CERESiS: ContaminatEd land Remediation through Energy crops for Soil improvement to liquid biofuel Strategies

D1.7: Integrated solution pathways

H2020-LC-SC3-2018-2019-2020
Contract No: 101006717
October 2022

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 101006717

This project has received funding from the Brazilian Fundação de Amparo à Pesquisa do Estado de Goiás under grant number 202110267000220

This project has received funding from the Canadian New Frontiers in Research Fund under grant number NFRFG-2020-00148 and the Canadian Fond de recherche Société et culture – Québec under grant number 308509

Document control sheet

Project	ContaminatEd land Remediation through Energy crops for Soil improvement to liquid biofuel Strategies
Call identifier	H2020-LC-SC3-2018-2019-2020
Grant Agreement N°	101006717
Coordinator	National Technical University of Athens
Work package	WP1 - Definition of requirements for determining integrated solution pathways
Work package leader	National Technical University of Athens
Related tasks	1.7 – Description and Validation of the integrated solution pathways
Deliverable title	Integrated Solution Pathways
Deliverable nature	Report
Dissemination level	PU
Lead Beneficiary	NTUA
Contributing partners	
Authors	Dimitrios Giannopoulos (NTUA), Ilias Katsifis (NTUA)
Reviewer(s)	Andrea Colantoni (UNITUS), Georgios Vourliotakis (EXE), Athanasios Rentizelas (NTUA)
Version	3.0
Total number of pages	
Issue date	

REVISION HISTORY			
Version	**Date**	**Author(s)**	**Changes made**
0.1	27/10/2022	Dimitrios Giannopoulos (NTUA), Ilias Katsifis (NTUA)	Final draft
0,2	2/11/2022	Andrea Colantoni (UNITUS)	Review
0.3	2/11/2022	George Vourliotakis (EXE)	Review
1.0	3/11/2022	Dimitrios Giannopoulos (NTUA)	Comments addressed
1.1	3/11/2022	Athanasios Rentizelas (NTUA)	2nd Review
2.0	7/11/2022	Dimitrios Giannopoulos (NTUA)	Comments addressed
2.1	14/11/2022	Athanasios Rentizelas (NTUA)	3rd Review – comments from M24 meeting
3.0	17/11/2022	Dimitrios Giannopoulos (NTUA)	Comments addressed

Contents

List of Tables

1 EXECUTIVE SUMMARY

In Deliverable 1.7: "Integrated Solution Pathways" full value chain alternative pathways are defined. These pathways include upstream agricultural methods, energy crop phytoremediation, midstream conversion to liquid biofuels with fast pyrolysis and gasification and downstream methods that include post-processing for decontamination of the biofuel in order to produce a "clean" product ready to be incorporated in catalytic processes (such as Fischer-Tropsch for gasification, or catalytic upgrading for pyrolysis).

Data from existing biofuel standards do not provide a clear threshold for heavy metal concentration in liquid biofuels. However, heavy metal thresholds are provided by EN ISO 17225-1:2021 for solid biofuels, and they are herewith adopted also for liquid biofuels. This value served as the "cornerstone" for forming the alternative value chains formulated under task T1.7. These value chains will be subjected to the life cycle assessment method to examine sustainability, which is included in the scope of WP4.

The alternative value chains are grouped according to their decontamination capacity. Consequently, the first category is defined as the **Full Decontamination Capacity – FDC alternative value chain,** and it refers to heavily contaminated biomass feedstock. Pre/post-treatment processes are assumed to ensure adequate decontamination, towards meeting the EN ISO 17225/2021 thresholds. The second category, **Medium Decontamination Capacity – MDC alternative value chain**, refers to moderately contaminated biomass feedstock that the core conversion processes alone can remove heavy metals. In addition, quantification of the four cases was realized (FDC- Pyrolysis, FDC- Gasification, MDC – Pyrolysis, MDC – Gasification), and contaminant decontamination efficiency was mentioned in each stage, with the information provided from Deliverable 1.3 and additional review of existing literature. The quantification stage assisted in the detailed calculation of the acceptable concentration of each heavy metal in the biomass feedstock.

The results from calculating the "acceptable" contaminant load in each case will set the system boundaries required for the life cycle assessment and the formation of relevant sustainability KPIs for the CERESiS project.

2 DEFINITION OF ALTERNATIVE VALUE CHAINS

This chapter contains the definition of the alternative value chain scenarios, after processing and summarizing the information presented in D1.3 and section 2.1 regarding upstream agricultural activities. The general overview of the value chains defined is presented in fig. 1.

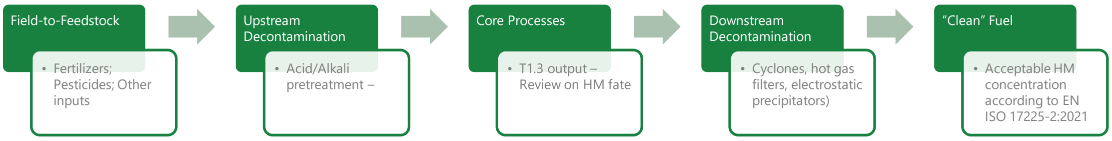


Figure 1 Overview of the value chains defined.

The goal of the alternative value chain scenarios formulated for the needs of the Life Cycle Assessment within the framework of WP4 of the CERESiS project is to produce liquid biofuel that can potentially replace fossil fuels or non-contaminated renewable fuels. Consequently, it is essential to examine existing standards or legislation that limit the heavy metal load in liquid biofuel.

More specifically, Directive 2009/30/EC determines the fuel quality specifications of petrol, diesel, and gas oil. The only heavy metal present in this directive is Pb with a limit of 5 mg/l and only in the case of petrol (not for diesel). Furthermore, there is no data available for heavy metal fuel limits for biofuels in the current standards related to the production, storage, transportation, and use of biofuels (EN590 (biodiesel); EN14214 (FAME); EN228; EN15736 (bioethanol). There is only one single reference in EN 14214, but it is not relevant to heavy metals (it refers to limits for Na+K (combined) and Ca+Mg (combined), both sums being below 5 ppm).

Pulles et al. [1] measured heavy metal concentrations in petrol and diesel fuel from different gas stations throughout Europe (Table 1). The results showed that heavy metal load in transport fuels varied over two orders of magnitude; however, they all remained in the ppb region. According to other literature sources, no general benchmark values have been set for the maximum acceptable level of inorganic compounds [2], [3], [4]. Lehto et al. [5] recommended a threshold of <0.10 wt% for the solid content of bio-oil.

Nevertheless, heavy metal thresholds are provided for solid biofuels in EN ISO 17225-2:2021 (Table 2). Among the various solid biofuels referenced in EN ISO 17225-2, wood pellets have been selected as the most common type of solid biofuel. The most conservative thresholds are adopted, referring to pellets for small scale use (Table 2). These particular values will be used for the needs of conceptualizing the alternative value chain pathways. In other words, this limit will indicate the level of decontamination required (in terms of pre-treatment and post-treatment) in order to acquire a "clean" product ready to be incorporated in catalytic processes (such as Fischer-Tropsch for gasification, or catalytic upgrading for pyrolysis). The concentration units of contaminants for both solid and liquid biofuels are herewith considered as "mg/kg" or "ppm" (which are identical). This is important because the heavy metal uptake of the feedstock might vary significantly, depending on whether the feedstock type is a hyperaccumulator (a plant that can extract large amounts of heavy metals) or normal biomass.

