any possible additional effect should be avoided, so the designed reactor does not plan the use of any solid heat carrier.

The design of the heating system has been done by the plant manufacturer and upgraded before the definition of the final configuration based the results of the preliminary set of experiments. The operational reactor operating parameters were used as input data for the definition of the electrical power to be installed on the reactor. Moreover, literature data reporting the pyrolysis reaction enthalpy and calculating the enthalpy needed to dry and heat up the biomass up to desired maximum temperature have been provided (Daugaard & Brown, 2003). A maximum initial moisture of the feedstock of 10 wt. % was considered for the calculations.

At the exit of the reactor the cyclone and the condensation section have been dimensioned accordingly to the considered temperature and flow rate ranges. Two condensers were designed similarly to those described by Papari et al. (2019). In particular, the first condenser is designed to function with diathermic oil at a temperature of about 110 °C, aiming to collect most of the high molecular weight compounds (oily phase), while the second condenser is designed to work with water at about 15 °C, collecting the water and low molecular weight compounds (aqueous phase). If fractional condensation is not needed, both the condensers can be used with water as cooling fluid.

Finally, at the end of the condensation section, there is an electrostatic precipitator (ESP) that aims to remove any residual mist prior to the discharge of the gas flow. The cyclone and all the pipelines that go from the exit of the reactor to the second condenser have been heated as well, to avoid bio-oil condensation along the line. The temperatures of the main elements of the condensation system are reported in Table 29.

Each device of the condensation section (i.e. cyclone, two condensers, ESP) is equipped with a dedicated bio-oil collection tank. Analyzing the products of this separate collection can give useful information on heavy metals distribution and transfer mechanisms.

Table 28 Main geometrical and operational features of the auger reactor

Biomass flow rate	N₂ flow	Solid residence time	Vapor residence time	Reactor diameter	Screw diamete	Reactor lenght
kg/h	NL/min	min	s	mm	mm	cm
2	12	5-30	2	60	50	150

Table 29 Operational temperatures of the pyrolysis system

Reactor	Operating temperature, °C						ESP
	Char collecting basket	Exit pipeline	Cyclone	I condenser	Mid- condenser pipeline	II condenser	
400-600	250	250	250	110	150	15	T _{amb}

6.4 System realization

The pyrolysis system has been realized and subsequently tested, revealing some criticality that led to several modifications in the reactor materials and heating system configuration.

For each configuration, the control and monitoring of the whole system has been developed using a dedicated software developed in Labview, coupled with a Data Acquisition System from National Instruments. In particular, the temperatures of the reactor and of the condensation section are monitored and used as control parameters to control the heating systems through proportional and ON/OFF controllers, respectively. The inert gas flow and the movement of the screw are also controlled digitally.

6.4.1 I configuration

The original configuration of the pyrolysis system is reported in Figure 37, whereas a picture of the reactor is shown in Figure 38.

