



D2.3

**Pre-treatment options and contaminant separation as well as
concentrated recovery**



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Statement of Originality

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Executive Summary

Soil contamination (contaminated sites) is a global problem, as these contaminated lands are not suitable for food production. The GOLD project aims to cultivate lignocellulosic energy crops (hemp, sorghum, miscanthus, switchgrass) on contaminated sites. The crops will phytoremediate the soil of metal contaminants, allowing for restoration of the sites back to agricultural production in the long-term. The harvested energy crops will also be used to produce biofuels. This report summarizes the outcomes of pre-treatment of metals-contaminated biomass upstream of biofuel production via downstream processes including entrained flow gasification (EFG). Three different pre-treatment processes are considered: 1) Torwash, 2) torrefaction and 3) slow pyrolysis.

NOTE: this deliverable will be updated upon completion of large-scale lab experiments for Torwash and Torrefaction pre-treatment of Miscanthus and Switchgrass biomasses. These experiments were delayed due to late delivery of the feedstock and issues with lab equipment (breakdowns).

Torrefaction

Torrefaction pre-treatment was conducted at TNO for contaminated Sorghum and Miscanthus (from the Lavrion site) feedstocks, at pilot-scale in a screw reactor. Torrefaction was done at a temperature of 280 – 285 °C and resulted in an upgraded product, with a mass yield of approximately 55 – 57%. Most metals remained in the biomass after torrefaction and thus are concentrated in proportion to the mass loss. However, some more volatile metals, including Cd, Pb, and Zn can be partially released to the gas phase during torrefaction. The properties of the torrefied biomass also change, in particular an increase in heating value, which highlights the value of torrefaction pre-treatment to upgrade biomass solids for downstream processing.

Torwash

Torwash pre-treatment was conducted at TNO at lab- and pilot-scale for Sorghum feedstock and at lab-scale (optimization tests) for contaminated Miscanthus and Switchgrass feedstocks. For all feedstocks, lab-scale testing indicated that optimized conditions for Torwash pre-treatment, with the goal of removing heavy metal contaminants from the solid fraction to the liquid fraction, is a temperature of 200 °C and an acidic pH (1 or 2), achieved with citric acid. These conditions produced a solid fraction that had reduced metals concentration compared to the original feedstock. The liquid fraction from Sorghum treatment, where the metals partitioned, could be further treated via acidification, to isolate humic substances in a concentrated fraction without the metal contaminants. This indicates the benefits of Torwash pre-treatment for solids cleaning upstream of gasification, while also presenting a route for valorising the liquid fraction obtained.

Slow pyrolysis

The slow pyrolysis pretreatment was carried out at lab-scale on five different biomass samples and the resulting char was characterized in terms of specific surface and metal concentration. The highest values of these two properties were observed at 600°C. Based on the results of the lab-scale experiments, the two most promising biomasses, i.e. sorghum and miscanthus from Lavrion, were treated at pilot-scale in a screw pyrolysis unit, where conventional and oxidative regime was investigated. The proximate and ultimate analysis of the char samples from conventional and oxidative pyrolysis were similar, but higher specific surface values were observed in the oxidative case. The condensates were collected and gravimetrically fractionated into an aqueous and an oil phase. The former was almost free of metal contaminants which tend to concentrate into the latter. Permanent gas was characterized in terms of volumetric composition: the oxidative runs led to a gas richer in carbon monoxide and carbon dioxide.

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Introduction

One of the goals of the GOLD project is to grow high-yielding lignocellulosic energy crops on contaminated sites to remediate the soil of heavy metals and to use the harvested energy crops for production of biofuels. Prior to biofuel production, harvested contaminated crops (Sorghum, Miscanthus, Switchgrass, Hemp) were subjected to pre-treatment. The goal of the pre-treatment steps were to improve performance of downstream processes for biofuel production by upgrading and improving the properties of the solid biomass (e.g., increased energy density, removing or concentrating metal contaminants, improving biomass grindability).

This report summarizes the outcomes of pre-treatment of metals-contaminated biomass for entrained flow gasification (EFG) and, ultimately, the production of biofuels. Three different pre-treatment processes are considered: 1) Torwash, 2) torrefaction and 3) slow pyrolysis. These processes are all thermo-chemical in nature, and result in different effects on the yield, metal partitioning and properties of the contaminated biomass, as discussed in this report. This report provides an overview of the biomass samples and the pre-treatment methods applied, results of pre-treatment processing and impacts of pre-treatment on the biomass solids.

1 Overview of contaminated biomass samples

Detailed descriptions of the contaminated biomass and their characterization is summarized in GOLD Deliverable 2.1. This section briefly describes the pre-treatment applied to the various contaminated biomass samples in the project (Table 1). All contaminated feedstock samples subjected to pre-treatment (upstream of gasification) were collected from either the Lavrion site or the Kozani site, both located in Greece. Sorghum, Miscanthus (from both sites) and Switchgrass were all subjected to pre-treatment via Torwash and slow pyrolysis, whereas Torrefaction pre-treatment was only applied to Sorghum and Miscanthus (Lavrion site) biomass feedstocks. Hemp was subjected to slow pyrolysis treatment at lab-scale only.

In general, the selection of feedstocks for different pre-treatments was based on level of contamination (with a preference for more contaminated feedstocks) and availability of the feedstock (quantity and timing for delivery to project partners).

Table 1: Summary of contaminated feedstocks (crop type), site of collection, main contaminants and type of pre-treatment applied in WP2 of the GOLD project.

Crop type	Site	Main heavy metal contaminants	Type of pre-treatment
Sorghum	Lavrion	Al, Cr, Cu, Fe, Pb, Zn	Torrefaction, Torwash, Slow Pyrolysis
Miscanthus	Kozani	Ni, Zn	Torwash, Slow Pyrolysis
Miscanthus	Lavrion	Cd, Ni, Pb, Zn	Torrefaction, Torwash, Slow Pyrolysis
Switchgrass	Kozani	Pb, Zn, Ni, Cd	Torwash, Slow Pyrolysis
Hemp	Lavrion	Pb, Zn, Ni, Cd	Slow Pyrolysis (lab-scale)

2 Methodology

2.1 Torwash

Torwash is a patented process developed at TNO. It is a mild form of hydrothermal carbonization (HTC), whereby samples are processed at temperatures from approximately 170 – 220 °C, under autogenous pressure. One of the advantages of the Torwash process is that it is suitable for direct treatment of wet biomass streams without pre-drying. For dry feedstocks, water is added for Torwash processing. The result of the Torwash process is that the biomass becomes more brittle and easier to dewater. Subsequent dewatering of the treated material gives a liquid fraction and a solid fraction, where many minerals and salts are “washed” out of the biomass into the liquid fraction, leaving a cleaner solid for use as a solid fuel or as a feedstock for downstream processes.

For the GOLD project, Torwash was applied at lab-scale to treat contaminated feedstocks (Sorghum, Miscanthus from Kozani, Miscanthus from Lavrion, Switchgrass). Initial screening tests were conducted in a multiclave apparatus (Figure 1), in Teflon-lined pots of volume 100 mL. In this way, multiple temperatures and pH adjustments, including the use of different acids, could be examined and the optimum conditions could be determined. Temperatures from 180 – 200 °C were investigated, as were pH values of 1, 2, 4 and no pH adjustment with citric acid and sulfuric acid. The treated samples were filtered to generate a liquid and solid fraction. The solid fraction was analysed to determine the heavy metals content and the partitioning of heavy metals between the liquids and solids post-Torwash. The optimal condition was chosen as the treatment condition which had the most metals partition to the liquid fraction (and thus were removed from the solids).



Figure 1: Multiclave apparatus (left) and 30 L autoclave reactor for Torwash pre-treatment optimisation and production experiments, respectively.

Based on the results of the screening tests, larger scale tests were performed in batch-mode in repeated experiments in a 30L autoclave (Figure 1). These larger scale tests were performed to produce approximately 10 kg of dry solids for downstream gasification processes at TUM. Following treatment, samples were filtered to generate a solid fraction and a liquid fraction. The solids were dried at 105 °C to a moisture content <10%.

The liquid fraction was further treated to isolate humic substances and investigate the fate of the metals that were partitioned out of the biomass (described in Section 2.4).

Feedstocks (untreated) as well as treated solids were analysed for fuel characteristics and elemental concentrations, including metals concentration. Dry matter content was determined via drying in an oven at 105 °C until no further mass loss was achieved. Volatile matter was measured according to standard method EN 15148. Ash content of solid samples was measured with a Nabertherm LV5/11/B180 oven following standard method EN 14775. Elemental analysis was conducted with a Thermo Scientific Element Analyser FLASH 2000. Carbon, hydrogen and nitrogen content was determined according to standard method EN 15104. The higher heating value (HHV) of the samples was determined according to standard method EN 14918 with a Parr 6300 Calorimeter. Elemental concentrations were measured by Inductively Coupled Plasma (ICP) analysis, with an ICAP6300 ICP-OES, according to methods NEN 6963 and NEN 6966. Elements F, Cl and Br were dissolved in water, and subsequently analysed with a Dionex ICS-2100 (Thermo Scientific) according to method NEN-EN-ISO 10304-1. Mercury was analysed by Cold vapour Atomic Fluorescence Spectroscopy (AFS).

2.2 Torrefaction

Torrefaction of contaminated Sorghum and Miscanthus (from Lavrion) was conducted at pilot-scale, in a continuous screw-type reactor (Figure 2).



Figure 2: Pilot-scale screw-type reactor used for torrefaction pre-treatment of contaminated biomass (Sorghum and Miscanthus from Lavrion)

Torrefaction is a process whereby biomass is heated to temperatures between 200 – 300 °C in the absence of oxygen. During the torrefaction process, and depending on the severity, moisture evaporates and components of lignocellulosic biomass are decomposed. Thus it is a common upgrading technique for solid biomass materials to increase the energy density, improve milling characteristics and pneumatic transport which may be important for downstream processes like entrained flow gasification.