Table 1: Average heavy metal concentration in petrol and diesel throughout Europe (ppb)

Heavy Metal	Average concentration in Petrol (ppb)	Average concentration in Diesel (ppb)
As	0.27	<0.05
Cd	0.26	<0.025
Cr	5.3	8.7
Cu	4.3	6.3
Hg	7.5	2.4
Ni	2.3	0.12
Pb	1.6	0.4
Se	0.18	<0.05
Zn	33	18

Table 2 Heavy metal requirements for wood pellets for small scale use. Source: EN ISO 17225-1:2021

Heavy Metal	Heavy metal requirements for wood pellets for small scale use (mg/kg dry)
As	≤ 1.0
Cd	≤ 0.5
Cr	≤ 10
Cu	≤ 10
Pb	≤ 10
Hg	≤ 0.1
Ni	≤ 10
Zn	≤ 100

2.1 Agricultural processes

An essential part of the biofuel value chain refers to the preliminary stage of biomass production, which involves processes related to agricultural activities. The major goals of these activities are to enhance soil conditions (through e.g. weed extraction and use of pesticides) [6] and to improve biomass properties and yields (through e.g. the use of fertilizers) [7]

The contribution of this value chain stage to the environmental impact is considered substantial. In a study conducted by Gasol et al. 2008[8], it was shown that in a life cycle assessment of the Ethiopian mustard bioenergy system, the use of fertilizer has a significant impact on global warming, freshwater aquatic ecotoxicity, marine aquatic ecotoxicity, and terrestrial ecotoxicity. In terms of indirect impacts, ammonia production for use by the fertilizer industry can also be very emissions-intensive in case fossil NG is used.

Fertilizers can be categorized into two main groups: organic and inorganic. Organic fertilizers are manure, compost, sewage sludge, and crop residues. These fertilizers were a core part of traditional farming that allowed the soil to preserve its beneficial qualities while at the same time providing the necessary nutrients. [9,10]

More specifically, composts can be made from feedstocks such as yard trimmings, food residuals, separated municipal solid waste, and municipal sewage sludge. In addition, a compost blanket can be used in biomass plantation, which is a layer of composted material that is loosely applied. It is then placed on the soil to help with problems such as stormwater runoff and erosion.[11] Research has also shown that composting is a low-cost and easily applied solution for soil remediation. Using a compost blanket, inorganic compounds (heavy metals) can be immobilized in the soil since the chemical composition can be altered through complexation with organic matter. [12,13]

However, due to the high demand for increased crop yields, modern agriculture has shifted attention towards mineral fertilizers, mainly nitrogen and phosphorus fertilizers. Many studies have shown that nitrogen is the primary nutrient that increases crop yield. [14,15] Furthermore, it has been confirmed that above-ground biomass is increased with the addition of nitrogen.[16,17] However, growing concern over the unreasonable use of nitrogen fertilizers has been reported due to nitrogen deposition in the atmosphere. Nitrogen deposition can affect the abundance of species and the plant community composition[18] and decrease biodiversity[19]. Phosphate fertilizers can help promote the maintenance of nutrients in the soil and enhance soil fertility[20–22]. High amounts of phosphate (P) and nitrogen (N) can cause eutrophication by soil erosion caused by rain and wind[7]. Potassium (K) fertilizers can contribute to overall plant function and performance. NPK (or complete) fertilizers contain all three macronutrients (nitrogen, phosphorus, and potassium).[23]

Pesticides are essential to crop production since they can ensure pest control and produce large quantities of food, fiber, etc. Herbicides are a significant subcategory of pesticides, aiding the management of persistent weeds[24]. Although, research has shown that pesticides can pollute water sources and are also toxic to humans and ecosystems. For example, weedkillers such as atrazine can hinder photosynthesis and cause health problems such as cardiac troubles, neuroepithelium degeneration, muscle worsening, and human malignancy[25].

In the context of contaminated land, sites with an industrial past can have specific characteristics that affect the value chain for biofuel production. Land previously used for an industrial purpose can often have inadequacies when compared with agricultural lands, such as low; organic matter content, water holding capacity, cation exchange capacity, and microbial function, as well as the presence of organic or inorganic contaminants and low nutrient concentrations. Importing large quantities of topsoil or clay to create a cap on contaminated sites to produce biofuel crops is cost prohibitive, as is the rising price of granular fertilizer [26,27]. An alternative for contaminated land is the use of waste products with high organic matter content known as organic waste soil amendments (OWSA), which can be used as both a fertilizer and a soil conditioner and thus are preferable to the use of only granular fertilizers [28].

Green waste compost (GWC) was applied at a rate of 500 t/ha by Lord et al. to enhance the growth of the biofuel feedstock crops *phalaris arundinacea, miscanthus, and Salix* on five brownfield sites, each with agronomic challenges [29]. Badmoss et al. found increases in nutrient concentrations, organic matter, and improvements in carbon to-nitrogen ratio following the amendment of soils from a former industrial site containing heavy metals and hydrocarbon contamination with GWC and the residue from the drinking water treatment process at rates of 90 and 180 t/ha [30]. Rodríguez et al. grew white lupin (*Lupinus albus*) in soils taken from a historic Pb/Zn mine which were amended with inorganic sugar production waste, drinking water treatment residue, organic waste from olive mill waste, and paper mill sludge. They found that all the amendments were capable of significantly decreasing extractable Pb, Zn, and Cu concentrations and the bioavailability of Pb and Zn to the lupine plants while also providing necessary growth conditions and plant nutrient requirements, leading to improved plant biomass [31]

From an LCA perspective, the use of ammonium nitrate fertilizer is connected with the energy use and CO_2 emissions from its manufacturing process from methane. In addition, the soil subsequently emits NO_x into the atmosphere. This can be avoided by using organic wastes instead of ammonium nitrate fertilizers, which also reduces NO_x emissions through soil carbon addition. Another issue that should be considered for life cycle assessment is indirect land-use change emissions. If agricultural land is used for biomass plantation, then food crops will be planted on other lands, leading to additional greenhouse gas emissions. However, in the CERESiS project, non-agricultural land is used since the soil is contaminated, so there will be no issue with indirect land-use change. However, some emissions should be expected from perennial crop growth, but this can be minimized with organic waste carbon addition to the soil.

Two studies focusing on life cycle assessment, one from Peters et al. [32] and the other from Han et al. [33], included parameters from upstream methods such as fertilizer, pesticides, herbicides, and water consumption which are all relevant to the agricultural stage of the biofuel value chains. The former studied a simulation of fast pyrolysis of hybrid poplar biomass, and the latter a simulation of fast pyrolysis of corn stover. Furthermore, Espada et al. [6] applied the LCA method for the plant *Festuca arundinacea,* which accumulated Pb. In the study, agriculture and cultivation were taken into account, precisely the type and amount of fertilizer (N, P_2O_5, K_2O), seeds, and diesel fuel used for labor machinery.

2.2 Alternative value chain 1: Sugar to alcohols

According to the information presented in D1.3 and section 2.1 of the present document, figures 2 and 3 present the value chain 1 "Sugar to alcohols", considering a normal and a contaminated feedstock, respectively.