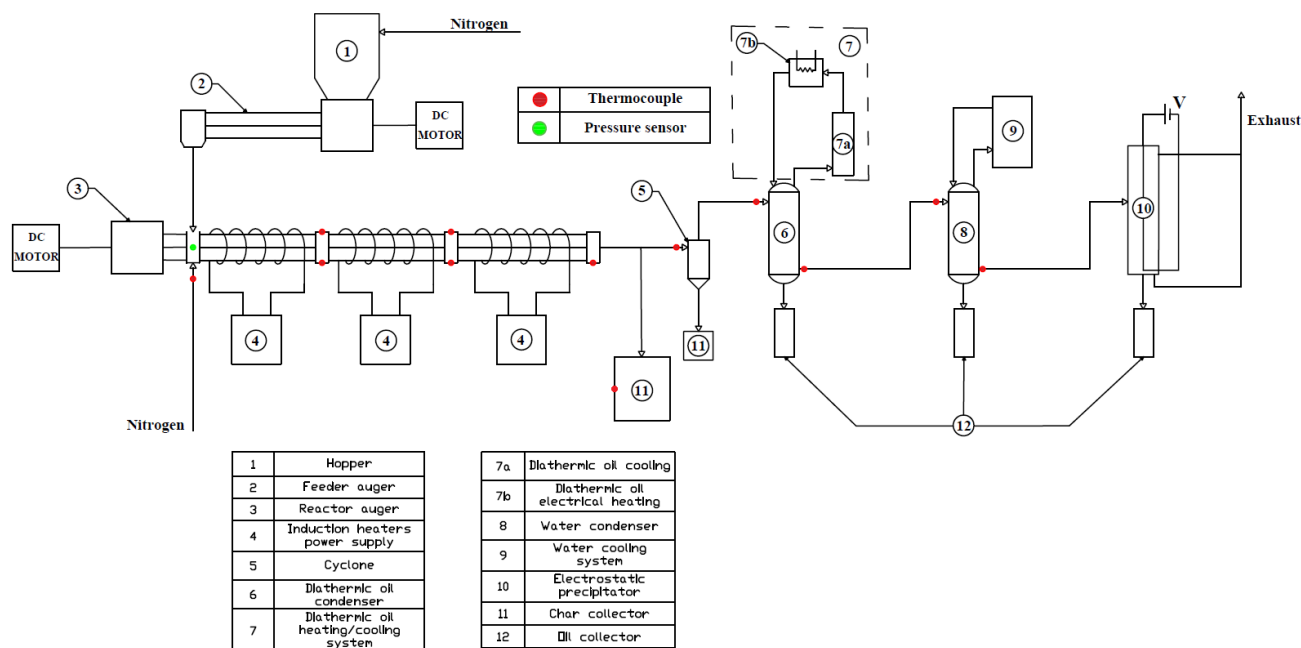


Figure 37 Scheme of the pyrolysis system

The absence of a solid heat carrier makes the realization of homogeneous biomass heating more difficult; moreover, the bio-oil could condensate on the shaft and flights of the screw, causing fouling problems and reducing the effective bio-oil yield. To overcome these issues, initially, induction

heaters were chosen for the reactor heating system, due to their efficiency and capability of achieving very fast heating rates. To deal with the bio-oil condensation problem, the induction system heats up only the screw inside of the reactor (in particular, the flights of the screw), and the heat is then transferred from the screw to the biomass. To this aim, the external shell of the reactor is realized in ceramic material. The entire plant has been provided with appropriate locations for thermocouples and pressure transducers and access points for sampling the gaseous stream. Specifically, the reactor has been equipped with an efficient temperature monitoring system, capable to monitor the temperatures along the screw (T_s), over the screw (T_{os}) in the volume typically occupied by the pyrolysis vapors and under the screw (T_{us}) in the volume typically occupied by the biomass. To introduce the thermocouples over and under the screw, it was necessary to divide the ceramic tube of the reactor external shell into three sections interrupted by metallic joints. Each reactor section is equipped with an independent induction heater, granting the possibility of realizing different temperature profiles along the reactor length (Figure 38).