Torrefaction of Sorghum was conducted at a temperature of 280 °C, at a feeding rate of 2-3 kg/hr and a target residence time of 30 minutes. Torrefaction of Miscanthus (from the Lavrion site) was conducted at similar conditions: a temperature of 285 °C, feeding rate of 2-3 kg/hr and a target residence time of 30 minutes. In total, including pre-heating time, the apparatus was operated for approximately 7 hours for each torrefaction test.

Samples of the feedstocks and the resulting torrefied material were analysed for element concentrations (including heavy metals), as well as proximate (moisture content, volatile material, mineral matter and heating value) and ultimate (carbon, hydrogen, nitrogen and oxygen) analyses, using methods as described in Section 2.1. Torrefied material was subsequently sent to TUM for use as feedstock for entrained flow gasification experiments.

2.3 Slow Pyrolysis

2.3.1 Lab-scale pyrolysis

Conventional lab-scale slow pyrolysis was carried out on sorghum, miscanthus from Kozani, miscanthus from Lavrion, switchgrass and hemp specimens. Biochar samples were produced in a macro thermogravimetric analyzer (LECO TGA 701, Figure 3) under nitrogen flow. This instrument is equipped with 19 ceramic crucibles (volume 20 mL each) with a sensitivity of mass measurement up to 0.1 mg.

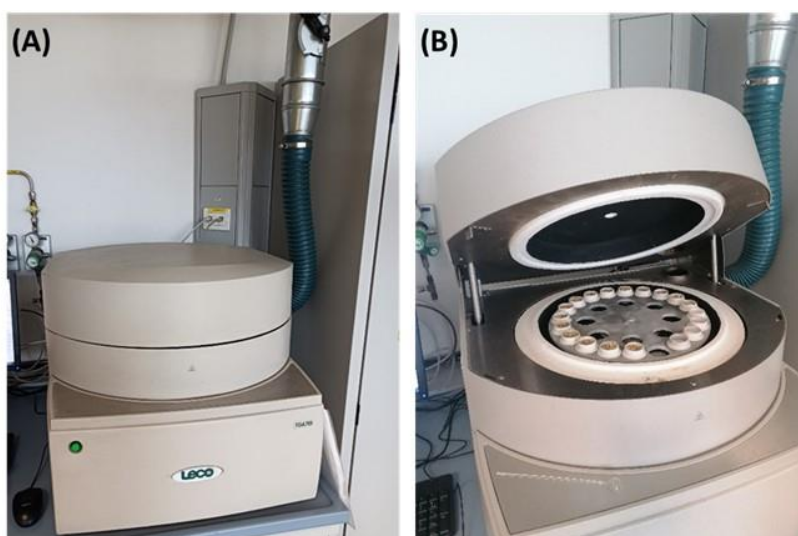


Figure 3: LECO TGA 701 at RE-CORD lab (A) and crucibles loaded with biomass samples (B).

The aim of these lab-scale experiments was to rapidly investigate the char yield and properties at different reaction temperatures and residence times. Specifically, two temperatures (500 and 600 °C) and two residence times at that temperature (30 and 60 min) were adopted as operating conditions. See Table 2 for the detailed set of process parameters.

Table 2: Conventional lab-scale pyrolysis process parameters.

Parameter	Value	U.M.
Nitrogen flow	10	L/min
Heating Rate	20	°C/min
Reaction temperature	500-600	°C
Residence time	30-60	min

The produced chars were characterized in terms of inorganic elements concentration and specific surface area, according to the methodology reported in Section 2.3.3.

2.3.2 Pilot-scale pyrolysis

The aim of the pilot-scale experiments was the production of 10 kg of char for its subsequent gasification. 5 kg of char were produced by conventional pyrolysis and other 5 kg by oxidative pyrolysis. To obtain the target amount of char, several replicate tests were carried out. Before each replicate, the feedstock was oven-dried to ensure a correct evaluation of products yields. No other pretreatment was carried out as the received feedstock already met the required specification for feeding, i.e. particle size lower than 8 mm.

Pilot scale production tests were performed in a continuous pyrolysis reactor (SPYRO) coupled with a condensation unit (Figure 4). SPYRO is an auger-type pyrolyzer. The unit can convert approx. 1-3 kg/h of biomass, with process temperature up to 600 °C and residence time in the range 5-60 min.

Solid biomass is introduced into the reactor by a dosing screw; the heat required for the pyrolysis process is provided by three radiative electric heaters along the length of the reactor, which are independently controlled in order to provide an extra degree of flexibility. The temperature feedback for each electric heater is provided through two K-type thermocouples, one monitoring the temperature of the reactor and the other between the heater and the reactor itself. Furthermore, two K-type thermocouples monitor the hot vapours temperature along the reactor. During the operation, sweep gas is fed into the reactor to determine inert (nitrogen) or oxidative atmosphere (nitrogen and air). The rotating speed of the reactor screw can be adjusted to vary the solids residence time, which can range from few minutes up to 1 hour, so that the effect of the latter on the pyrolysis products yield and quality can be investigated. The char is collected by gravity in a sealed vessel, while hot vapours are constantly withdrawn by a fan placed in the cold section, downstream of the condensation unit. Both outlets are heat-traced by independent conductive electric heaters to avoid organics condensation. A hot filter installed at the pyrogas reactor's outlet limits the amount of entrained particulates flowing into in the condensation unit. The latter consists of:

- a tube-in-tube heat exchanger, named the hot condenser, operating up to 120 °C, in which the heavier fraction of the condensed vapours is collected,
- two shell-and-tube heat exchangers, operating respectively around ambient and 0 °C, in which most of the aqueous phase is collected,
- an electrostatic precipitator (ESP),
- a filtration section,
- a fan, which provides the suction for the pyrogas.

Volatiles are separated into a pyrolysis liquid, which is collected in glass bottles, and an off-gas stream composed of permanent gas. Three J-type thermocouples are installed along the pyrogas line to monitor the temperature drop across each condenser. Two pressure transducers are installed, measuring the relative pressures in the reactor and upstream of the blower.



Figure 4: SPYRO pilot unit at RE-CORD experimental area (Scarperia e San Piero, Florence, Italy).

Table 3 reports the operating parameters adopted in the conventional and oxidative experimental runs. The equivalence ratio is defined as the ratio between the injected air and the air needed for complete combustion. The amount of air to be injected for reaching the desired equivalence ratio was calculated from the elemental composition of the feedstock. In each test, the first heating section was set to 150°C in order to control the heating rate, but, being the process carried out in a continuous unit, the heating rate is governed by the screw velocity and by the heaters temperature, and resulted almost doubled with respect to the lab-scale TGA pyrolysis.

Table 3: Operating conditions selected for the pilot-scale production tests.

Parameter	Conventional pyrolysis	Oxidative pyrolysis	U.M.
Equivalence ratio	0	0.06	-
Calculated Heating Rate	40	41	°C/min
Reaction temperature (set temperature of section 2 and 3 of reactor)	600	600	°C
Solids residence time	30 and 60	30 and 60	min

The volumetric composition of the gas species in the pyrolysis permanent gas was evaluated via an online Agilent microGC. After each run, the char and the condensates were collected, and the latter were gravimetrically separated in a funnel to obtain an aqueous and an oil phase.

2.3.3 Analytical methods for characterization of biomass and pyrolysis products

The pyrolysis products yields were evaluated as the ratio of the mass of the product and the mass of the dry feedstock.

The moisture, ash and volatile matter contents were analysed using a Leco Thermogravimetric Analyzer TGA 701. The moisture content was measured at 105 °C following the UNI EN ISO 18134-2 standard, the ash content was measured at 550 °C according to UNI EN ISO 18122, and the volatile matter at 900 °C according to UNI EN ISO 18123. The fixed carbon was calculated according to UNI EN 1860-2, i.e. by difference from moisture, volatiles and ash.

The total carbon (C), hydrogen (H), nitrogen (N) contents were analysed in a Leco TruSpec CHN analyser according to UNI EN ISO 16948. Sulphur content (S) was analysed using a TruSpec S module (LECO, USA) according to ASTM D 4239: samples of about 60–100 mg was weighted on ceramic boats and incinerated at 1350 °C in presence of oxygen to convert sulphur to sulphur dioxide, and quantified for S after a 5 points calibration with a certified reference standard. The oxygen content was evaluated by difference from C, H, N, S and ash concentration.

The concentration of inorganic elements was determined after a mineralization step using an Agilent microwave plasma atomic emission spectrometer (Agilent 4200 MP-AES), previously calibrated with a multielement standard solution. 0.05 g of biochar were weighted. 3 mL of H₂O₂ and 8 mL of HNO₃ were then added to the sample. Sample was then mineralized in a Milestone Start D Microwave Digestor System. HNO₃ at 1% concentration was added to the collected mineralized solution to reach 20 mL in volume.

The specific surface area (BET) of char was determined by N₂ adsorption isotherms in a Quantachrome NOVA 2200E instrument.

2.4 Torwash effluent treatment for separation of metals and humic acids

Following Torwash treatment (at 30L batch scale) and subsequent filtration to separate solids and liquids, the liquid fraction was further processed to separate out humic acids for use as a soil amendment. The fate of the humic substances as well as the heavy metals present in the liquid fraction was also examined. Following humic acid removal, the remaining liquid (and metals therein) is subjected to adsorption testing on biochar samples, including samples generated via slow pyrolysis of the contaminated biomass.

2.4.1 Humic acids separation and the fate of metals

The resulting Torwash liquid fraction is a dark brown colour and rich in organic matter that is removed from the biomass feedstock during treatment. Much of this organic matter is humic substances, including humic acids, which are useful as a soil amendment during plant production. The liquid fraction obtained after Torwash was treated to concentrate humic acids via two methods: 1. Acidification, and 2. Membrane filtration.