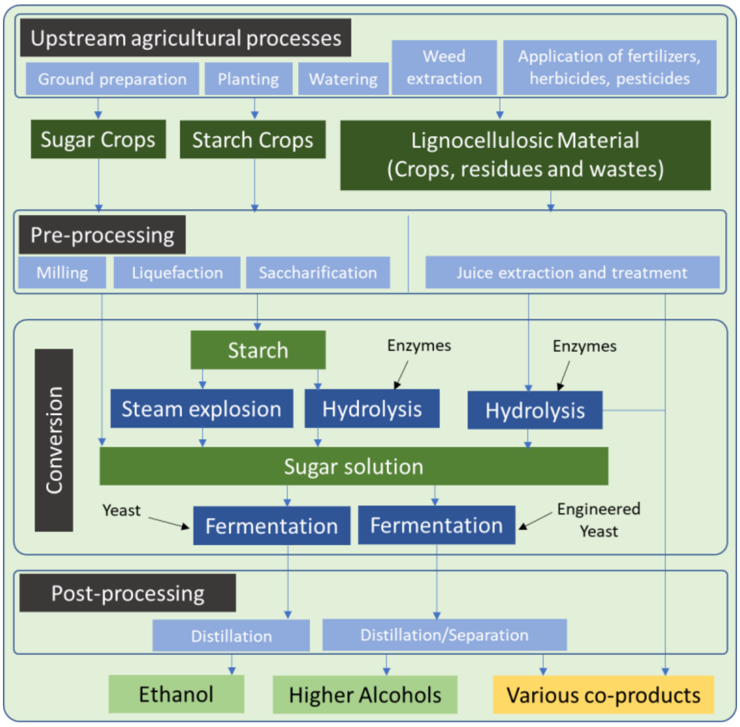
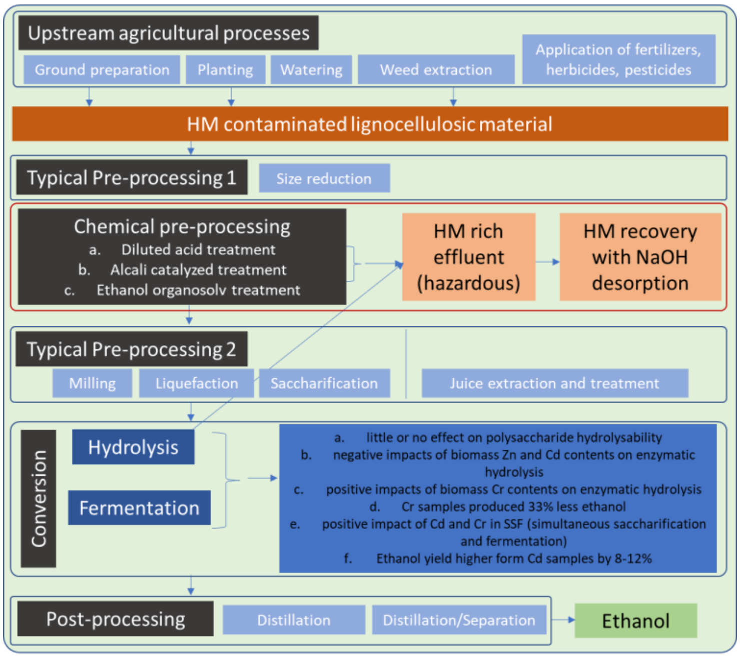


Figure 2 Alternative value chain 1 "Sugar to alcohols". Non-contaminated feedstock.



a. little or no effect on polysaccharide hydrolysability
b. negative impacts of biomass Zn and Cd contents on enzymatic hydrolysis
c. positive impacts of biomass Cr contents on enzymatic hydrolysis
d. Cr samples produced 33% less ethanol
e. positive impact of Cd and Cr in SSF (simultaneous saccharification and fermentation)
f. Ethanol yield higher form Cd samples by 8-12%

Figure 3 Alternative value chain 1 "Sugar to alcohols". Heavy metal contaminated feedstock.

2.3 Alternative value chain 2: Oil crops to biodiesel

According to the information presented in D1.3 and section 2.1 of the present document, figure 4 presents the value chain 2 "Oil crops to biodiesel", considering only non-contaminated feedstock. Unfortunately, as explained in D1.3, there is no information retrieved regarding the effects or possible adaptations regarding the production of biodiesel from HM contaminated feedstocks.

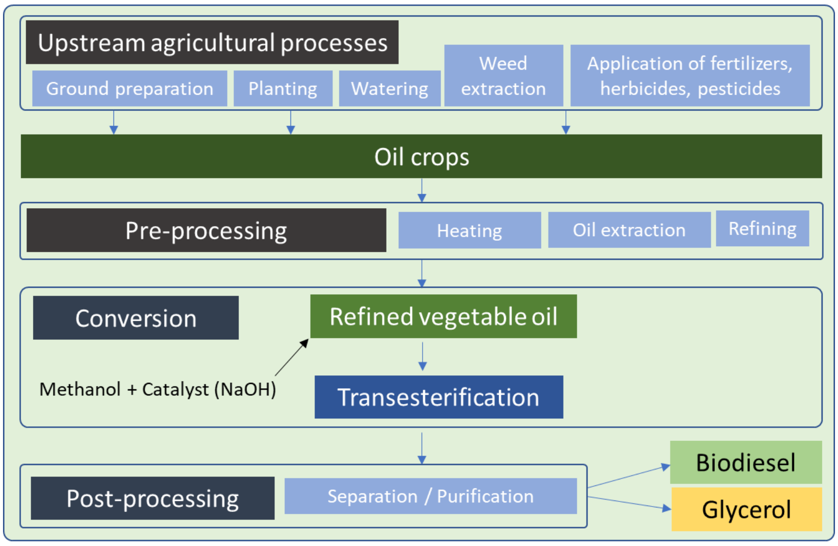


Figure 4 Alternative value chain 1 "Oil crops to biodiesel". Non contaminated feedstock.

2.4 Alternative value chain 3: Biomass to Liquids (BtL) via gasification

According to the information presented in D1.3 and section 2.1 of the present document, figures 5 and 6 present the value chain 3 "Biomass to Liquids (BtL) via gasification", considering a normal and a contaminated feedstock, respectively. The following figures 7 and 8 refer to the case of Supercritical Water Gasification (SCWG), which is one of the core CERESiS conversion technologies.

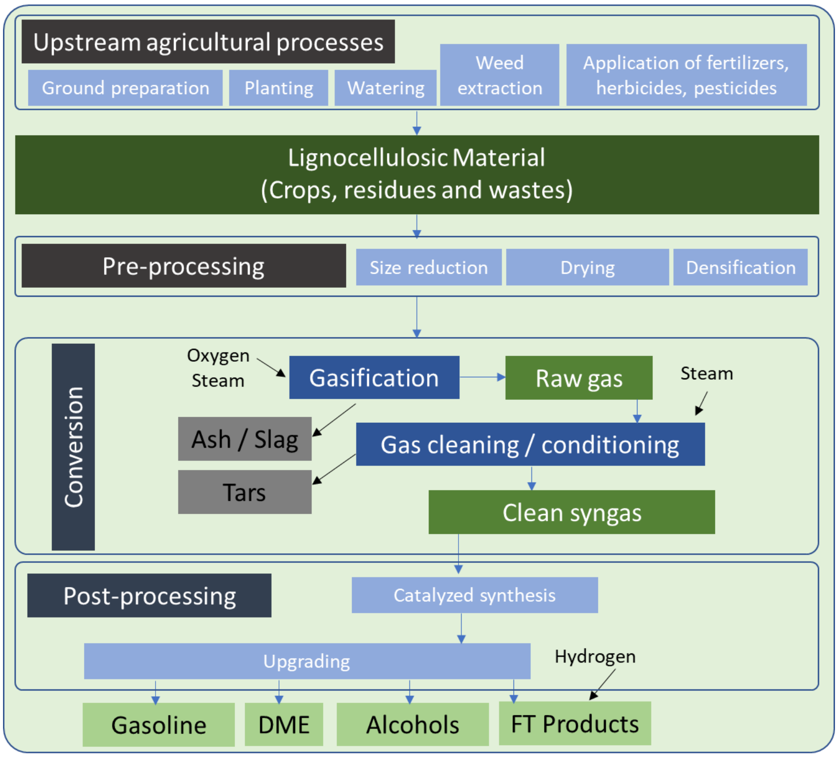


Figure 5 Alternative value chain 3a "Biomass to Liquids (BtL) via gasification". Non contaminated feedstock.