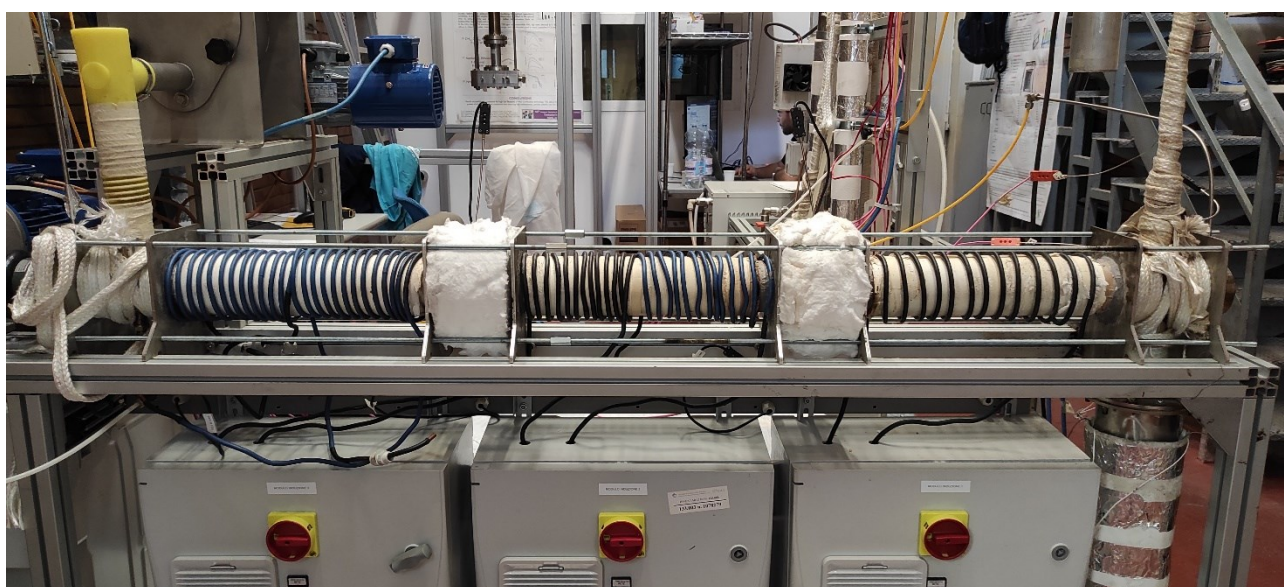


Figure 38 First configuration of the auger reactor

In this configuration, the screw is able to reach the design temperature, while the reactor walls remain at a lower temperature (about 350°C). This has two beneficial effects: it can avoid the condensation of bio-oil in the screw and, at the same time, keeps the walls reactor quite cold to reduce the extent of the secondary decomposition reactions that occur in the gas and vapor phase. However, the presence of unheated metallic joints results in cold spots between the heated sections of the reactor, introducing discontinuities in the temperature profiles along the reactor.

The main difficulty encountered with this configuration is represented by the sealings between the ceramic tubes and the metallic joints. It was not possible to identify a commercial economically affordable solution.

6.4.2 II configuration

To overcome the coupling problems between ceramic material and metallic joints, the reactor external shell was substituted with a stainless steel tube, with a greater number of thermocouple accesses (Figure 39). The induction heating system was retained, as shown in Figure 40.

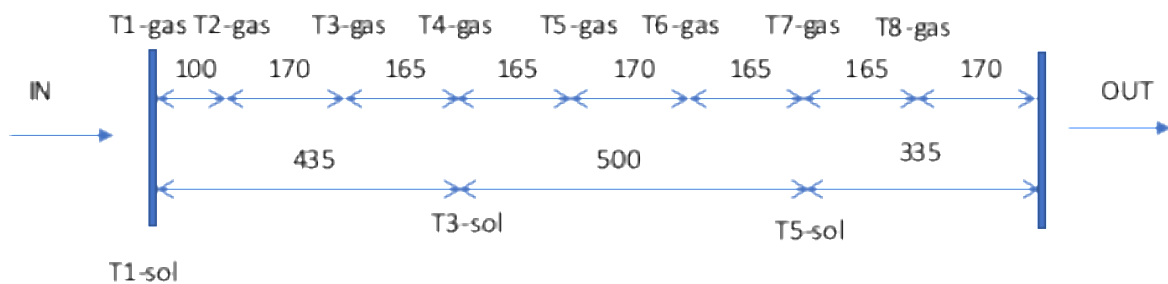


Figure 39 Schematization of thermocouples axial position along the reactor. The distances are reported in mm

