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Effect of Feedstock and Temperature on the Distribution of Heavy Metals in Char from Slow Steam Pyrolysis of Contaminated Biomasses

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Restoration of soils contaminated by potentially toxic elements (PTEs) can be carried out through phytoremediation technique able to reduce bioavailable PTEs by translocation them from the soil to the different organs of the plants. The European LIFE ECOREMED project is now implementing an eco-compatible protocol for soil restoration through phytoremediation in Litorale Domitio - Agro Aversano NIPS (South Italy, Campania region). *Populus nigra* (*P. nigra*) is among the fastest-growing trees among the short rotation coppice with an annual dry matter production of 17.8 Mg ha^{-1} y^{-1}. Poplar trees, though not hyperaccumulators, are effective in uptaking PTEs from a very deep layer due to the efficiency of their root systems.
However, after soil restoration, the problem of a safe disposal of the contaminated biomasses should be faced. Pyrolysis could be an eco-sustainable post-processing treatment capable to reduce the mass of the contaminated biomass, concentrate the PTEs in the residual char and produce a vapor phase heavy metal free energy carrier. In addition there are many possibilities for valorizing char as fuel in traditional and advanced power generation facilities, in the agronomic field for carbon sequestration and as fertilizer, as contaminant adsorbent in wastewater and soil, as adsorbent or catalyst for gas cleaning, as catalyst for syngas conversion to liquid hydrocarbons and biodiesel production, as raw material for supercapacitors and, finally, as filler in wood and polymer composites. The stability of PTEs and the physico-chemical properties of the produced chars are relevant to assess if such material could be converted into a valuable resource. Steam assisted pyrolysis tests of *P. nigra*, contaminated by Cd, Cu, Pb and Zn, have been conducted under slow pyrolysis conditions.
The effect of the pyrolysis final temperature has been investigated in the temperature range 653-873 K in order to study the distribution of heavy metals in the pyrolysis products. The results show that the concentration of the metals in the chars along the temperature has a non-monotonous trend for *P. nigra* branches. The maximum concentration of Cd and Pb is measured in the chars produced at 653 K and 753 K, respectively. In chars derived from leaves Cd concentration shows the same trend as in branches, whereas the concentration of Cu, Pb, Zn increases in the whole temperature range.
The metals recovery in the chars slightly decreases with temperature in all the examined cases, except for Cd that show a quite complete devolatilization even at temperature higher than 753 K.

1. Introduction

Soil contamination is compromised by bioavailable potentially toxic elements (PTEs) due to industrial activities, mismanagement of wastes, sludge and illegal dumping. Phytoremediation can be considered a low cost technique able to reduce bioavailable PTEs by translocating them from the soil to the different organs of specific plants known as hyperaccumulators (Fiorentino et al., 2013; Barbosa et al., 2015). However, after soil

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restoration, the problem of a safe disposal of the contaminated biomasses should be faced. Prolysis can represent an environmentally sustainable strategy combining both the concentration of heavy metals in the char, thus reducing the volume and weight of contaminated matter with respect to the original biomass, and producing a gaseous phase free of heavy metals (Stals et al., 2010; Lievens et al., 2008). The stability of PTEs and the physico-chemical properties of the produced chars are relevant to assess if such bio-waste could be converted into a valuable resource. Literature evidences show that under nitrogen atmosphere pyrolysis temperature affects both the behavior of PTEs during the thermal treatment (Stals et al., 2010; Lievens et al., 2008) and the bioavailability of PTEs in the char (Buss et al., 2016). However, previous works on the production of activated carbon show that in order to develop high levels of porosity in the char, fundamental in determining the suitability of char in many applications, steam has to be preferred to nitrogen (Savova et al., 2001). At the same time, it has been proven that steam induces modifications in devolatilization mechanism of the organic matrix. The aim of this study is to study the steam assisted pyrolysis of contaminated biomasses with two main goals:

- to concentrate the PTEs in the solid product, thus producing a combustible gaseous product containing no or limited amounts of heavy metals that can be used to assist energetically the pyrolysis process;
- to find an optimal temperature that could be a good compromise between the weight reduction of the contaminated material and good structural quality of the solid residue.