Acidification of the effluent involved adjusting the pH of the liquid to pH 1 with nitric acid. This pH adjustment causes the organic matter to precipitate. The liquid fraction was treated with nitric acid and allowed to stand overnight for the organics to precipitate. The precipitate was then filtered from the remaining liquid, and reconstituted with some distilled water and pH adjusted with sodium hydroxide back to the starting pH of the Torwash effluent (pH 5 – 6).

The precipitated organic material, as well as the remaining liquid fraction, were analysed for Total Organic Carbon (TOC) as a proxy for humic substances content. The samples were also analysed for elemental

concentrations, including heavy metals via ICP (as described in Section 2.1). Subsequent detailed analysis of the organic fraction was conducted via resin fractionation [1] based on hydrophobicity and functional groups.

Membrane filtration tests were also conducted to separate the Torwash liquid effluent based on size fractions, to isolate and concentrate the humic substances. A nanofiltration (NF) membrane from Alfa Laval (NF-3838/48, MWCO 1-10 kDa, spiral-wound configuration) was used to concentrate and filter Torwash effluent from treated Sorghum feedstock.

2.4.2 Adsorption of metals onto biochars

Following concentration and removal of organic matter (humic substances) from the Torwash effluent from treated contaminated feedstocks, the remaining liquid fraction (and any metals therein) are subjected to adsorption testing with biochar. Biochar samples (from slow pyrolysis of Sorghum and Miscanthus as part of the GOLD project), as well as other types of biochar, were used as adsorbents in batch, lab-scale adsorption tests. The aim of this testing is to investigate the potential for char samples to adsorb and remove metal contaminants from liquid samples. Concentration of metals in the liquid samples pre- and post-adsorption will be analysed via elemental analysis (ICP, as previously described in Section 2.1).

3 Torwash pre-treatment

Torwash pre-treatment of contaminated biomass was optimized for removal of metals from the solid fraction. In general, Torwash optimization tests showed that similar conditions are required for the treatment of the different types of biomass (sorghum, miscanthus, switchgrass) when targeting metals removal. Namely, a temperature of 200 °C and a pH of 1-2 are optimum for partitioning of heavy metals out of the solid biomass, for all types of biomass investigated.

3.1 Optimization of Torwash conditions

3.1.1 Partitioning of heavy metals

During Torwash pre-treatment, metals can be partitioned out of the solid fraction to the liquid fraction with a low pH (1-2) and a treatment temperature of 200 °C, for all biomass types investigated. The type of acid was also found to be important to the metals partitioning, with organic acid (i.e., citric acid) resulting in a better removal of metals from the solid when compared with inorganic acid (i.e., sulfuric acid). Lower temperatures and higher pH were associated with more metals staying in the solid fraction. These trends are demonstrated with contaminated Sorghum feedstock in the figures below.

The impacts of pH and temperature on metals concentration in the solid fraction of treated Sorghum are shown in (Figure 5) for Al, Fe and Zn and in (Figure 6) for Cd and Pb. Results show that Torwash treatment results in partitioning of some metals from the solids at all conditions, but more metals are removed with decreasing pH (adjusted with citric acid) and with increasing temperature.

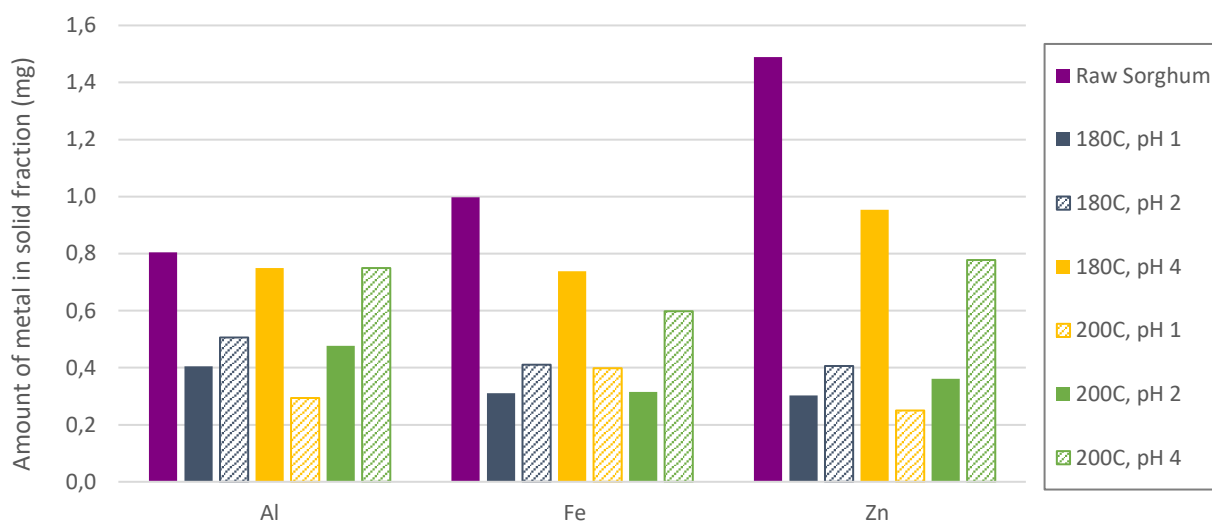


Figure 5: Concentration of Al, Fe and Zn in raw contaminated sorghum and Torwash-treated Sorghum solid fraction at various pH and temperature values; pH adjustment with citric acid.

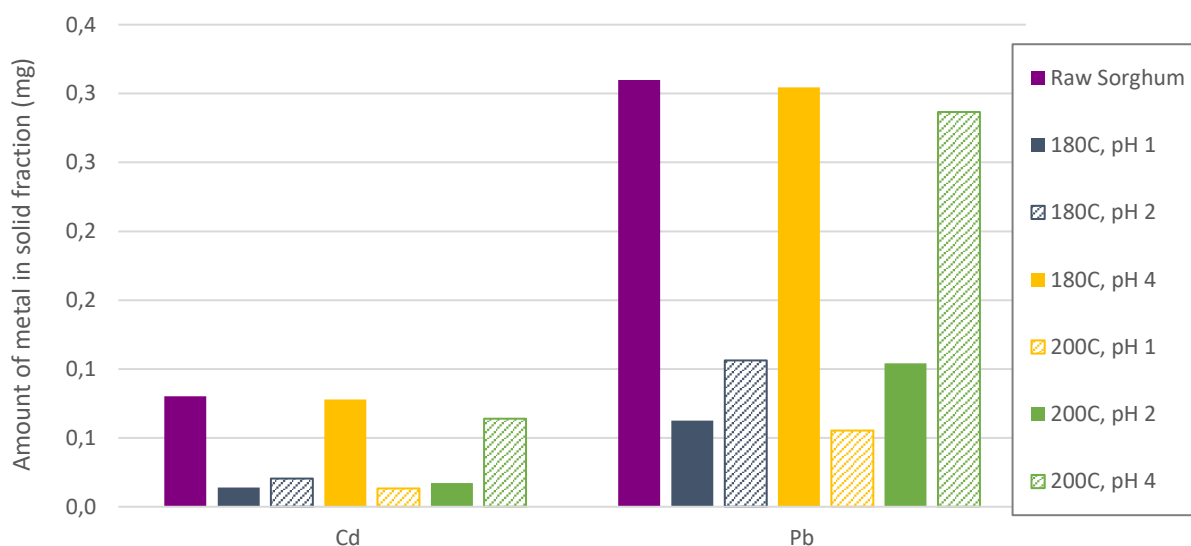


Figure 6: Concentration of Cd and Pb in raw contaminated sorghum and Torwash-treated Sorghum solid fraction at various pH and temperature values; pH adjustment with citric acid.

The impact of pH and acid type was also explored in optimization tests. The impacts for Sorghum are presented here, representative of all feedstocks. Results indicate that the use of citric acid for pH adjustment results in more metals partitioning out of the solids than use of sulfuric acid. This was the case for all metals in the biomass, and representative results for Al, Fe, and Zn in Sorghum are shown in Figure 7. Citric acid partitioning metals to the liquid fraction more than sulfuric acid is likely due to the chelating nature of citric acid, and therefore its ability to solubilize and bind metals.

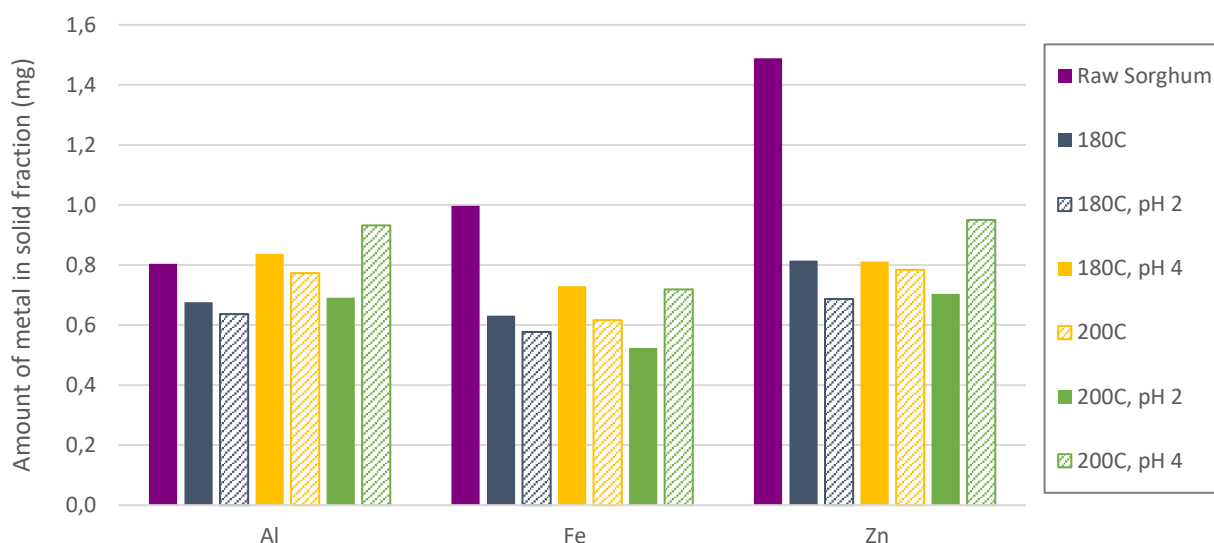


Figure 7: Concentration of Al, Fe and Zn in raw contaminated sorghum and Torwash-treated Sorghum solid fraction at various pH and temperature values with pH adjustment using sulfuric acid.