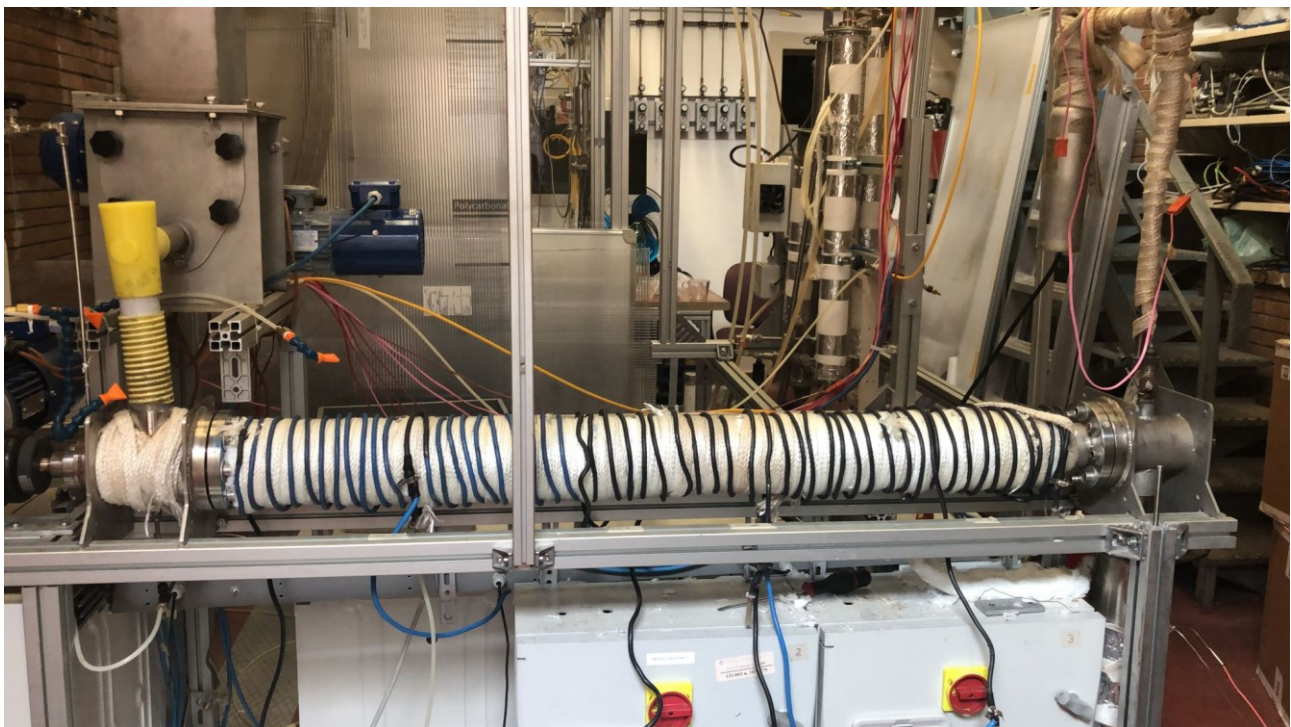


Figure 40 Second configuration of the auger reactor

Some difficulties were encountered with the efficiency of the heat transfer to the reactor. The power of the induction system was initially designed to heat up only the screw inside the reactor, so with the introduction of an additional metal mass it resulted insufficient. It was still possible to reach the design

operational temperatures on the empty reactor with a higher uniformity along the reactor axis, even if the heating rate resulted to be lower than for the original configuration. However, the introduction of the biomass caused an unacceptable lowering of the reactor temperature (about 420 °C).

Some attempts were made to increase the heating efficiency of the induction system by increasing the number of reaction coils and rearranging their position to increase the power density in the first 30 cm of the reactor., but without any relevant improvement.

6.4.3 III configuration

Given the difficulty of hosting an increasing number of induction coils, the heating of the reactor was eventually deemed to conventional electrical heating, using four semi-cylindrical heating elements supplied by Watlow with a nominal power of 2.5 kW each (Figure 41).