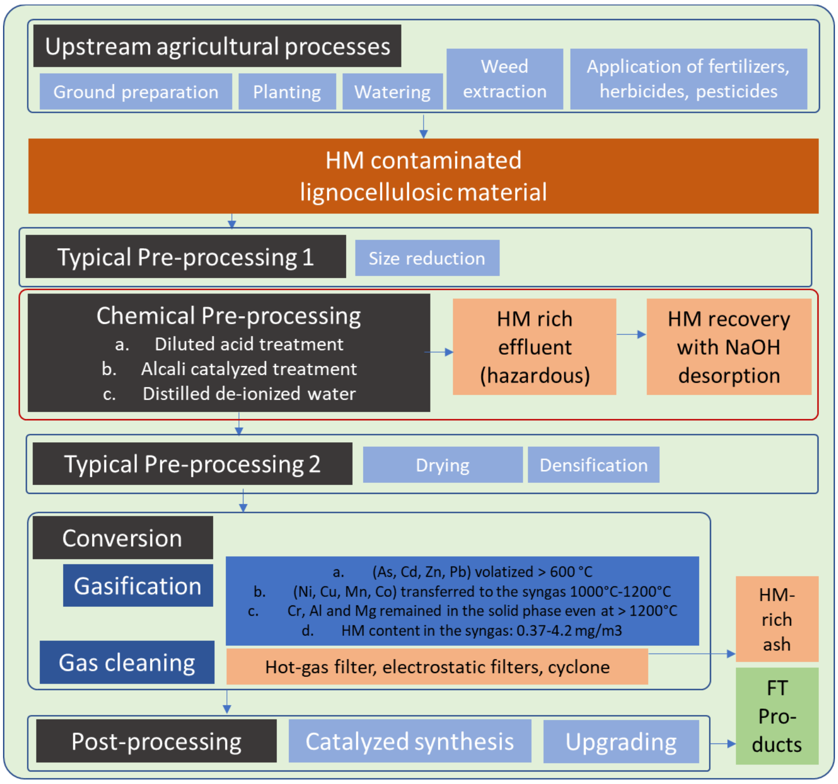


Figure 6 Alternative value chain 3a "Biomass to Liquids (BtL) via gasification". Heavy metal contaminated feedstock.

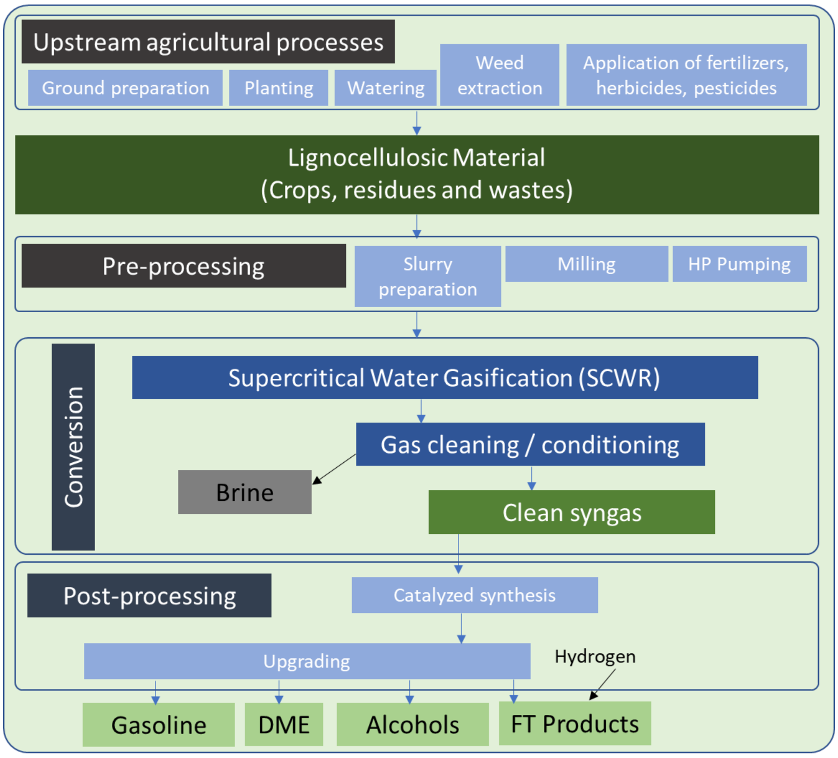


Figure 7 Alternative value chain 3b "Biomass to Liquids (BtL) via SCWG". Non contaminated feedstock.

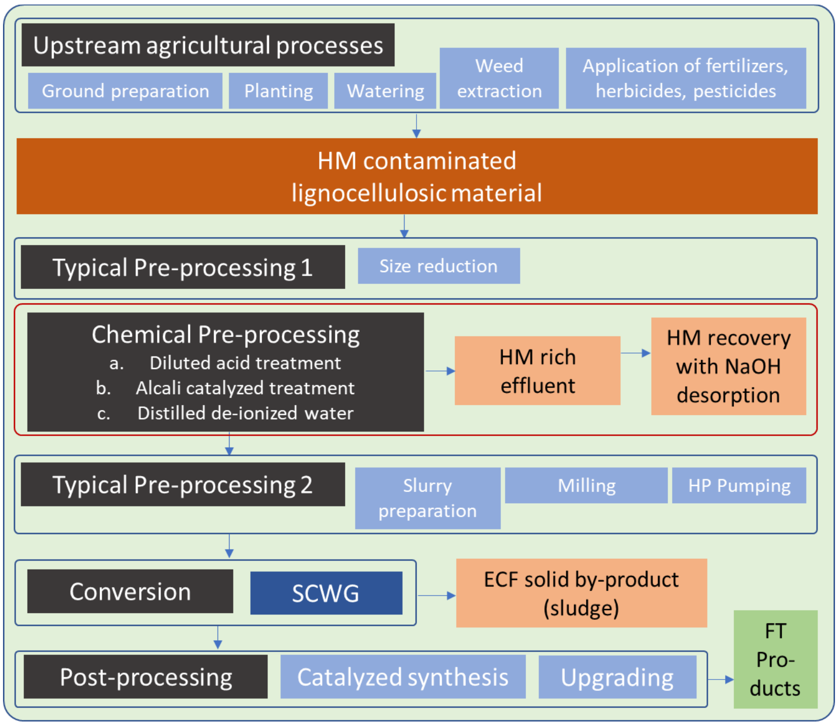


Figure 8 Alternative value chain 3b "Biomass to Liquids (BtL) via SCWG". Heavy metal contaminated feedstock.

2.5 Alternative value chain 4: Biomass to Liquids (BtL) via fast pyrolysis

According to the information presented in D1.3 and section 2.1 of the present document, figures 9 and 10 present the value chain 4 “Biomass to Liquids (BtL) via fast pyrolysis”, considering a normal and a contaminated feedstock, respectively.