Figure 8 summarizes the partitioning of heavy metals between the liquid and solid fraction during Torwash, with Sorghum as a representative feedstock. Results are presented for the optimized conditions, i.e., pH 1 with citric acid and a temperature of 200 °C.

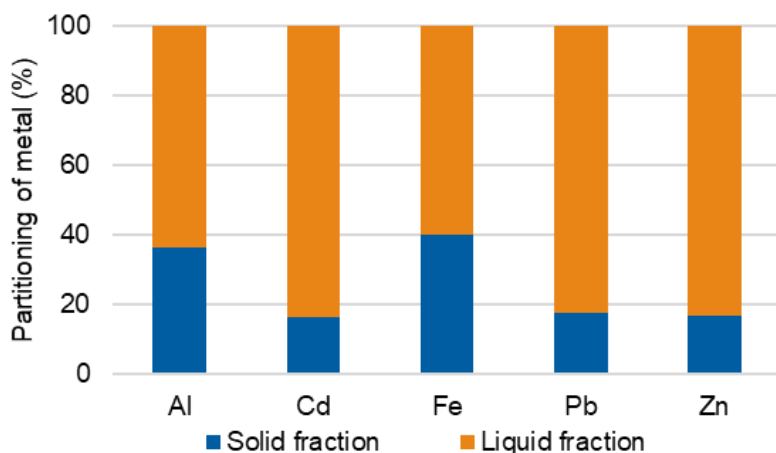


Figure 8: Partitioning of heavy metal contaminants between solid and liquid fractions of Torwash-treated Sorghum contaminated biomass.

3.2 Results of Torwash treatment of contaminated biomass

3.2.1 Sorghum feedstock

Sorghum feedstock, contaminated with heavy metals Al, Cd, Fe, Pb, and Zn, was treated at optimized conditions of 200 °C and a pH of 2 (with citric acid) in batch experiments of 30L volume for each batch to produce solids for gasification tests (Figure 9). A pH of 2 was chosen (instead of pH 1) to limit the amount of citric acid that needed to be used. A total of 6.3 kg of dried solids was produced in 5 batch experiments.



Figure 9: Sorghum solids post-Torwash at 200 °C and pH 2, adjusted with citric acid.

At these conditions, the heavy metals (with the exception of Al) partially end up in the liquid fraction and are thus removed from the solids (Table 4). In particular, Cd, Pb, and Zn partition >50% to the liquid fraction. The Torwash treatment also removes some ash and volatile matter from the solids and increases the heating value and carbon content of the treated solids.

Table 4: Characteristics and metals concentration in Sorghum feedstock and Torwash-treated Sorghum solids (pH = 2 with citric acid and 200 °C temperature).

Component (units)	Raw Sorghum feedstock	Torwash-treated Sorghum solid fraction
Fuel Analysis		
Ash (550 °C) (% db)	8.5	4.3
Ash (815 °C) (% db)	5.3	3.8
Volatile matter (% db)	73.7	65.3
Moisture content (% ar)	8.1	4.3
Higher heating value (MJ/kg db)	17.4	22.4
Carbon (% db)	43	55.7
Nitrogen (% db)	1.0	1.1
Hydrogen (% db)	5.8	5.4
Oxygen (%db)	42.5	32.8
Heavy Metals (mg/kg db)		
Al	480	1300
Cd	15	4.7
Fe	580	310
Pb	140	64
Zn	370	130

3.2.2 Miscanthus feedstocks

To-date, large-scale tests have not been done on Miscanthus feedstocks (to be included in an updated version of this deliverable). Some results of optimization tests for Miscanthus are presented in this section as an interim report.

Miscanthus feedstock (from the Lavrion site) has been optimized for Torwash treatment conditions. The Miscanthus, contaminated with Al, Fe, Ni, and Zn, shows a similar pattern of partitioning to liquids with varying pH and temperature. In particular, Ni displays a strong response to pH, partitioning completely to the liquid phase at a pH of 1 (with citric acid) (Figure 10).

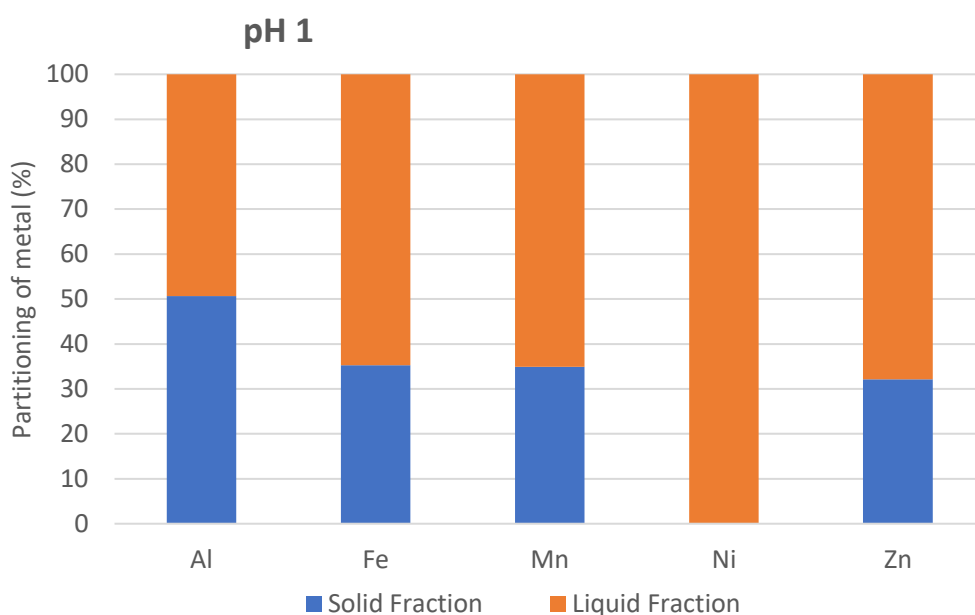


Figure 10: Partitioning of heavy metals in contaminated Miscanthus between the solid and liquid fraction post-Torwash at 200 °C and pH 1 with citric acid.

When the pH is increased to 2 or 4, more of the metals stay in the solid fraction (Figure 11). Therefore, achieving a low pH with citric acid is particularly important for the removal of metals, especially Ni, from contaminated biomass. However, the feasibility of using large quantities of citric acid to scale up this process remain uncertain as citric acid is quite expensive. Therefore, investigations into acid blends and recovery of the citric acid should be investigated.

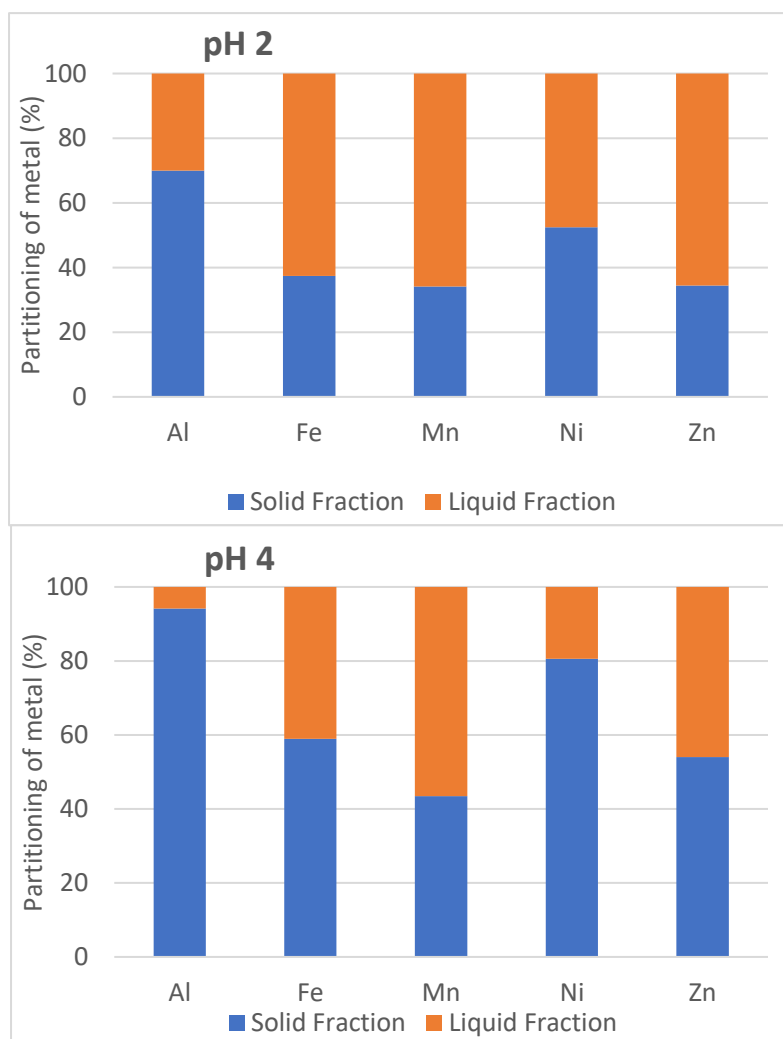


Figure 11: Partitioning of heavy metals in contaminated *Miscanthus* between the solid and liquid fraction post-Torwash at 200 °C and pH 2 and pH 4 with citric acid.

3.2.3 Switchgrass feedstock

To-date, large-scale tests have not been done on Switchgrass feedstock (to be included in an updated version of this deliverable). Some results of optimization tests for Switchgrass are presented in this section as an interim report.