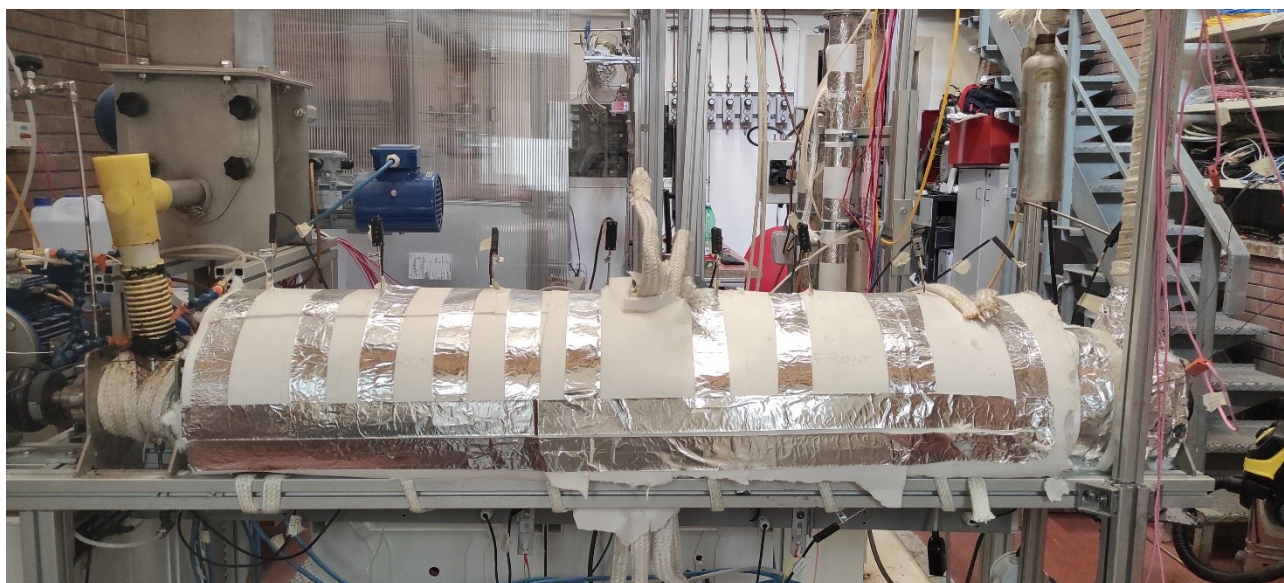


Figure 41 Third configuration of the auger reactor

In this configuration the design operational temperatures were reached successfully and with an even greater temperature homogeneity in the whole reactor body.

This final configuration was then used to run preliminary tests verifying the proper functioning of the pyrolysis system.

6.5 Test under design operational conditions

Preliminary tests were conducted on Phalaris (Reed canary grass), an herbaceous biomass characterized by high ash content. Figure 42a and Figure 42b report the temperature profiles registered by the thermocouples along the reactor during Phalaris processing at 550 °C, which is the highest tested temperature. The tests at 420, 450 and 500 °C returned identical temperature profiles.

