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Research paper

Torrefaction and pyrolysis of metal-enriched poplars from phytotechnologies: Effect of temperature and biomass chlorine content on metal distribution in end-products and valorization options

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ABSTRACT

Torrefaction (290 °C) and pyrolysis (450 and 800 °C) trials were performed at pilot scale with a patented reactor on metal-enriched poplars from a contaminated soil managed by phytotechnologies and poplars cultivated on uncontaminated soil, for comparison. This study emphasized the influence of temperature on end-product yield, metal distribution in end-products and metal behavior. Results showed that the evolution of the end-product yield, i.e. biochar, bio-oil and gas fractions, was depending on temperature rather than other parameters such as the origin or metal content of the tested poplars. Torrefaction decreased the processed poplars weight, leading to metal-enriched torrefied biomass as a major end-product. At 450 and 800 °C, metal behavior was governed by temperature. Nevertheless, the different chlorine content of initial biomass was hypothesized to be an important factor that could modify the metal behavior by increasing metal volatilization at process temperatures. Amongst the studied metals, Zn and Pb were hypothesized to form volatile metal chlorides, therefore increased metal volatilization from Control poplar biomass could be explained by increased chlorine content of such biomass. At 450 °C, metals were recovered in biochar, then in bio-oil and finally in gases. At 800 °C, similar results were obtained for Cu, confirming that Cu was not easily volatilized. On the contrary, Zn, Pb and Cd were mostly recovered in gases, which became the second metal recovery compartment. According to metal concentrations, valorization options were discussed for end-products.

1. Introduction

The Renewable Energy Directive (RED) [1] encourages the restoration of degraded and contaminated land by cultivating biomass to produce biofuels and bioliquids in compliance with sustainability criteria that ensure biofuel/bioliquid production in a sustainable and environmentally friendly manner [1].

In this context, plant-based options for the management of contaminated land seem relevant strategies to contribute to the RED objectives. These options, grouped under the term phytotechnologies, are mainly based on the combined use of plants and their associated microorganisms, partly assisted by the use of various amendments and soil management practices. In addition to potentially restoring soil structure, functions and quality, and

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positively influencing other ecosystem services, phytotechnologies may also provide valuable sources of renewable biomass for the bio-based-economy (e.g. bioenergy, biocatalysis and platform molecules for green chemicals, and ecomaterials) [2]. Indeed, crop management results in herbaceous or woody biomass which could be recovered and valuated in various processes. Depending on the phytotechnology set up on the contaminated site and the type of plant used, harvested plant parts may contain concentrations of trace elements (TE) that may be higher than those found in similar vegetation grown on uncontaminated soils. Phytoextraction leads to metal-enriched plant biomass whereas (aided) phytostabilization leads mostly to plants with metal concentrations in the range of physiological levels. These plants may enter valorization pathways if (i) TE do not disturb the functioning and the performance of the processes, (ii) if the TE transfer is controlled and impacts on the environment are prevented, and (iii) if such plant use complies with current regulation.

Several studies have been performed with metal-enriched plant biomass cultivated for phytoremediation purpose as potential fuel to produce bioenergy using thermal treatment such as combustion [3–6], gasification [7], torrefaction [8] and pyrolysis [9–14]. All trials, except those from Chalot et al. and Delplanque et al. [5,6] on combustion, were conducted in laboratory reactors. These trials were performed with willows [4,6,7,11,12,13], birches [9,10], sunflowers [10], reed canary grass [8], poplars [5,13], *Sorghum bicolor* [14] and hyperaccumulators [3]. From these studies, it can be concluded that the distribution of TE in end-products highly depends on the process used, notably the temperature as a major parameter. The valorization objective of end-products (biochar/ash, bio-oil or gases) will lead to the choice of one biomass conversion process rather than another.

In the present study, torrefaction (290 °C) and pyrolysis (450 and 800 °C) trials were performed at a pioneering pilot scale on metal-enriched (M-enriched) poplars from a contaminated soil managed by phytotechnologies and poplars cultivated on uncontaminated soil, for comparison. The aim of the study was to determine the fate of the metals present in the poplars (Cd, Zn, Cu, Pb) in the end-products of the torrefaction and pyrolysis processes. As the trials took place in France, the possibilities of valorization of end-products according to both current French regulation and literature were reported.