Switchgrass feedstock has been optimized for Torwash treatment conditions. Large-scale tests are pending and will be included in an updated version of this deliverable. The Switchgrass feedstock demonstrates the importance of Torwash treatment temperature on the partitioning of heavy metal contaminants. A temperature of 200 °C was the optimum temperature; at lower temperatures (180 °C), more metals remained in the solid fraction (Figure 12). Nickel shows temperature sensitivity in this case, partitioning entirely to the liquid fraction at a temperature of 200 °C, while over 60% of Ni remains in the solids at a temperature of 180 °C.

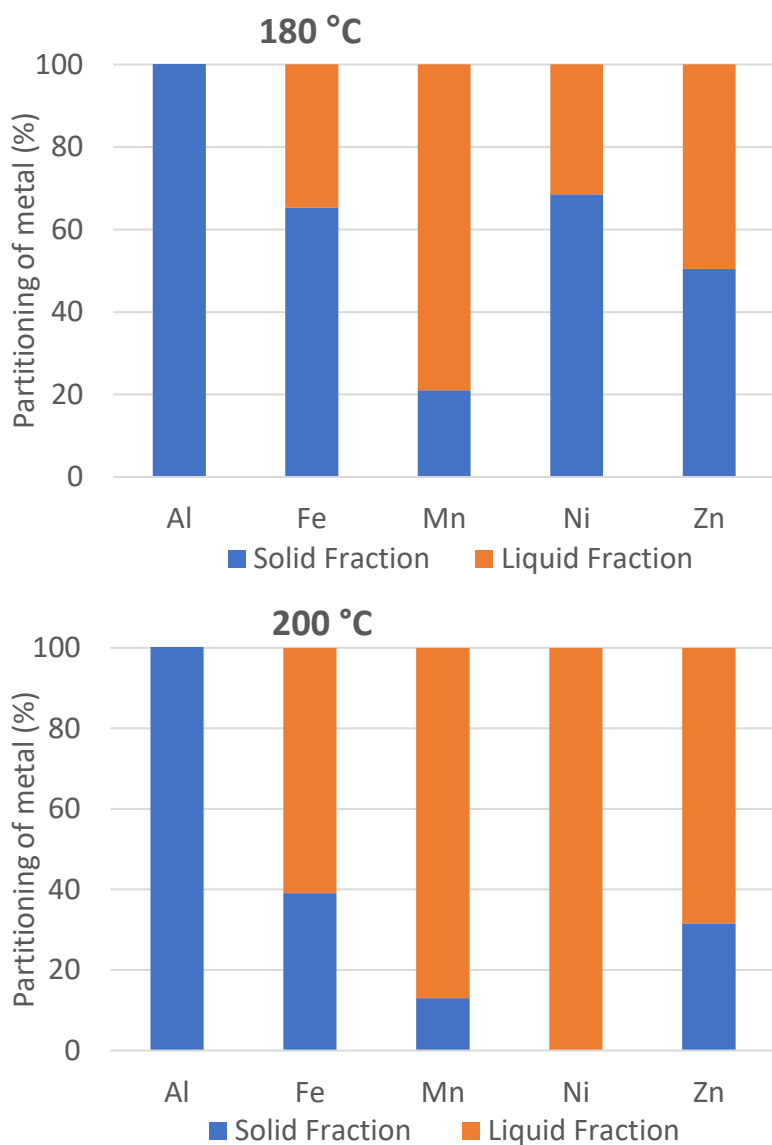


Figure 12: Partitioning of metal contaminants in Switchgrass feedstock between the solid and the liquid fractions after Torwash at 180 °C (top) and 200 °C (bottom), at a pH of 1 with citric acid.

4 Torrefaction pre-treatment

Torrefaction pre-treatment of contaminated Sorghum and Miscanthus (from the Lavrion site) were conducted at pilot scale to generate torrefied solids for gasification tests. *Analysis of the Miscanthus samples (chemical analysis) is still pending and will be included in an updated version of this deliverable.*

4.1 Results of Torrefaction pre-treatment of contaminated biomass

4.1.1 Sorghum feedstock

Contaminated sorghum was torrefied to produce a solid product (Figure 13). The resulting torrefied material had a reduced moisture content and volatile matter content compared to the feedstock. The biomass was

upgraded to a higher energy density (higher heating value), and increased carbon content relative to the feedstock (Table 5).



Figure 13: Raw Sorghum feedstock (left) and torrefied sorghum, following continuous pilot scale torrefaction at 280 °C.

The overall mass yield in the torrefaction process was 54.7%. With respect to heavy metals in the biomass, most of the metals stayed in the solids during torrefaction, with some of the more volatile metals (Cd, Pb, Zn) partially being volatilized and released to the gas phase and thus removed from the solid fraction. Less volatile metals (Al, Fe) stay in the solid fraction and are concentrated in the torrefaction process.

Table 5: Characteristics and metals concentration in Sorghum feedstock and torrefied Sorghum (280 °C temperature).

Component (units)	Raw Sorghum feedstock	Torrefied Sorghum
Fuel Analysis		
Ash (550 °C) (% db)	8.5	18.4
Ash (815 °C) (% db)	5.3	13.4
Volatile matter (% db)	73.7	48.9
Moisture content (% ar)	8.1	3.7
Higher heating value (MJ/kg db)	17.4	21.6
Carbon (% db)	43	52.9
Nitrogen (% db)	1.0	1.4
Hydrogen (% db)	5.8	4.7
Oxygen (%db)	42.5	25
Heavy Metals (mg/kg db)		
Al	136	1451
Cd	14	24
Fe	136	1993
Pb	114	368
Zn	245	567

4.1.2 Miscanthus feedstock

Miscanthus feedstock (from the Lavrion site) was torrefied at pilot scale at 285 °C and a feeding rate of around 3-4 kg/hr. The overall mass yield in the torrefaction process was 56.5%. A picture of the miscanthus material before and after torrefaction is presented in Figure 14.



Figure 14: Raw miscanthus feedstock (left) and torrefied miscanthus following continuous pilot scale torrefaction at 285 °C.

Analytical results of the torrefied *Miscanthus* are pending and will be included in an updated version of this deliverable.

5 Slow Pyrolysis pre-treatment

Slow pyrolysis is one of the foreseen pretreatment methods involved in the first thermochemical conversion route: its aim is to concentrate the biomass contaminants in an intermediate carrier (char) to be further processed via gasification. RE-CORD carried out conventional lab-scale pyrolysis experiments on five different biomass samples and conventional and oxidative pilot-scale experiments on two selected biomasses (sorghum and miscanthus from Lavrion).

5.1 Results of slow pyrolysis pre-treatment

5.1.1 Sorghum feedstock

Around 50 kg of sorghum were shipped to RE-CORD for the slow pyrolysis pretreatment (Figure 15). This material was subjected to lab-scale conventional pyrolysis and pilot-scale conventional and oxidative pyrolysis.



Figure 15: Sorghum sample as received at RE-CORD.

Concerning the lab-scale experiments, char yields were above 30 wt% d.b. for all the investigated reaction conditions. At a reaction temperature of 500 °C the char yields were 33.1 and 32.6 wt% d.b. at 30 and 60 min, respectively. By increasing the temperature to 600 °C the yields decreased to 31.3 wt% d.b. at 30 min and 30.3 wt% d.b. at 60 min. Figure 16 shows the four char samples obtained after the sorghum conventional pyrolysis. The feedstock and char properties are shown in Table 6 and Table 7. Interestingly, the specific surface area of the chars produced at 500 °C was negligible (2 m²/g for both chars obtained at 30 and 60 min), while that of the chars obtained at 600 °C was two orders of magnitude higher and increased with residence time, i.e. reaction severity. At 600 °C, 30 min, this value was 113 m²/g, whereas at 600°C, 60 min reached 155 m²/g.

Table 6: Sorghum properties; w.b.: wet basis, d.b.: dry basis.

Parameter	Value	U.M.
Moisture content	5.7	wt% w.b.
Volatiles	73.0	wt% d.b.
Ash content @ 550°C	9.0	wt% d.b.
Ash content @ 710°C	8.8	wt% d.b.
Fixed carbon	17.9	wt% d.b.
C	43.7	wt% d.b.
H	5.6	wt% d.b.
N	0.9	wt% d.b.
S	0.2	wt% d.b.
O	40.7	wt% d.b.

Table 7: Main metal elements concentration in sorghum and char samples from lab-scale conventional pyrolysis. Values are in mg/kg d.b.; b.d.l.: below detection limit.

Element	Sorghum feedstock	Char 500 °C 30 min	Char 500 °C 60 min	Char 600 °C 30 min	Char 600 °C 60 min
Al	239	1163	2200	1480	1270
Cd	9	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Fe	235	1208	2870	1634	1269
Mn	71	272	271	277	269
Ni	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Pb	56	265	289	309	259
Zn	194	897	817	1058	933

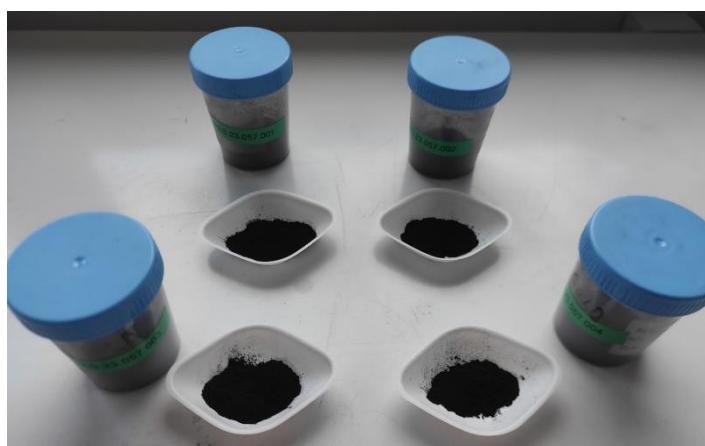


Figure 16: Char samples from lab-scale conventional pyrolysis of sorghum.