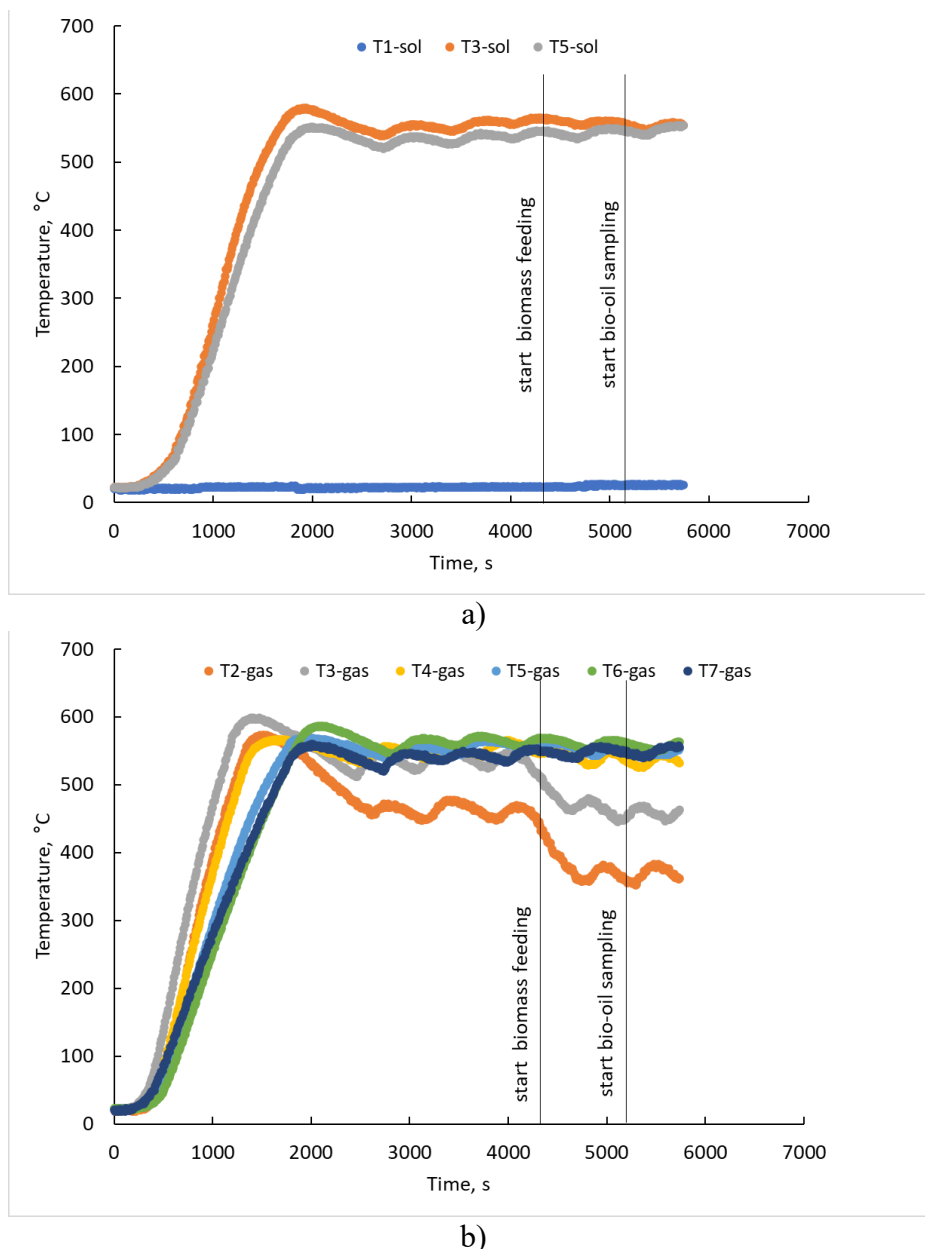


Figure 42 Typical temperature profiles (a) under the screw; (b) over the screw

The first noticeable result is the uniformity of the temperatures along the reactor that was achieved after the parameters for the proper control of the supplied electrical power were optimized. The maximum temperature gradient along the assail coordinate of the reactor is 30 °C for both the gas and solid phase temperature sets. The only temperatures that differ from the described trend are the ones registered at the inlet of the reactor: T1-sol is situated outside the heated zone, in correspondence with the biomass feeding point, while T2-gas is at the edge of the heated zone, as reported in Figure 37. When the biomass is fed, there is a decrease of the temperatures in the first part of the reactor (i.e. T2-gas and T3-gas), while the other temperatures remain unbothered. This means that the most of biomass pyrolysis takes place in the initial 40-50 cm of the reactor, and the system adjust to the fed conditions reaching a new quasi-stationary temperature profile after

10-15 minutes. Roughly the same transitory times were registered during the pyrolysis tests at 420, 450 and 500 °C.

Two set of data regarding bio-oil yield were recorded: "oil yield batch operation" refers to all the oil collected simulating batch operation (oil in the collecting pots+oil stuck on the pipelines+ oil in the EPS before the exhaust pipe) and is therefore useful for reactor modeling; "oil yield continuous operation" refers to the real output of the whole pyrolysis plant (oil in the collecting pots) and is useful for modeling of the whole pyrolysis system. To evaluate the "oil yield continuous operation" a sampling time of about 10 minutes was considered during the quasi-stationary temperature phase, after the transitory temperature phase caused by the start of the biomass feeding.

The batch oil yields obtained are in agreement with the results reported in literature (see Table 30) for other herbaceous biomasses pyrolyzed in screw reactors in the same temperature range, confirming that the reactor performances are satisfactory.