In the present work *P. nigra* has been selected and cultivated on industrial sites contaminated with Cd, Pb, Zn and Cu. Different parts of the tree have been sorted and used as feedstock for pyrolysis tests: branches and leaves. Steam assisted pyrolysis tests have been conducted under slow pyrolysis conditions (heating rate = 4 K/min) in the temperature range 653-873 K. The distribution of the heavy metals in the chars has been studied and the dependence of char porosity on the process final temperature has been assessed.

2. Materials and Methods

2.1 Feedstock preparation and characterization

For pyrolysis tests, branches and leaves samples of *P. nigra* have been milled and sieved. The collected fractions between 400 and 600 μm have been characterized and used for pyrolysis tests. The ultimate and the proximate analyses of the samples have been performed using a CHN 2000 LECO analyzer with EDTA as standard and a TGA 701 LECO thermogravimetric analyzer, respectively, applying ASTM procedures. The content of major inorganic elements has been determined by Inductively Coupled Plasma Mass Spectrometry (ICP/MS) using an Agilent 7500CE instrument after dissolving the biomass samples by means of microwave assisted acid digestion in agreement with US-EPA 3051 and 3052 methods. All the biomass samples have been dried in an electric oven at 105°C for 2h to remove moisture before pyrolysis tests.

2.2 Experimental apparatus for pyrolysis tests

The pyrolysis reactor, described in detail in Giudicianni et al. (2014a), consists of a jacketed prismatic chamber in which 6 g of biomass are spread in thin layers over 4 trays along the rectangular cross-section of the inner reaction chamber. Steam produced by a steam generator and heated to the programmed temperature in a super heater enters the reaction chamber through a flow straightener and invests tangentially the samples on the sample trays. The residence time of the gas phase in the reactor ranges from 1.5 to 3 s depending on the reactor temperature and it is adjusted in order to minimize the extent of secondary reactions in the gas phase. The gaseous stream exiting the reaction unit passes through a condensation device and a flask submerged in a thermostatic bath at 273 K is used to collect the condensable fraction. Non-condensing gases flow through a silica gel trap in order to reduce their moisture content before being fed to the analytical system. Pyrolysis experiments have been carried out at constant heating rate (HR_{sp}=4 K/min) and pressure ($P=5\times10^5$ Pa). Temperature and pressure are monitored using N-type thermocouples and pressure transducers along the steam supply line and at the inlet and the exit of the test chamber.

2.3 Products characterization

The yields of gaseous species have been measured integrating along the time of the test the corresponding releasing rate curves. Temporal profiles of the releasing rate of all the gaseous species of interest (CO, CO_2, H_2, CH_4, N_2 and O_2) have been obtained monitoring carrier (N_2) flow rate and gas composition by mean of a gas chromatograph equipped with a thermal conductivity detector (Agilent 3000 Quad) every 171.5 s. The yield of char has been determined gravimetrically respect to the amount of fed sample, while liquid yield has been evaluated as the amount needed to complete the mass balance. The content of the major inorganic elements in the chars was determined by ICP/MS (see section 2.1). The specific surface area has been evaluated from the Brunauer–Emmett–Teller (BET) equation by mean of gas adsorption porosimetry tests. Before the analysis, the samples were degassed at 573 K for 5 h under vacuum conditions.