Considering that the maximum concentration of metal contaminants such as Pb and Zn was observed at 600°C-30 min and that the specific surface area was greatly enhanced at 600 °C, while having a char yield still above 30 wt% d.b., 600 °C and 30 min were selected as the operating conditions for the pilot scale experiments. 5 conventional and 4 oxidative runs were carried out to produce the required amount of char, which was sent to TUM for gasification, to CERTH for characterization and to TNO for adsorption testing.

Table 8 reports the average mass yields of the pyrolysis products in the conventional and oxidative operation. In the oxidative test, char yield was slightly decreased, aqueous fraction of the condensates increases, oil fraction of condensates halves, permanent gases yield only marginally increases compared to conventional pyrolysis test. Figure 17 depicts the volumetric composition of the latter stream: the oxidative operation led to an increase in CO and CO₂ and a decrease in H₂ concentration. These values have been normalized, removing the detected fractions of nitrogen and oxygen.

Table 8: Sorghum pyrolysis yields.

Product yield (wt%) d.b.	Conventional	Oxidative
Char	32.0	29.3
Aqueous phase	20.8	28.0
Oil phase	5.3	2.1
Gas	42.0	40.6

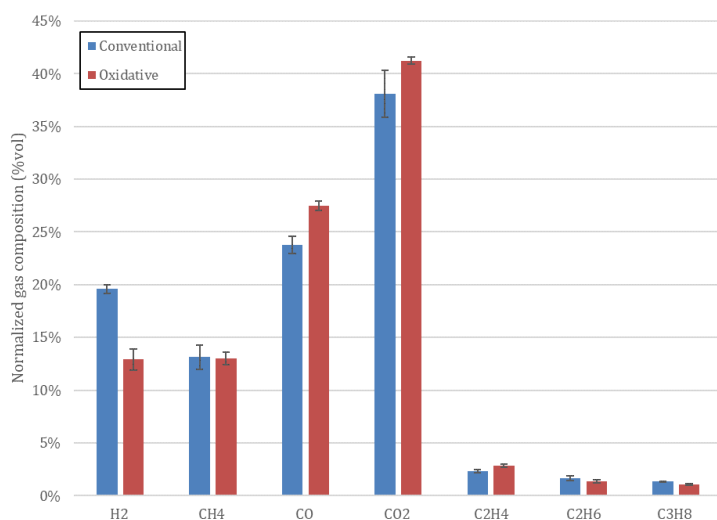


Figure 17: Composition of permanent gas from sorghum pyrolysis.

Figure 18 shows two char samples. Referring to Table 9, no relevant differences in proximate and ultimate analysis of char from conventional and oxidative pyrolysis were observed, and only the surface area presented noticeable differences, with BET specific surface area of char obtained in oxidative atmosphere higher than conventional pyrolysis.

Concerning the content of contaminants in the pyrolysis products (

Table 10), these are generally concentrated in the char. The aqueous phase was almost free of inorganics: the most abundant elements were K and P, which are not shown in the table as they are not considered contaminants. The main contaminants detected in the oil phase were Cd, Pb and Zn. It is worth noting that cadmium concentration in the feedstock was relatively low (9 mg/kg) and this element was not observed in the char; however, it was detected in the oil phase, confirming the volatility of the element [2].



Figure 18: Conventional (left) and oxidative char (right) from sorghum pyrolysis.

Table 9: Properties of sorghum char samples.

Parameter	Conventional	Oxidative	U.M.
Volatiles	9.9	9.9	wt% d.b.
Ash content @ 550°C	25.9	25.7	wt% d.b.
Ash content @ 710°C	25.4	25.1	wt% d.b.
Fixed carbon	64.2	64.4	wt% d.b.
C	68.4	68.0	wt% d.b.
H	1.7	1.7	wt% d.b.
N	1.4	1.5	wt% d.b.
S	0.4	0.5	wt% d.b.
O	2.3	2.7	wt% d.b.
Specific surface area	76	122	m ² /g

Table 10: Concentration of main metal elements in sorghum char and liquid samples. Values are in mg/kg d.b.; b.d.l.: below detection limit.

Element	Conventional Char	Oxidative Char	Conventional Aqueous phase	Oxidative Aqueous phase	Conventional Oil phase	Oxidative Oil phase
Al	2131	903	b.d.l.	b.d.l.	2	9
Cd	b.d.l.	b.d.l.	b.d.l.	b.d.l.	54	74
Fe	1640	1324	b.d.l.	b.d.l.	22	b.d.l.
Mn	275	238	b.d.l.	b.d.l.	b.d.l.	2
Ni	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Pb	351	249	b.d.l.	b.d.l.	23	45
Zn	837	793	b.d.l.	b.d.l.	82	b.d.l.

5.1.2 Miscanthus feedstock

Two samples of miscanthus (1 kg each) were provided by partners for the slow pyrolysis pretreatment: a sample from Kozani (Figure 19) and another one from Lavrion (Figure 20). Both samples were subjected to lab-scale pyrolysis; however, being the latter more contaminated with metals, in agreement with the other WP2 partners, it was selected as the second biomass sample to be treated at pilot-scale.

5.1.2.1 Miscanthus from Kozani

At a reaction temperature of 500 °C the char yields were 31.1 and 30.4 wt% d.b. at 30 and 60 min, respectively. By increasing the temperature to 600 °C the yields decreased to 29.0 wt% d.b. at 30 min and 28.4 wt% d.b. at 60 min. The feedstock and char properties are shown in Table 11 and Table 12. The values of the specific surface area followed a trend that is similar to that observed in the sorghum pyrolysis, but in the miscanthus case higher values were reported. The BET area of the chars produced at 500 °C was rather low (27 and 30 m²/g for the chars obtained at 30 and 60 min respectively), while that of the chars obtained at 600°C was higher and slightly increased with residence time. At 600°C, 30 min, this value was 224 m²/g, whereas at 600°C, 60 min it reached 240 m²/g.



Figure 19: Miscanthus sample from Kozani as received at RE-CORD.

Table 11: Miscanthus (Kozani) properties.

Parameter	Value	U.M.
Moisture content	5.9	wt% w.b.
Volatiles	75.5	wt% d.b.
Ash content @ 550°C	7.9	wt% d.b.
Ash content @ 710°C	7.8	wt% d.b.
Fixed carbon	16.5	wt% d.b.
C	42.7	wt% d.b.
H	6.0	wt% d.b.
N	0.3	wt% d.b.
S	0.2	wt% d.b.
O	42.9	wt% d.b.

Table 12: Concentration of main metals in miscanthus (Kozani) and char samples from lab-scale conventional pyrolysis. Values are in mg/kg d.b.; b.d.l.: below detection limit.

Element	Miscanthus (Kozani) feedstock	Char 500 °C 30 min	Char 500 °C 60 min	Char 600 °C 30 min	Char 600 °C 60 min
Al	161	408	365	432	425
Cd	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Fe	210	525	474	564	584
Mn	92	254	250	286	262
Ni	7	34	32	36	36
Pb	2	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Zn	9	b.d.l.	b.d.l.	b.d.l.	b.d.l.

5.1.2.2 Miscanthus from Lavrion

The char yields of the two miscanthus sample were similar, however, slightly lower values were observed at the maximum reaction severity (600 °C and 60 min) for the Lavrion sample. At a reaction temperature of 500°C the char yields were 31.5 and 30.0 wt% d.b. at 30 and 60 min, respectively. By increasing the temperature to 600 °C the yields decreased to 29.0 wt% d.b. at 30 min and 27.3 wt% d.b. at 60 min. The feedstock and char properties are shown in Table 13 and Table 14. The values of the specific surface area followed the same trend as the other biomasses. The BET area of the chars produced at 500 °C was low (26 and 31 m²/g for the chars obtained at 30 and 60 min respectively), while that of the chars obtained at 600 °C was higher and increased with residence time. At 600 °C, 30 min, this value was 226 m²/g, whereas at 600 °C, 60 min it reached 260 m²/g.



Figure 20: Miscanthus (Lavrion) sample as received at RE-CORD.

Table 13: *Miscanthus (Lavrion) properties.*

Parameter	Value	U.M.
Moisture content	8.8	wt% w.b.
Volatiles	74.5	wt% d.b.
Ash content @ 550°C	5.9	wt% d.b.
Ash content @ 710°C	5.8	wt% d.b.
Fixed carbon	19.6	wt% d.b.
C	42.9	wt% d.b.
H	6.1	wt% d.b.
N	0.4	wt% d.b.
S	0.1	wt% d.b.
O	44.6	wt% d.b.

Table 14: *Main metal elements concentration in miscanthus (Lavrion) and char samples from lab-scale conventional pyrolysis. Values are in mg/kg d.b.; b.d.l.: below detection limit.*

Element	Miscanthus (Lavrion) feedstock	Char 500°C 30 min	Char 500°C 60 min	Char 600°C 30 min	Char 600°C 60 min
Al	163	484	371	514	591
Cd	3	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Fe	149	425	286	398	598
Mn	114	321	255	369	374
Ni	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Pb	26	62	45	58	77
Zn	109	374	304	369	386

Differently from sorghum, the bulk density of Lavrion miscanthus was too low as-received (98 kg/m³) and compaction by pelletization was required to feed the pilot-scale pyrolysis unit. Pellets with a diameter of 6 mm (Figure 21) were obtained with a Smartwood PLT-100 pelletizing machine, increasing the bulk density of the sample to 549 kg/m³.



Figure 21: Pelletized miscanthus (Lavrión) sample.

Taking into account that the maximum concentration of metal contaminants was observed at 600°C-60 min and that the specific surface area was maximum at these conditions, 600°C and 60 min were selected as the operating conditions for the pilot scale experiments. Since the pelletization allowed for an increased biomass flowrate, only 2 conventional and 2 oxidative runs were needed to produce the required amount of char, which was sent to TUM for gasification, to CERTH for characterization and to TNO for adsorption testing.