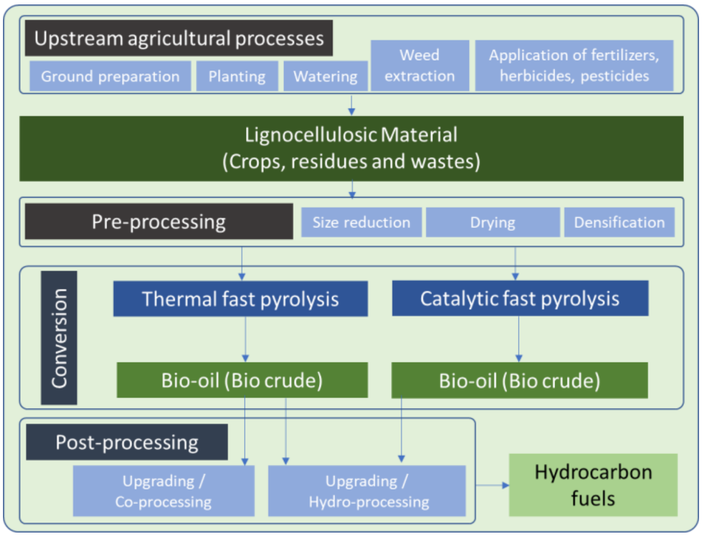
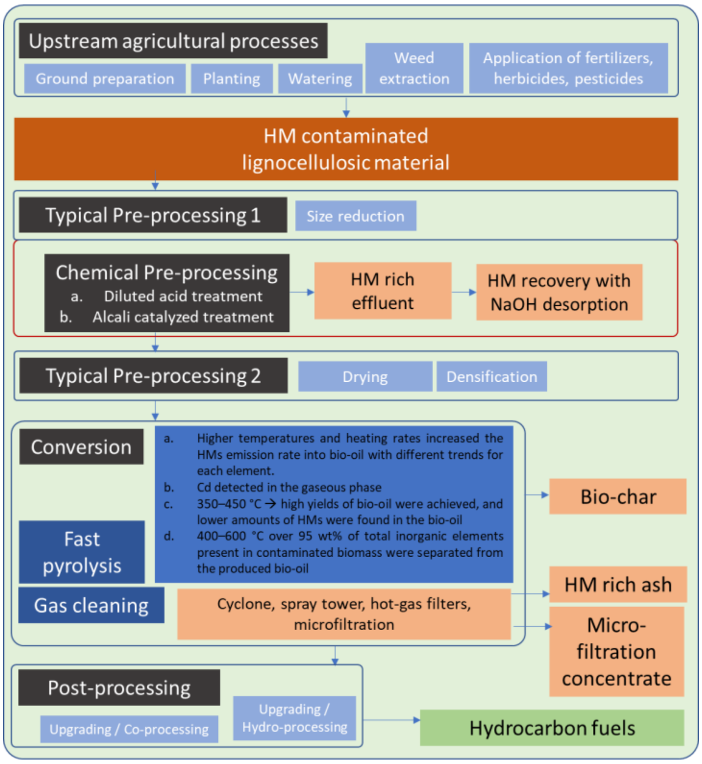


Figure 9 Alternative value chain 4 “Biomass to Liquids (BtL) via fast pyrolysis”. Non contaminated feedstock.



a. Higher temperatures and heating rates increased the HMs emission rate into bio-oil with different trends for each element.
b. Cd detected in the gaseous phase
c. 350–450 °C → high yields of bio-oil were achieved, and lower amounts of HMs were found in the bio-oil
d. 400–600 °C over 95 wt% of total inorganic elements present in contaminated biomass were separated from the produced bio-oil

Figure 10 Alternative value chain 4 “Biomass to Liquids (BtL) via fast pyrolysis”. Heavy metal contaminated feedstock.

3 DISTINCTION OF VALUE CHAINS ACCORDING TO THE RESPECTIVE DECONTAMINATION CAPACITY

According to the level of contaminant load in the biomass feedstock, there can be two alternative value chain scenarios for acquiring “clean” liquid product ready to be incorporated in catalytic processes.

In case the feedstock contains a large amount of heavy metal (i.e., if a hyperaccumulator is planted), then additional processes apart from fast pyrolysis and supercritical water gasification must be added to the value chain to ensure full decontamination. Relevant processes facilitating the extraction of heavy metals are presented in D1.3 can be distinguished to upstream (related to agricultural and cultivation stages and chemical pre-treatment techniques) and downstream methods. This value chain type shall be named **Full Decontamination Capacity (FDC)** alternative value chain scenario (fig.11).

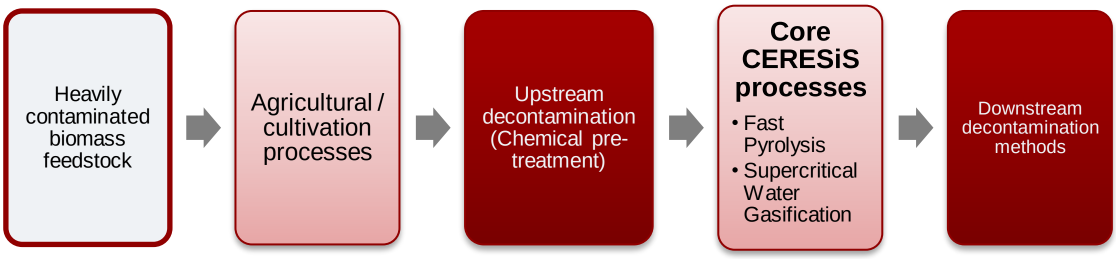


Figure 11: Full Decontamination Capacity Alternative Value Chain

If a manageable contaminant load has contaminated the feedstock, then the core processes of fast pyrolysis and gasification will be sufficient to remove heavy metals and form clean biofuel. Since this value chain contains a moderate level of contamination compared with the FDC value chain, it will be named **Medium Decontamination Capacity (MDC)** alternative value chain scenario (fig. 12).

The level feedstock contamination that decides which of the two types of chains is applicable is estimated in Section 5 of the present deliverable. These two main categories are pictured in the figures below:

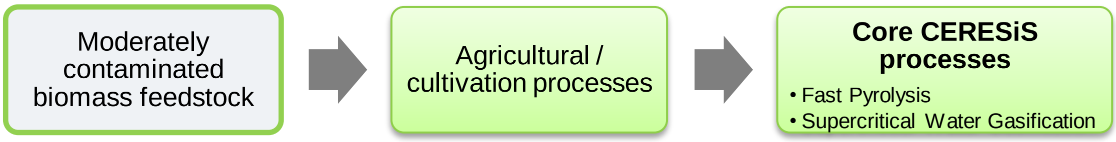


Figure 12: Medium Decontamination Capacity Alternative Value Chain

4 QUANTIFICATION OF DECONTAMINATION CAPACITY

For the CERESiS project, two core processes will be utilized: fast pyrolysis and supercritical water gasification. Each process will correspondingly have two distinct value chains according to the decontamination capacity. However, no data are currently available on the ratio of heavy metals still present in the syngas in the case of supercritical water gasification. Therefore, the present deliverable analyzes the case of conventional gasification, according to the findings of D1.3.

4.1 Upstream decontamination processes

In general, according to literature, wet pre-treatment processes such as chemical methods can facilitate decontamination before the pyrolysis process.

Asad et al. [34] studied the effect that pre-treatment methods such as ethanol organosolv, soda, and dilute acid pretreatments had on non-woody lignocellulosic (tobacco) and woody (birch, willow) biomass that was contaminated with trace elements. In the case of the dilute acid pretreatment, 2% sulfuric acid at a temperature of 170 °C was utilized, and the results showed that 90% of Mn and Zn were extracted in the water effluent. Furthermore, the alkali pretreatment with 15% NaOH resulted in the extraction of metals in the cellulosic pulp in a range of 70-98%. Lastly, the efficiency of organosolv for removing heavy metals was considered "generally low," and therefore, it will not be considered in the alternative value chain scenarios. In another study by Yu et al. [35], the pretreatment method of leaching was used for agricultural, forestry, and energy crop biomass (rice straw, wheat straw, corn stover, switchgrass, miscanthus, etc.). The study concluded that through leaching, the ash content is drastically reduced; however, the extraction of contaminants leads to fuels with complex properties. From the information above, an approximate decontamination efficiency of 90% for pre-treatment is a realistic value for the Pyrolysis-FDC value chain.