3. Results and discussion

3.1 Feedstock characterization

In this section results obtained from *P. nigra* branches and leaves have been presented. Results of elemental and proximate analysis are listed in Table 1. Hydrogen content doesn't exhibit large variations between leaves and branches, whereas the content of carbon and oxygen is lower in the leaves due to the presence of large amount of ashes. Nevertheless, the O/C and H/C atomic ratio is 0.69 and 1.48 for branches and 0.62 and 1.38 for the leaves because of the lower content of carbon on dry ash free basis in the branches. This result allows to postulate a higher content of holocellulose in the branches. It is well known that the relative content of cellulose, hemicellulose and lignin determines a different pyrolytic behavior and different characteristics of the final solid residue (Giudicianni et al., 2014b).

Table 1: Feedstock characterization: elemental and proximate analysis, HHV.

	C	H	N	S	O	moisture	volatiles	fixed carbon	ash
	wt% dry basis					wt% as received			
Branches	47.7	5.9	0.0	0.1	44.2	7	74.3	16.7	1.9
Leaves	41.6	4.8	1.0	0.1	34.7	8.7	60.8	14.2	16.4

The concentrations of the major inorganic elements and of the heavy metals have been reported in Table 2. Cd, Cu, Pb and Zn have been detected in all the samples, but leaves are characterized by the highest concentration of all the contaminants as well as the other detected inorganics, except for K. This finding is consistent with previous literature data on *Populus* used for phytoremediation (Rafati et al., 2011).

Table 2: Feedstock characterization: ICP/MS analysis.

	Na	Al	P	K	Ca	Mg	Fe	Cd	Cu	Pb	Zn
	mg/kg dry basis										
Branches	206	248	468	4477	9407	836	132	2	8	60	50
Leaves	573	1854	1088	3596	38015	2325	477	10	63	423	118

3.2 Pyrolysis test

Figure 1, panels a and b, shows the products yields obtained from pyrolysis tests of branches and leaves, respectively, at three different temperatures 653, 753 and 873 K. For both the samples, the char yield decreases with pyrolysis temperature due to the increased loss of condensable volatiles (indicated in the figure as “liquid”) and permanent gases (indicated in the figure as “gas”). Variations of the liquid yield are negligible because most of them are released at temperature lower than 653 K. This is due to the fact that condensable volatiles are mainly released by holocellulosic fraction of the biomass and holocellulose decomposition occurs mainly at temperature lower than 673 K (Giudicianni et al., 2014b). The yield of the gas increases abruptly for branches heating up the biomass from 753 to 873 K, whereas it gradually increases for leaves in the same temperature range. Pyrolysis of branches produces lower amounts of char and higher yields of the whole vapor phase (liquid and gas) in agreement with the higher content of volatiles in the raw feedstock. The higher alkali and earth alkali metals content in leaves contributes to enhance char yield at the expense of liquid yield in the whole temperature range (Gargiulo et al., 2015).

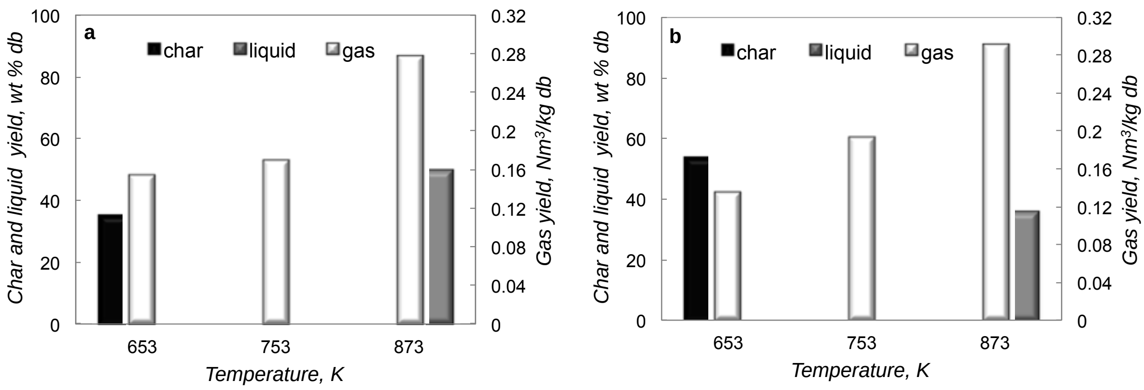

Figure 1: Products yield obtained at different pyrolysis temperature from branches (a) and leaves (b).