Table 8 reports the average mass yields of the pyrolysis products in the conventional and oxidative operation. The same char yield was observed, a slight increase in the aqueous fraction and a decrease in the oil fraction of the condensates was measured for the oxidative regime. Permanent gases yield was slightly higher in the conventional case.

Figure 22 depicts the normalized volumetric composition of the produced permanent gases: similar trends as those obtained with the sorghum pyrolysis were observed. The oxidative operation led to an increase in CO and CO₂ and a decrease in H₂ concentration.

Table 15: Miscanthus (Lavrión) pyrolysis yields.

Product yield (wt%) d.b.	Conventional	Oxidative
Char	31.1	31.3
Aqueous phase	24.4	26.5
Oil phase	3.0	2.2
Gas	41.6	40.0

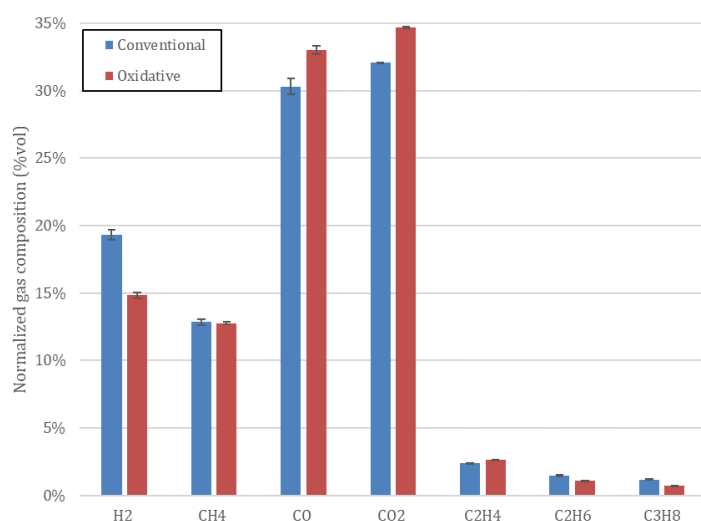


Figure 22: Composition of permanent gas from *Miscanthus (Lavrion)* pyrolysis.

Figure 23 shows two char samples; the pellet shape is partially maintained after the process. Referring to Table 16, as in the sorghum case, no relevant differences in proximate and ultimate analysis of char from conventional and oxidative pyrolysis were observed. If compared to the lab-scale run at 600°C-60 min, the char surface area was lower (51 and 98 m²/g with respect to 260 m²/g). This fact may be mainly due to the pelletization pretreatment. But the same trend of an enhanced porosity is observed as the surface area of the char from the oxidative pyrolysis was higher than that obtained in conventional pyrolysis.

Concerning the inorganic composition of the pyrolysis products (Table 17), the char samples exhibited a higher concentration due to the volatilization of organics during the pyrolysis process. The aqueous phase was almost free of inorganics and traces of Cd (2 mg/kg) were found in the sample from conventional pyrolysis. The inorganics in the oil phase were more concentrated and the main contaminants detected were Cd, Pb, Fe and, to a lower extent, Al, Zn and Mn. In general, the oil phase from the oxidative pyrolysis exhibited a higher concentration of contaminants. This fact can be explained by the higher gas flowrate of the oxidative runs, which may cause a stronger char particles entrainment into the condensation system.



Figure 23: Conventional (left) and oxidative char (right) from *Miscanthus (Lavrion)* pyrolysis.

Table 16: Properties of *Miscanthus (Lavrion)* char samples.

Parameter	Conventional	Oxidative	U.M.
Volatiles	6.9	6.8	wt% d.b.
Ash content @ 550°C	19.8	20.3	wt% d.b.
Ash content @ 710°C	19.7	20.2	wt% d.b.
Fixed carbon	73.3	72.9	wt% d.b.
C	74.5	74.1	wt% d.b.
H	1.7	1.6	wt% d.b.
N	0.9	0.9	wt% d.b.
S	0.1	0.2	wt% d.b.
O	3.0	3.0	wt% d.b.
Specific surface area	51	98	m ² /g

Table 17: Main metal elements concentration in *Miscanthus (Lavrion)* char and liquid samples. Values are in mg/kg d.b.; b.d.l.: below detection limit.

Element	Conventional Char	Oxidative Char	Conventional Aqueous phase	Oxidative Aqueous phase	Conventional Oil phase	Oxidative Oil phase
Al	1214	985	b.d.l.	b.d.l.	6	5
Cd	b.d.l.	b.d.l.	2	b.d.l.	12	55
Fe	1417	1170	b.d.l.	b.d.l.	7	21
Mn	374	330	b.d.l.	b.d.l.	0.4	3
Ni	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Pb	144	143	b.d.l.	b.d.l.	12	47
Zn	456	544	b.d.l.	b.d.l.	1	7

5.1.3 Switchgrass feedstock

1 kg of switchgrass was provided for the lab-scale conventional pyrolysis experiments (Figure 24). The feedstock and char properties are shown in Table 18 and Table 19. At a reaction temperature of 500 °C the char yields were 31.9 and 31.0 wt% d.b. at 30 and 60 min, respectively. By increasing the temperature to 600 °C the yields decreased to 29.4 wt% d.b. at 30 min and 29.0 wt% d.b. at 60 min. The feedstock and char properties are shown in Table 20 and Table 21. The values of the specific surface area followed the same trend, but switchgrass yielded the highest BET values: at 500 °C it was low (36 and 60 m²/g for the chars obtained at

30 and 60 min respectively), while at 600 °C 243 m²/g were obtained at 30 min residence time and 259 m²/g were observed at 60 min.



Figure 24: Switchgrass sample as received at RE-CORD.

Table 18: Switchgrass properties.

Parameter	Value	U.M.
Moisture content	7.1	wt% w.b.
Volatiles	75.3	wt% d.b.
Ash content @ 550°C	8.5	wt% d.b.
Ash content @ 710°C	8.0	wt% d.b.
Fixed carbon	16.2	wt% d.b.
C	41.7	wt% d.b.
H	5.9	wt% d.b.
N	0.3	wt% d.b.
S	0.1	wt% d.b.
O	43.4	wt% d.b.

Table 19: Main metal elements concentration in switchgrass and char samples from lab-scale conventional pyrolysis. Values are in mg/kg d.b.; b.d.l.: below detection limit.

Element	Switchgrass feedstock	Char 500°C 30 min	Char 500°C 60 min	Char 600°C 30 min	Char 600°C 60 min
Al	214	277	392	405	500
Cd	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Fe	311	336	537	516	623
Mn	59	201	125	179	188
Ni	7	20	30	33	40
Pb	2	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Zn	9	b.d.l.	b.d.l.	b.d.l.	b.d.l.

5.1.4 Hemp feedstock

1 kg of hemp was provided for the conventional slow pyrolysis pretreatment (Figure 25), which was carried out at lab-scale. At a reaction temperature of 500 °C the char yields were 31.6 and 31.0 wt% d.b. at 30 and 60 min, respectively. By increasing the temperature to 600 °C the yields decreased to 29.5 wt% d.b. at 30 min and 28.2 wt% d.b. at 60 min. The feedstock and char properties are shown in Table 20 and Table 21. The values of the specific surface area were the lowest among all the lab-scale produced chars. The BET area of the char produced at 500 °C was low (17 and 10 m²/g for the chars obtained at 30 and 60 min respectively), and only a slight increase was observed when increasing the reaction temperature: 49 m²/g were obtained at 600 °C, 30 min and 70 m²/g at 600 °C, 60 min.



Figure 25: Hemp sample as received at RE-CORD.

Table 20: Hemp properties.

Parameter	Value	U.M.
Moisture content	6.0	wt% w.b.
Volatiles	73.9	wt% d.b.
Ash content @ 550°C	8.1	wt% d.b.
Ash content @ 710°C	7.2	wt% d.b.
Fixed carbon	17.9	wt% d.b.
C	41.4	wt% d.b.
H	5.9	wt% d.b.
N	0.9	wt% d.b.
S	0.2	wt% d.b.
O	43.5	wt% d.b.

Table 21: Main metal elements concentration in hemp and char samples from lab-scale conventional pyrolysis. Values are in mg/kg d.b.; b.d.l.: below detection limit.

Element	Hemp feedstock	Char 500°C 30 min	Char 500°C 60 min	Char 600°C 30 min	Char 600°C 60 min
Al	438	1538	2401	1954	1490
Cd	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Fe	438	1534	2208	1764	1429
Mn	104	509	433	534	441
Ni	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
Pb	82	291	353	350	264
Zn	71	331	392	377	281

5.1.5 Lab-scale pyrolysis comparison

Figure 26 depicts a comparison among the results of the lab-scale pyrolysis of the investigated biomasses in terms of char yield and char specific surface (BET). All the char samples follow the same trends: with an increase in reaction severity the yield decreases while the BET surface increases. The latter parameter, however, shows a sharp increase when the reaction temperature is raised from 500 to 600 °C. It is observed that sorghum is the specie leading to the highest char yield, which is above 30 wt% d.b. for all the investigated conditions. Regarding the BET surface, at 500 °C the maximum value is obtained with switchgrass at 60 min

(60 m²/g). At a reaction temperature of 600 °C, switchgrass and the two miscanthus samples show the highest values, ranging from 224 to 243 m²/g at 30 min and from 240 to 260 m²/g at 60 min. On the other hand, sorghum and hemp lead to lower values, i.e. 113 and 155 m²/g for sorghum and 49 and 70 m²/g for hemp.