2. Materials and methods

2.1. Poplars characteristics and sample preparation

The poplar cultivar 'SKADO' (*Populus maximowiczii* x *P. trichocarpa*) used in this study was grown on a soil contaminated with Cd and Zn (Leforest, Nord Pas de Calais, France, 50°25′39.7″N, 3°02′39.8″E) for 7 years as short rotation coppice (SRC). In December 2013, the entire SKADO plot (i.e. 72 trees) was harvested (Fig. 1). These poplars are termed metal-enriched (M-enriched) in the text below. At the same period, 500 kg of 4-year-old 'SKADO' poplars (i.e. 150 trees) were harvested on an uncontaminated soil in Belgium (Bosstraat 31, 9080 Lochristi, Belgium, 51° 06′ N, 03° 51′ O) (Fig. 1) and used as control (Control). Both types of poplar biomasses were manually cut with a chainsaw and the whole trees (with bark) crushed on site with a wood chipper at 25 × 25 (VANDAELE TV 250, Vandaele Konstruktie company, Oostrozebeke, Be) and 30 × 30 mm (STARFORST, Seppy M. company, Caldaro, Italy) for Control and M-enriched poplars, respectively. For each poplar type, two big bags of wood chips were transported by truck to ETIA (Engineering company, Compiègne, France) facilities for processing. Before processing, wood chips were dried with a continuous flow conveyor system (123B BOM B.N.W. Industries, www.belt-o-matic.com) for 15 min at 120-150 °C to reach 10% of humidity. Wood chips were then crushed more finely to reach 5 mm diameter and 3 mm thickness (T25 Toy, www.broyeur-sas-renetoy.fr). Wood chips were put back in their respective big bags. To ensure homogenization, the wood chips of each big bag was spread on a tarpaulin, mixed with a shovel and divided in 10 heaps, each heap corresponding to two shovels. Half of one heap from one big bag was then mixed with half of one heap from the second big bag and put in a concrete mixer. Another mixture prepared in the same way was added to the concrete mixer. Both mixtures were homogenised for 5 min. From this mixture, around 1 kg of wood chips were taken off for analyses while the remaining wood chips were put in new big bags. The operation was repeated 10 times leading to homogenised wood chips for each poplar type and 10 samples per poplar type for analyses. The fines formed during the handling and preparation of wood chips were not considered in this work. Before use, the concrete mixer was carefully cleaned by tap water, acidic solution (3.3% $HN0_3$ at 65% and 1.5% H_20_2 at 30%) and mineral water and finally dried with compressed air.

2.2. Poplar analysis

Ten samples of 1 kg per poplar type, packed in plastic bags, were used for analyses. Ten g of each sample were picked up and analysed separately for Cd, Cu, Pb and Zn. For this trace element (TE) concentration analysis, 500 mg wood chips were ground and digested (microwave Mars Xpress, CEM) at 180 °C during 20 min using 10 m L of 67% nitric acid (HNO_3). Extracts were filtered using 0.45 μm Whatman filter paper and analysed using ICP- MS (Agilent 7500) for trace elements. 'BCR-679' standard reference of plant material (white cabbage; community bureau of reference, http://www.irmm.jrc.be/mrm.html) were included for analytical quality control. Lead was not present in this material. Recoveries were 0.95 for Cd, 0.90 for Cu and 1.17 for Zn. The remaining 990 g of each sample per poplar type were grouped in one sample and sent to an external laboratory (Socor, Dechy, France) for the following analyses: lower and higher heating values (LHV and HHV, respectively) [15], elemental analysis (C, H, O, N, S, Cl), dry matter [16] and ash content [17].

2.3. Thermochemical conversion processes

In March and April 2014, torrefaction and pyrolysis trials were carried out with the Biogreen process (Biogreen BGR130L2) patented by ETIA (patent registration 07082015 on 23/11/2007, France), equipped with the Spirajoule technology. It is designed with a low voltage electrically heated screw conveyor. The product was heated by solid-solid heat transfer from the screw surface to the biomass, the joule effect taking place inside the screw. The screw temperature was precisely controlled and regulated, which led to a stable and constant product temperature as the product flow and the process temperature were kept constant. The residence time was regulated by the screw rotation rate. The residence time of the product varied according to the speed rotation (ω in rpm/min) of the screw. For a screw with a length L (mm) and a screw pitch P (mm), the residence time (in min) was L/(ω x P). Temperature adjustment varied between 200 and 900 °C depending on required specifications. Residence time of the product was adjusted from 5 to 30 min. Adjustment of operating conditions defines the ratio of bio-oil, biochar and gas produced with the process. Biogreen BGR130L2 (30 kW, 2 kg h^{-1}) was used for trials (Fig. 2). The design of the pilot allowed the extrapolation of the results to industrial module, which could process 100–500 kg h^{-1}.

Before trials, the chamber was carefully cleaned with a vacuum cleaner to remove solid residues and soaked in a phosphate free