4.2 Core and downstream processes

4.2.1 Pyrolysis – FDC (Full Decontamination Capacity)

An extensive literature review of experiments and simulations of the pyrolysis process was carried out in Task 1.3. Consequently, in the table below are cases of pyrolysis and their respective efficiency in removing heavy metals from contaminated biomass.

Table 3: Removal of heavy metals in pyrolysis

Experiment	Contaminant	Type of Pyrolysis	Fraction of contaminant removed
Han et al., 2018 [36]	Cd	Slow	0.657
	Cu		0.735
Zhong et al., 2016 [37]	Cd	Slow & Fast	0.125
	Zn		0.956
	Pb		0.264
Wiinikka et. al 2015 [4]	Zn	Fast	0.968
Liu et. al 2012 [38]	Cu	Fast	0.999
Mullen and Boateng, 2013 [39]	Cu	Fast	0.993
Leijenhorst et. al 2016 [3]	Ni	Fast	1
	Pb		0.399
	Zn		0.405
	Mn		1

What can be derived from the information above is that the values for the pyrolysis efficiency vary depending on the method and the contaminant type. For example, Cu can be removed quite effectively, whereas Cd tends to remain in the bio-oil during the pyrolysis process. However, in order to acquire a decontamination ratio for each metal species, the following assumptions will be adopted:

- Literature on fast pyrolysis is more relevant to CERESiS than slow pyrolysis, since slow pyrolysis is connected to solid biofuel production. Therefore, corresponding fast pyrolysis data will be preferred.
- Extreme values (>0.995) will be rounded to 0.99.
- Cr is assumed to have the behaviour of Pb, according to relevant literature references in D1.3.

The decontamination ratio of pyrolysis to be adopted for the most common heavy metal species are therefore the following:

Cd: 0.167; Pb: 0.333; Cr: 0.333, Zn: 0.95; Ni: 0.99; Cu: 0.99.

Downstream methods for Pyrolysis

After pyrolysis, the downstream processes available can facilitate further decontamination if needed. The gaseous stream (before condensation of bio-oil) can be treated with cyclones and hot gas filtration, while the bio-oil can be purified by microfiltration.

Cyclones

Another option for downstream methods is cyclones capable of reducing particle content. The control efficiency for a conventional cyclone is estimated at 70-90% for PM lager than

2.5 µm [44]. Table 4 also provides corresponding removal efficiency values for multicyclones.

Table 4 Collection efficiencies (in %) of several particulate control devices. Source: [50]

Control device	Removal efficiency (%)			
	< 1 µm	1-3 µm	3-10 µm	> 10 µm
High efficiency ESP	96.5	98.25	99.1	99.5
Multicyclones	11	54	85	95

Hot gas filtration

According to Stals et al. [45], hot gas filtration significantly reduced Zn and Cd. Specifically for Cd, the amount transferred after the hot gas filter was 3.9, 0.7, 3.6 times lower at 350, 450, and 550 °C, respectively. As for Zn, the transfer was decreased by a factor of 1.0 (350 °C), 2.0 (450 °C), and 2.6 (550 °C). Moreover, it was reported that the concentration of K, Ca, P, and Si was reduced by a hot gas filter by 97%, 91%, 98%, and 88%, respectively [46].

Microfiltration

This method can remove heavy metal char particles less than 10 µm from the bio-oil. [40] Arevalo et al. [41] reported that microfiltration in wastewater that contained Cu, Zn, and Cd had removal efficiencies of up to 80%. Moreover, Liu et al. [42] experimented on removing nanoparticles and heavy-metal ions (Cd, Cr). The results showed that the rejection ratios for composite microfiltration membranes were 99,3%. Finally, a literature review for microfiltration in oily wastewater by Behroozi and Ataabdi [43] featured numerous cases with a removal ratio higher than 95%.

From the information provided by Deliverable 1.2 [40], cyclone and hot gas filtration have been applied to remove char particles before the condensation of bio-oil. Nevertheless, these treatment methods are efficient for solid particles greater than 10 µm, and microfiltration is a feasible alternative.

Considering the alternative value chain FDC with pyrolysis, a conservative assumption for a combination of cyclone/hot gas filter would be a decontamination ratio of 80%. The same conservative value is considered for the microfiltration.

Upgrading process

Bio-oil is usually incompatible with existing infrastructure, due to its high water and oxygen content. Processes like catalytic cracking and hydrocracking require the presence of catalysts that are poisoned from contaminants [47]. According to the literature, which is shown in Table 5 (adapted from Ma et al. [48]), different contaminants have different effects on the performance of iron (Fe) and Cobalt (Co) catalysts.

Table 5 Thresholds (ppm) and level of impact of poisonous substances in Fe and Co catalysts

Poisonous substance	Iron Catalyst		Cobalt Catalyst	
	ppm	**impact**	**ppm**	**impact**
NaCl	100	slight	50	slight
KCl	20	negligible	100	slight
$NaHCO_3$	40	negligible	1000	none
$KHCO_3$	40	negligible	1000	slight
HCl	20	major	20	moderate
HBr	20	major	20	moderate
HF	20	major	-	-
NH_3	200	none	1	moderate
H_2S	0.3	major	1	major
HCN	6	slight	-	-

The impact of contaminants that poison the catalyst on a moderate to major level have values in the range of 0.3-20 ppm. However, these contaminants are not heavy metals, and the literature does not provide sufficient information on catalyst poisoning from heavy metals. Therefore, for this project's scope, the heavy metal thresholds of Table 2 will be assumed for the not upgraded bio-oil entering the relevant catalytic processes. Since all contamination levels of Table 2 are in the "ppm" order of magnitude, no major problems would be expected in terms of catalyst contamination.

4.2.2 Pyrolysis – MDC (Medium Decontamination Capacity)

In this case, the feedstock used in the pyrolysis process will be moderately contaminated. Therefore, the pyrolysis process alone, with the contamination efficiencies presented in Table 3, should be sufficient for reducing the contaminant load at a satisfactory level in the biofuel to be considered "clean."

4.2.3 Gasification – FDC (Full Decontamination Capacity)

In Deliverable 1.3, in a similar fashion to pyrolysis, a couple of cases of decontamination with gasification were considered. These can be seen in the table below

Table 6: Removal of heavy metals in gasification

Gasification	Contaminant	Fraction of contaminant removed
Syc et al., 2011 [2]	Cd	0.1
	Zn	0.75
	Pb	0.82
	Cu	0.85
	Mn	1
	Ni	0.79
Pudasainee et. al 2013 [49]	Cd	0.17
	Pb	0.86
	Ni	0.28

The available data (Table 6) show an agreement of the two sources regarding the decontamination ratios of Cd and Pb, while a difference is observed for Ni. For the case of Ni, a value close to the most conservative value will be adopted.

Adopted values: Cd: 0.167; Ni: 0.33; Zn: 0.75; Pb: 0.85; Cr: 0.85; Cu: 0.85.

Downstream methods/Upgrading for gasification

In conventional gasification, cyclones and electrostatic precipitators (ESPs) are used to remove remaining contaminants in the form of particles from the syngas [2], [49]. According to the efficiency data presented in Table 4, the decontamination efficiencies of 80% and 90% will be adopted for cyclones and ESPs, respectively.

4.2.4 Gasification – MDC (Medium Decontamination Capacity)

For this chain, gasification is the only process that removes contaminants from the syngas since the feedstock used has a medium level of contamination. As mentioned in the Gasification – FDC value chain, the decontamination efficiency will be assumed according to section 4.2.3.