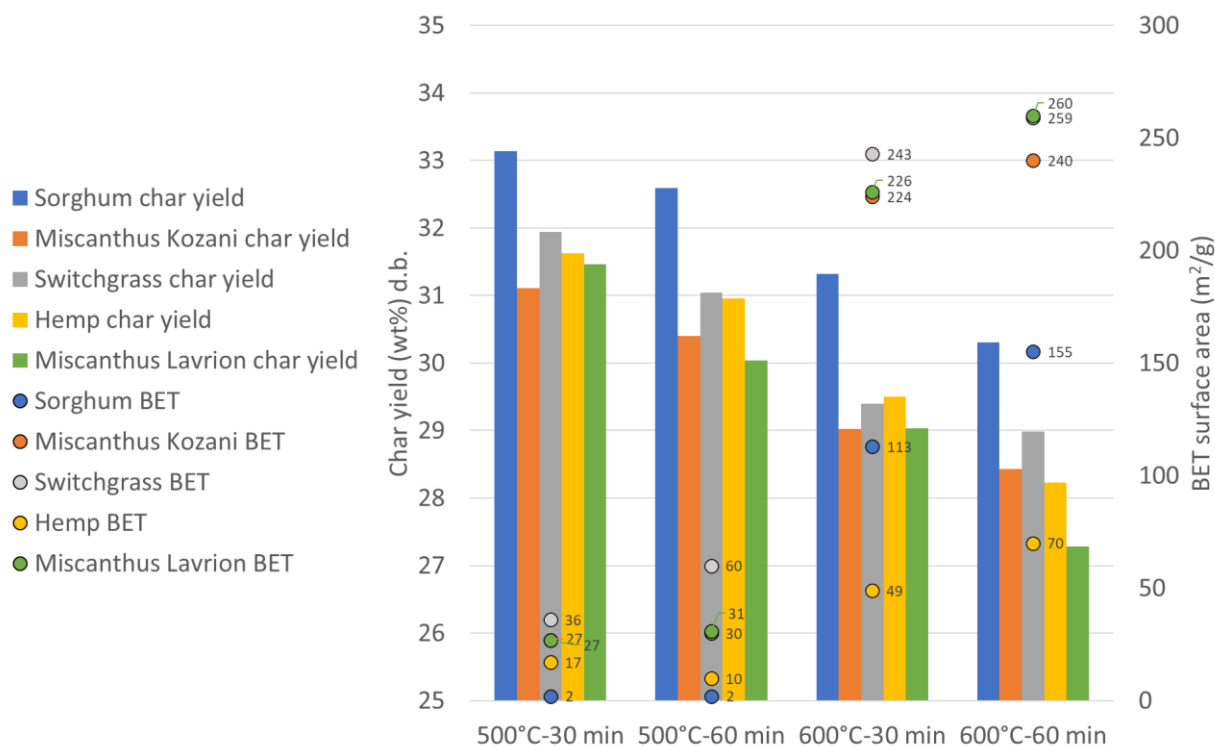


Figure 26: Char yields and specific surface area comparison in lab-scale pyrolysis.

6 Metals concentration and recovery

6.1 Separation of metals from Torwash effluent

Following Torwash treatment of Sorghum and separation of the liquid and solid fraction, the resulting liquid was a rich, dark brown colour indicating a high concentration of natural organic matter (

Figure 27). The acidification and precipitation of this liquid effluent resulted in the separation of a precipitate rich in organics, as measured by Total Organic Carbon (TOC) (Figure 28). Since TOC is used as a representative

measurement of humic acids (our target component), this indicates that the precipitate represents a concentrated form of humic acids.

Furthermore, the precipitate and the remaining liquid fraction were analysed for metals concentrations, and results show that the metals stay in solution and do not precipitate with the organic matter (Figure 29). This is a positive result for the creation of concentrated humic acids to be used as a potential soil amendment.



Figure 27: Liquid effluent from Torwash treatment of contaminated Sorghum.

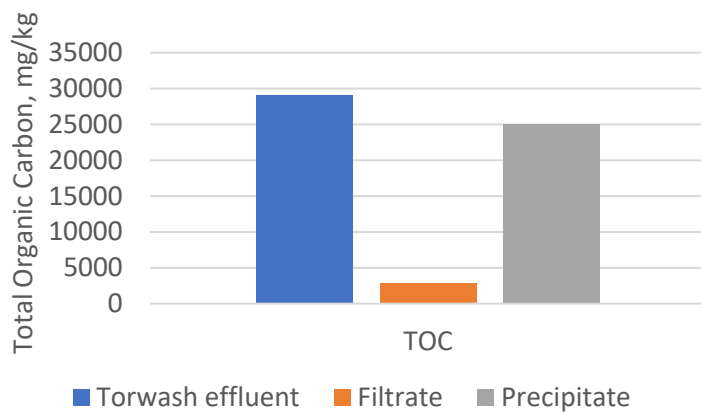


Figure 28: Concentration of organic matter (measured as total organic carbon) in the Torwash effluent of treated Sorghum, the precipitate after acidification and the remaining filtrate.

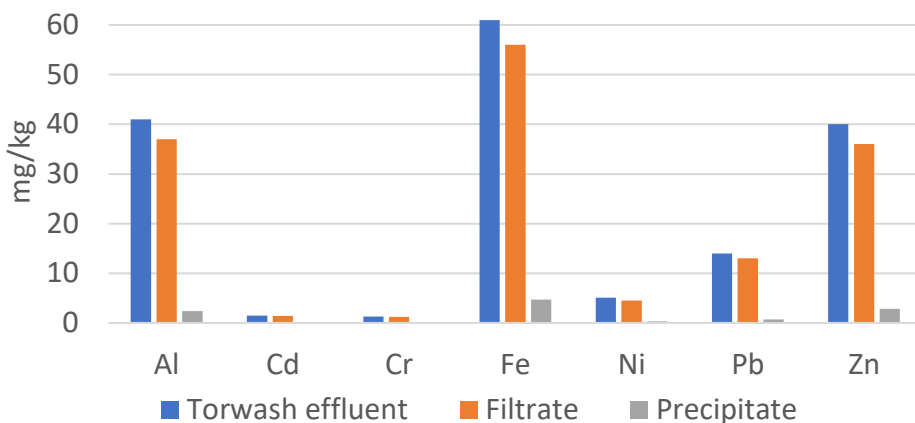


Figure 29: Distribution of heavy metals in Torwash effluent of treated Sorghum, the precipitate after acidification (humic-acid rich) and the remaining filtrate.

6.1.1 Humic substances concentration

Fractionation of the organic matter-rich precipitate to determine the concentration of humic acids (as well as other organic fractions) has not been done yet. This will be included in an updated version of the deliverable.

6.1.2 Adsorption testing

Adsorption of metals in the filtrate after organic removal has not been done yet. This will be included in an updated version of the deliverable.

7 Conclusions and further steps

Pre-treatment of energy crops (Sorghum, Miscanthus, Switchgrass, Hemp) grown on sites contaminated with heavy metals can be achieved by various thermo-chemical processes. This pre-treatment changes the characteristics of the biomass, potentially making it more suitable for downstream processes, including gasification. In general, pre-treatment of the contaminated biomass improves the energy density of the biomass, reduces the moisture and oxygen contents and increases the carbon content.

Torwash pre-treatment was conducted at lab-scale (optimization tests) for Sorghum, Miscanthus and Switchgrass. For Torwash pre-treatment, pH, type of acid, and treatment temperature are important factors for removing metal contaminants from the biomass solids and partitioning them to the liquid phase. In particular, a pH of 1 or 2 with citric acid and a temperature of 200 °C are optimal conditions for pre-treatment of contaminated biomass (Sorghum, Miscanthus, and Switchgrass). The liquid fraction obtained from the Torwash process is rich in organic matter, which can be concentrated and recovered without metal contaminants. Torwash of Sorghum was conducted at larger scale to produce solids for downstream gasification. Larger-scale Torwash of Miscanthus and Switchgrass are pending and will be included in an

updated version of this deliverable.

Torrefaction pre-treatment of contaminated Miscanthus and Sorghum was conducted at pilot scale in a screw-type reactor. Torrefaction at 280 – 285 °C resulted in a product that had improved energy density (higher heating value) and carbon content compared to the feedstock. In general, with torrefaction the heavy metal contaminants mostly stayed in the solid product. More volatile metals, such as Cd, Pb and Zn, were partially released to the gas phase, whereas less volatile metals such as Fe and Al were concentrated in the solid biomass. Mass yield in the torrefaction process was approximately 55 - 57%.

Lab-scale slow pyrolysis pretreatment was carried out on five biomasses. The most promising ones, sorghum and miscanthus from Lavrion, were treated at pilot-scale. Lab-scale conventional pyrolysis was carried out in a thermogravimetric analyser. Four operating conditions were investigated for each biomass (500-600 °C, 30-60 min), evaluating char yield, char specific surface area (BET) and concentration of metal contaminants. Generally, the latter parameter reached maximum values when the reactor temperature was higher, i.e. 600 °C. Similarly, the BET specific surface at 500 °C was lower than that observed at higher temperature.

Pilot runs were carried out in a screw pyrolyzer, investigating conventional and oxidative operation. Reaction temperature and residence time were selected after the results from the lab-scale tests. Due to the low bulk density of miscanthus, this biomass had to be pelletized to feed the reactor. Pilot-scale conventional and oxidative runs produced char with similar proximate and ultimate analyses, but a higher specific surface value was observed in the oxidative case, although lower than that obtained in the lab-scale experiments. Pyrolysis condensates from the pilot experimental campaign were collected and separated in an aqueous and an oil phase and their concentration of metal contaminants was measured. The oil phase exhibited a higher concentration of metal contaminants with respect to the aqueous phase, whose inorganic element concentrations were mostly below the detection limit. The volumetric composition of the permanent gases was evaluated via an online micro-GC analyser: the slow pyrolysis of sorghum and miscanthus from Lavrion yielded a permanent gas stream with very similar composition. Generally, conventional pyrolysis produced a gas phase richer in hydrogen, while in the oxidative case, the share of CO and CO₂ was higher.

This report demonstrates the impact of different pre-treatment processes on the properties of contaminated biomass feedstocks. The use of these pre-treated feedstocks will be explored in downstream entrained flow gasification, with the ultimate goal of producing clean liquid biofuels.

8 References

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