The concentration of heavy metals in the solid residue as a function of temperature is shown in Figure 2, panels a and b, for branches and leaves, respectively, whereas in Figure 2, panels c and d, the corresponding ion recovery is shown. The metal concentration is intended as mass of ion per mass of char and it is used to calculate the Ion Recovery obtained multiplying it by char yield and dividing by the mass of ion in the raw biomass. The concentration of Cd in both branches and leaves chars shows a maximum at 653 K. At this temperature Cd Ion Recovery slightly decreases and the organic matrix of the original feedstock strongly looses weight resulting in char yields equal to 35.4 and 53.6 wt % for branches and leaves, respectively. This determines the increase of Cd concentration in the char produced at 653 K. The increase is more significant for branches, whereas is slighter for leaves. At higher temperatures Ion Recovery decreases suddenly because of a significant devolatilization of Cd in agreement with previous literature results obtained under nitrogen assisted pyrolysis (Bert et al., 2017; Stals et al., 2010). At the same time the decrease of char yield is slighter thus determining the decrease of Cd concentration in the solid residue.

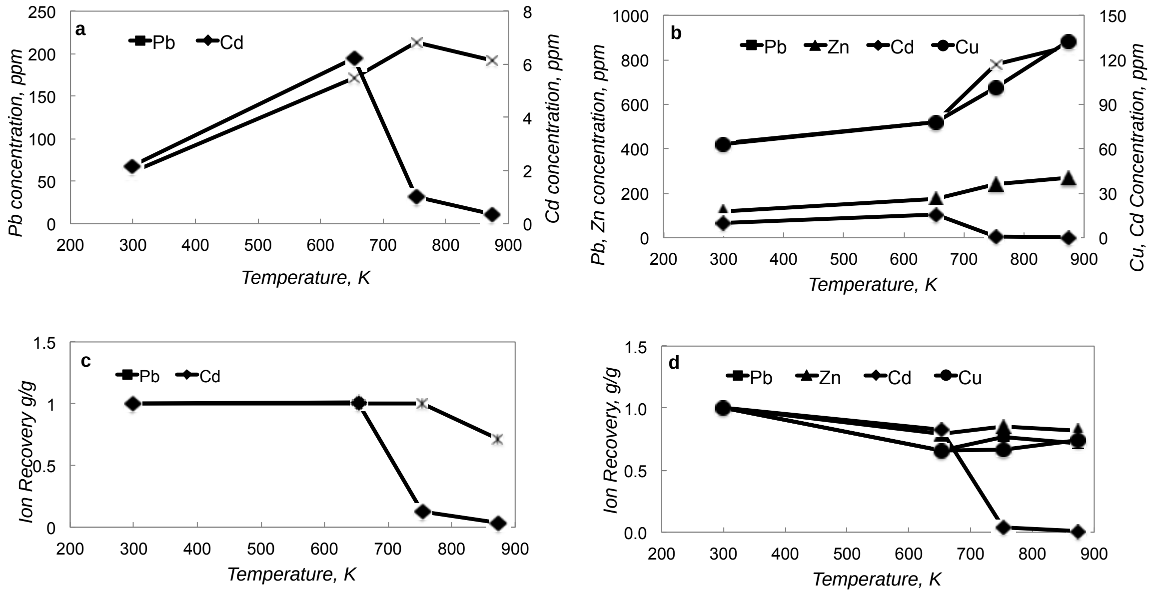

Figure 2: Concentration and Ion Recovery of PTEs in the chars from branches (a and c, respectively) and leaves (b and d, respectively).