Table 30 Bio-oil yields of various biomass processing in auger reactors

Feedstock		Oil yield, wt%
Phalaris	1	25.0
	2	27.7
	3	28.3
Oak wood (a)		42.7
Pine wood (a)		44.8
Eucalyptus (a)		41.1
Wheat straw (b)		30.1
Sunflower stalks (b)		17.8
Rape stalks (b)		17.9
Corn stover (b)		31.5
a) (Ingram et al., 2008)		
b) (Tröger et al., 2013)		

6.6 Pyrolysis tests on poplar (P)

After the successful preliminary tests, a set of experiments was conducted to evaluate the effect of gas flow rate on the intermediate pyrolysis system. The employed biomass is plain poplar wood (P), that was pelletized in cylinders of 6 mm diameter and 5 to 10 mm length. The use of a doped biomass was not considered in this preliminary phase for two main reasons: the difficulty to treat

such great amounts of biomass obtaining a uniform distribution of heavy metals and the possible health hazards derived from the processing of high quantities of heavy metals.

The biomass was pyrolyzed at 600 °C under a N₂ flow in the range of 3-12 nL/min; for each test char yield and "oil yield continuous operation" are calculated. Moreover, the solid content of the produced bio-oils is determined following the Standard Test Method ASTM D7579–09. The obtained results are reported in Table 31.

As expected, the variation of gas flow rate does not affect the char yield in the whole considered range: the obtained yield is always 21-22 wt.%, that is also coherent with the results obtained from slow pyrolysis experiments (Figure 12) and thermogravimetric analysis (Figure 10). On the other hand, the oil yield results to be affected by N₂ flow variations: in particular, the "oil yield continuous operation" sharply decreases from around 35 wt.% to around 27 wt.% when the gas flow is lower than 9 nL/min. Two reasons can be invoked for these results: (i) a higher residence time of the pyrolysis vapors inside the reaction chamber favor the secondary decomposition of vapors to form lighter volatiles and gas; (ii) the lower carrier gas flow rate determines a lower heat transfer coefficient thus decreasing the condensation and oil collection efficiency of the intermediate pyrolysis system.

The solid content of the produced bio-oils does not show great changes, assessing around 0.1 wt.% for a nitrogen flow between 12 and 6 nL/min. Only in the case of N₂ flow equal to 3 nL/min it is possible to appreciate a diminution in the solid particles transported to bio-oil.

However, these are preliminary results that must be confirmed.

Table 31 Operational conditions and main results of the preliminary tests on poplar (P) on the auger reactor

Biomass			Conditions						Output		
#	Type	Shape	Biomass Inlet Flow Rate	Solid Residence Time	N2 Stream Flow Rate	Gas Residence Time	Temperature	Pressure	Char yield	Oil yield continuous operation	Oil solid content
			(kg/h)	(min)	(nL/min)	(s)	(°C)	(bar)	(wt.%)	(wt.%)	(wt.%)
1	Poplar (P)	Pellet	1.923	13.3	12	2.3	apx. 600	1 ± 0.2	21	35	0.12
2					9	2.4			22	38	0.09
3					6	2.4			22	27	0.10
4					3	2.5			21	28	0.03

7 Conclusions and future perspectives

Pyrolysis of heavy metals contaminated biomass is a subject that is gaining a lot of attention, given the possibility of combining the phytoremediation strategies for marginal lands with the valorization of phytoremediation residue by the production of bio-fuels and bio-materials. However, as was highlighted in a literature review, there are many aspects of heavy metals contaminated biomass pyrolysis that must be deeply investigated. During this PhD thesis, the effects of Pb speciation and type of contamination on the pyrolysis products and Pb retention and speciation in the char were studied considering the pyrolysis of poplar supplied from a phytoremediation site. To take into account the effect of Pb chemical speciation, the poplar biomass was doped with two different salts, lead nitrate ($\text{Pb}(\text{NO}_3)_2$) and lead acetate $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$. To evaluate the influence of the Pb contamination type, the poplar biomass was demineralized and doped with lead acetate following three different procedures that simulate different contamination types.