5 CALCULATION OF ACCEPTABLE FEEDSTOCK LOAD FOR EACH HEAVY METAL

For the calculation of acceptable heavy metals load for the MDC value chains, the following equation is used

$$C_{acceptable\_MDC} = \frac{C_{limit}}{1 - a_{pyrolysis\ or\ gasification}}$$

For the FDC value chain:

$$C_{acceptable\_FDC} = \frac{C_1}{1 - c_{microfiltration\ or\ ESP}}, \text{ where}$$

$$C_1 = \frac{C_2}{1 - c_{cyclones}}; C_2 = \frac{C_3}{1 - a_{pyrolysis\ or\ gasification}}; C_3 = \frac{C_{limit}}{1 - b_{pre-treatment}}$$

$C_{acceptable\_MDC}$: Acceptable contaminant load in feedstock (ppm). The maximum value of contaminant concentration in the feedstock, that is expected to lead to product heavy metal concentrations lower than the EN ISO 17225-1:2021 thresholds under the MDC value chain.

$C_{acceptable\_FDC}$: Acceptable contaminant load in feedstock (ppm). The maximum value of contaminant concentration in the feedstock, that is expected to lead to product heavy metal concentrations lower than the EN ISO 17225-1:2021 thresholds under the FDC value chain.

C_{limit}: Adopted limit for contaminant in biofuel for CERESiS according to EN ISO 17225-1:2021 (Table 2).

α: Adopted decontamination for the core processes (percentage of contaminant removed). See sections 4.2.1 and 4.2.3.

b: Adopted pre-treatment (acid/alkali) decontamination (percentage of contaminant removed). See section 4.1.2.

c: Adopted decontamination of downstream processes for CERESiS (percentage of contaminant removed). See sections 4.2.1 and 4.2.3.

The results are summarized in Table 7. The reference for the HM thresholds that define a hyperaccumulator feedstock are also presented in column HFT (Hyperaccumulator Feedstock Thresholds). The results show that the FDC chains are capable of providing a “clean” output even when fed with a feedstock well above the corresponding HFT.

Table 7: Acceptable load ($C_{acceptable}$) in feedstock for each alternative value chain (ppm). *Hyperaccumulator feedstock thresholds - HFT (see D1.3, section 2.1)

	Pyrolysis		Gasification		HFT	
	$C_{acceptable\_MDC}$ (ppm)	$C_{acceptable\_FDC}$ (ppm) (=250×$C_{acceptable\_MDC}$)	$C_{acceptable\_MDC}$ (ppm)	$C_{acceptable\_FDC}$ (ppm) (=500×$C_{acceptable\_MDC}$)	(ppm)	
Cd	0.6	1.5 × HFT_{Cd}	0.6	3 × HFT_{Cd}	HFT_{Cd}	100
Cu	1000	250 × HFT_{Cu}	65	32.5 × HFT_{Cu}	HFT_{Cu}	1000
Ni	1000	250 × HFT_{Ni}	15	7.5 × HFT_{Ni}	HFT_{Ni}	
Pb	15	3.75 × HFT_{Pb}	65	32.5 × HFT_{Pb}	HFT_{Pb}	
Zn	2000	50 × HFT_{Zn}	400	20 × HFT_{Zn}	HFT_{Zn}	10000
Cr	15	3.75 × HFT_{Cr}	65	32.5 × HFT_{Cr}	HFT_{Cr}	1000

6 CONCLUSIONS

The objective of this deliverable was to define the full alternative value chain scenarios, including upstream, midstream, and downstream processes utilized for energy crops contaminated with heavy metals.

The alternative value chains are formulated according to the contaminant level in the biomass feedstock. The corresponding acceptable load of the feedstock is estimated, so as to acquire a "clean" product ready to be incorporated in catalytic processes (such as Fischer-Tropsch for gasification, or catalytic upgrading for pyrolysis). The acceptable level of feedstock contamination is defined by the equivalent heavy metal thresholds for solid biofuels are provided by EN ISO 17225-1:2021. Therefore, the ISO EN values served as the "cornerstone" for forming the alternative value chains formulated under T1.7.

In order to assume a chain configuration tailored to possible heavy metal loads, two alternative value chains will be considered for each core process (pyrolysis and gasification). In the Medium Decontamination Capacity (MDC) group of chains, only the core process is considered, referring to moderately contaminated biomass feedstocks that the pyrolysis or gasification processes alone can remove heavy metals down to an acceptable level. The Full Decontamination Capacity (FDC) group of chains refers to heavily contaminated biomass feedstock. Upstream and downstream treatment processes are thus assumed, so as to ensure an adequately decontaminated intermediate product, ready to be further processed in terms of catalytic upgrading or transformation towards the final biofuel.

As expected, the FDC value chain allows a more significant amount of heavy metals to be present in the biomass feedstock compared with the MDC value chain, exceeding the heavy metal loads typically carried by hyperaccumulating species. More specifically, in the case of Cd, a heavy metal that tends to stay in the bio-oil after the core processes, with the addition of a pre-treatment and post-treatment stage, the heavy metal tolerance of the FDC chain can be increased in the level of achieving utilization of hyperaccumulating species. Pb input in the FDC chain can exceed the value of 1000 ppm for both core processes.

However, it must be noted that the approach to conceptualizing the value chains is based only in a limited amount of available literature data regarding the fate of heavy metals during the core transformation stages of pyrolysis and gasification. Moreover, the decontamination efficiencies of upstream and downstream methods have also been estimated according to literature. Therefore, the final results acquired can only be considered as estimations and only utilized towards formulating representative value chains, capable of producing a "clean" output under a variety of heavy metal loads carried by possible feedstocks.

The value chains herewith formulated will set the system boundaries needed for the life cycle assessment and the formation of sustainability KPIs for Task 4.3 and 4.4. Additionally, they will provide supporting information for Task 4.2 for supply chain optimization.