The same behavior is observed for Pb in the branches, but its concentration in the char has a maximum at 753 K because of the highest thermal stability of this metal as shown by the slow decrease of Pb Ion Recovery. As shown in Figure 2d, in the leaves, Pb, Cu and Zn show a slight devolatilization at 653 K and are retained in the char at higher temperatures, thus determining an increase of their concentration in the char in the whole temperature range (see panel c).

The final pyrolysis temperature has a crucial role in determining the structural characteristics of the char. The influence of temperature on specific surface area of chars has been shown in figure 3. At low heating rates, biomass structure is preserved during thermal treatment and the pore development and internal surface area are strictly correlated to the degree of devolatilization and to the formation of cracks inside the char matrix. For both branches and leaves chars, up to 753 K, the removal of a great amount of volatile matter created sparse void volume regions giving rise to a macroporous structure characterized by a low BET surface value. At 873 K, the formation of cracks in the material caused a great increase in surface area and porosity probably due to the development of micropores and mesopores (Lehmann et al., 2009).

The differences in the structure and in the chemistry of the different parts of the plant affect significantly the BET surface of the residual chars. Char obtained from branches has the highest BET surface at 873 K, namely 325.3 m^2/g, and this is probably correlated to the higher content of volatiles and the lower content of ashes. BET surface of char from branches is slightly higher than the values obtained for the whole biomass sample (mixed branches and leaves) processed under similar conditions (Giudicianni et al., 2017) and significantly higher than the values reported in the literature for the same biomass processed under similar thermal conditions in nitrogen atmosphere (Zheng et al. ,2013), thus confirming the positive effect of steam on char structure.

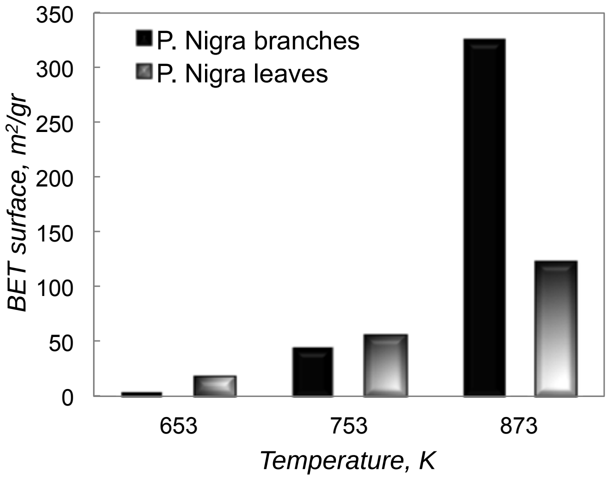

Figure 3: BET surface of char obtained from pyrolysis of branches and leaves at different temperatures.

4. Conclusions

Slow steam assisted pyrolysis of *Populus N.* branches and leaves derived from soil phytoremediation process were pyrolyzed up to a final temperature varying in the range 653-873 K. The concentration of four heavy metals, namely Cd, Cu, Pb and Zn, in the char was monitored in order to investigate the possibility of concentrating the contaminants in the solid products thus obtaining a heavy metals free vapor phase.
The behavior of the monitored heavy metals during pyrolysis is similar in both the organs of the plant: Cd is more volatile and undergoes to a significant devolatilization even at low temperature (653 K), whereas Cu, Pb and Zn are more thermally resistant in the examined temperature range.
The results showed that, in presence of Cd, if pyrolysis temperature is higher than 653 K, it is not possible to obtain a free heavy metals vapor phase. Nevertheless, at this temperature the char cannot be valorized due to the low value of its BET surface. In this case a low temperature process, such as torrefaction, is preferable with the aim to reduce the contaminated material and combine the production of both a stabilized waste and valuable liquid chemicals (such as furan derivatives). On the contrary, in presence of Cu, Pb and Zn pyrolysis temperature can be increased up to 873 K without a significant devolatilization of the metals, thus allowing the development of the internal porosity. In this case, char deriving from branches is characterized by a higher BET surface and it is more suitable for application in processes involving solid/fluid interface phenomena.

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