The prepared feedstocks were pyrolyzed under slow pyrolysis conditions at 465, 600 and 800 °C. The major observed results are summarized below:

- The Pb initial chemical speciation affects only slightly pyrolysis products yield and the effect is different for the two considered salts. In particular, lead nitrate causes a decrease in char and gas yields and an increase in bio-oil yield, while lead acetate slightly promotes char formation at the expense of gas yield, with bio-oil yield almost unaffected. However, the presence of inherent inorganics cannot be neglected in the determination of the products yield. The effect of Pb speciation on product properties and compositions is clearly appreciable. The lead salts affect the char elemental composition in a similar way, causing an increase of O/C ratio at 800 °C, differently from the expected trend observed for plain poplar. Both the salts depress CO_2 production at 800 °C, whereas Pb nitrate express the same effect also at lower temperatures. Coherently, the levoglucosan production is depressed by both the Pb salts as well as the production of H_2O .
- The Pb contamination type alters the pyrolysis mechanisms as well. The yield variations were only slightly affected by the contamination type, which on the other hand results in a strong effect on char and bio-oil compositions. Regarding the char elemental composition, for example, the ion exchange procedure did not alter qualitatively the decreasing trend of O/C observed for the reference biomass; on the contrary, dry mixing and wet impregnation doping procedures returned and increase of O/C at 800 °C.

- Pb displacement in pyrolysis products is affected by Pb speciation and by contamination type. In general, the Pb coming from lead nitrate is more thermally stable, resulting in higher Pb recovery in char produced at high pyrolysis temperatures (600 and 800 °C); moreover, BCR sequential extraction revealed a lower Pb mobility and bioavailability in lead nitrate doped char when compared with lead acetate doped char.

Pb contamination type shows a huge influence on Pb displacement, which follows a unique qualitative trend with pyrolysis temperature in the case of detrital contamination. The corresponding Pb recovery is lower than for any other considered feedstock at 465 and 600 °C, while at 800 °C it reaches 25 % of the initial biomass Pb content. This is an unreported behavior, which clearly represents the influence of the type of bond that exists between the heavy metals and the biomass tissues.

As general comment the obtained results clearly show that the contamination type, more than Pb speciation, should be considered during pyrolysis of contaminated biomass, highlighting a different effect of detrital and authigenic contaminations.

The obtained results and acquired knowledge were then applied to the conceptualization, design and realization of a continuous pyrolysis system for contaminated biomass processing. The system is based on a screw reactor and is equipped with a complex condensation section, able to deal with solid particle elutriation and capable of fractional condensation. These features are relevant when dealing with contaminated biomass in order to obtain a bio-oil as free of heavy metals as possible. After its realization, the screw reactor configuration was modified to ensure the achievement of the design operational conditions and was successfully tested with a reference biomass.

The findings of this PhD research can lay the foundation for the development of a phenomenological model capable of predicting and describing Pb behavior during contaminated biomass pyrolysis. This model could provide great assistance during the design of heavy metal contaminated biomass pyrolysis processes, providing information on Pb effects and stability in connection with biomass properties, contamination characteristics and pyrolysis operational conditions.

The described approach can be extended to the study of the behavior of other relevant heavy metals in order to achieve a more comprehensive description of heavy metals contaminated biomass pyrolysis. The methodical study of other heavy metals is particularly relevant for real phytoremediation residual biomass, considering that usually the soil contamination can include more than a single heavy metal. In this regard, a further step in the study of contaminated biomass pyrolysis

should be the evaluation of cross-effects given by the presence of multiple heavy metals. However, this can be achieved only with proper knowledge on specific elements behavior.

Finally, the realized intermediate pyrolysis system will be optimized for heavy metals contaminated biomass processing. By doing so, it will be possible to collect insights on the influence on Pb displacement of other parameters tied to the reactor configuration, expanding the information on Pb transformations and transfer phenomena.

Acknowledgments

The work has received financial support through the project: “CERESiS - ContaminatEd land remediation through energy crops for soil improvement to liquid biofuel strategies”, funded through HORIZON2020 (Project No 101006717).

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