7 REFERENCES

1. Pulles, T.; Denier van der Gon, H.; Appelman, W.; Verheul, M. Emission Factors for Heavy Metals from Diesel and Petrol Used in European Vehicles. *Atmos Environ* **2012**, *61*, 641–651, doi:10.1016/j.atmosenv.2012.07.022.
2. Šyc, M.; Pohořelý, M.; Jeremiáš, M.; Vosecký, M.; Kameníková, P.; Skoblia, S.; Svoboda, K.; Punčochář, M. Behavior of Heavy Metals in Steam Fluidized Bed Gasification of Contaminated Biomass. *Energy and Fuels* **2011**, *25*, 2284–2291, doi:10.1021/ef1016686.
3. Leijenhorst, E.J.; Wolters, W.; van de Beld, L.; Prins, W. Inorganic Element Transfer from Biomass to Fast Pyrolysis Oil: Review and Experiments. *Fuel Processing Technology* **2016**, *149*, 96–111, doi:10.1016/j.fuproc.2016.03.026.
4. Wiinikka, H.; Carlsson, P.; Johansson, A.C.; Gullberg, M.; Ylipää, C.; Lundgren, M.; Sandström, L. Fast Pyrolysis of Stem Wood in a Pilot-Scale Cyclone Reactor. *Energy and Fuels* **2015**, 29, 3158–3167, doi:10.1021/acs.energyfuels.5b00174.
5. Lehto, J.; Oasmaa, A.; Solantausta, Y.; Kytö, M.; Chiaramonti, D. Review of Fuel Oil Quality and Combustion of Fast Pyrolysis Bio-Oils from Lignocellulosic Biomass. *Appl Energy* 2014, *116*, 178–190.
6. Espada, J.J.; Rodríguez, R.; Gari, V.; Salcedo-Abraira, P.; Bautista, L.F. Coupling Phytoremediation of Pb-Contaminated Soil and Biomass Energy Production: A Comparative Life Cycle Assessment. *Science of the Total Environment* **2022**, *840*, doi:10.1016/j.scitotenv.2022.156675.
7. Tong, Z.; Quan, G.; Wan, L.; He, F.; Li, X. The Effect of Fertilizers on Biomass and Biodiversity on a Semi-Arid Grassland of Northern China. *Sustainability (Switzerland)* **2019**, *11*, doi:10.3390/su11102854.
8. Gasol, C.M.; Gabarrell, X.; Anton, A.; Rigola, M.; Carrasco, J.; Ciria, P.; Rieradevall, J. LCA of Poplar Bioenergy System Compared with Brassica Carinata Energy Crop and Natural Gas in Regional Scenario. *Biomass Bioenergy* **2009**, *33*, 119–129, doi:10.1016/j.biombioe.2008.04.020.
9. E. Frossard; E. Bünemann; J. Jansa; A. Oberson; C. Feller *Concepts and Practices of Nutrient Management in Agro-Ecosystems: Can We Draw Lessons from History to Design Future Sustainable Agricultural Production Systems?*; 2009;
10. Watson C.A.*; Atkinson, D.; Gosling, P.; Jackson, L.R.; Rayns, F.W. Managing Soil Fertility in Organic Farming Systems. *Soil Use Manag* **2002**, *18*, 239–247, doi:10.1079/sum2002131.
11. EPA USEPA *Stormwater Best Management Practice: Compost Blankets*;
12. Bolan, N.; Kunhikrishnan, A.; Thangarajan, R.; Kumpiene, J.; Park, J.; Makino, T.; Kirkham, M.B.; Scheckel, K. Remediation of Heavy Metal(Loid)s Contaminated Soils - To Mobilize or to Immobilize? *J Hazard Mater* 2014, 266, 141–166.
13. Brown, S.L.; Chaney, R.L. Use of Amendments to Restore Ecosystem Function to Metal Mining-Impacted Sites: Tools to Evaluate Efficacy. *Curr Pollut Rep* 2016, 2, 91–102.
14. Khan, N.A. Response of Mustard to Ethrel Spray and Basal and Foliar Application of Nitrogen. *J. Agronomy & Crop Science* **1996**, 175, 331–334.

15. Guo, J.H.; Liu, X.J.; Zhang, Y.; Shen, J.L.; Han, W.X.; Zhang, W.F.; Christie, P.; Goulding, K.W.T.; Vitousek, P.M.; Zhang, F.S. Significant Acidification in Major Chinese Croplands. *Science (1979)* **2010**, *327*, 1008–1010, doi:10.1126/science.1182570.
16. Liu, W.; Jiang, L.; Hu, S.; Li, L.; Liu, L.; Wan, S. Decoupling of Soil Microbes and Plants with Increasing Anthropogenic Nitrogen Inputs in a Temperate Steppe. *Soil Biol Biochem* **2014**, *72*, 116–122, doi:10.1016/j.soilbio.2014.01.022.
17. Liu, L.; Greaver, T.L. A Global Perspective on Belowground Carbon Dynamics under Nitrogen Enrichment. *Ecol Lett* **2010**, *13*, 819–828, doi:10.1111/j.1461-0248.2010.01482.x.
18. Payne, R.J.; Dise, N.B.; Stevens, C.J.; Gowing, D.J.; Duprè, C.; Dorland, E.; Gaudnik, C.; Bleeker, A.; Diekmann, M.; Alard, D.; et al. Impact of Nitrogen Deposition at the Species Level. *Proc Natl Acad Sci U S A* **2013**, *110*, 984–987, doi:10.1073/pnas.1214299109.
19. Stevens, C.J.; Dise, N.B.; Mountford, J.O.; Gowing, D.J. Impact of Nitrogen Deposition on the Species Richness of Grasslands. *Science (1979)* **2004**, *303*, 1876–1879, doi:10.1126/science.1094678.
20. Selim E.M.; A.S. El-Neklawy; Soad, M.E.-A. Beneficial Effects of Humic Substances Ferrtigation on Soil Fertility to Potato Grown on Sandy Soil. *Aust J Basic Appl Sci* **2009**, *3*, 4351–4358.
21. Demirsoy, L.; Demirsoy, H.; Balci, G. *DIFFERENT GROWING CONDITIONS AFFECT NUTRIENT CONTENT, FRUIT YIELD AND GROWTH IN STRAWBERRY*; 2012; Vol. 44;.
22. Mehrunisa, M.; Jamro, G.M.; Noor-un-Nisa, M.; Memon, K.S.; Akhtar, M.S. *MICRONUTRIENT AVAILABILITY ASSESSMENT OF TOMATO GROWN IN TALUKA BADIN, SINDH*; 2012; Vol. 44;.
23. Fertilizers Europe Types of Fertilizers Available online: https://www.fertilizerseurope.com/fertilizers-in-europe/types-of-fertilizer/ (accessed on 17 September 2022).
24. Abid Subhani; Ayman M. El-ghamry; Huang Changyong; Xu Jianming Effects of Pesticides (Herbicides) on Soil Microbial Biomass - A Review. *Pakistan Journal of Biological Sciences* **2000**, *3*, 705–709, doi:10.3923/pjbs.2000.705.709.
25. Jatoi, A.S.; Hashmi, Z.; Adriyani, R.; Yuniarto, A.; Mazari, S.A.; Akhter, F.; Mubarak, N.M. Recent Trends and Future Challenges of Pesticide Removal Techniques - A Comprehensive Review. *J Environ Chem Eng* **2021**, *9*, doi:10.1016/j.jece.2021.105571.
26. Summersgill, M. Remediation Technology Costs in the UK & Europe; Drivers and Changes from 2001 to 2005. In Proceedings of the Proceedings of the 5th International GeoEnviro Conference; 2006.
27. Ali, A.M.; Habib, A.A.M. Estimation of the Economic Optimum Rates of Nitrogen Fertilizer for Maize Grown in a Calcareous Soil in Combination with Organic Manure Applications. *Commun Soil Sci Plant Anal* **2022**, *53*, 2484–2496, doi:10.1080/00103624.2022.2071933.
28. Larney, F.J.; Angers, D.A. The Role of Organic Amendments in Soil Reclamation: A Review. *Can J Soil Sci* **2012**, *92*, 19–38, doi:10.4141/cjss2010-064.
29. Lord, R.A. Reed Canarygrass (Phalaris Arundinacea) Outperforms Miscanthus or Willow on Marginal Soils, Brownfield and Non-Agricultural Sites for Local,

Sustainable Energy Crop Production. *Biomass Bioenergy* **2015**, *78*, 110–125, doi:10.1016/j.biombioe.2015.04.015.

30. Badmos, B.K.; Sakrabani, R.; Lord, R. A Glass House Trial to Investigate the Impact of Water Treatment Sludge and Green Waste Compost to Enhance the Revegetation of Contaminated Sites. *Arch Agron Soil Sci* **2015**, *62*, 865–876, doi:10.1080/03650340.2015.1093622.
31. Rodríguez, L.; Gómez, R.; Sánchez, V.; Alonso-Azcárate, J. Chemical and Plant Tests to Assess the Viability of Amendments to Reduce Metal Availability in Mine Soils and Tailings. *Environmental Science and Pollution Research* **2016**, doi:10.1007/s11356-015-4287-z.
32. Peters, J.F.; Iribarren, D.; Dufour, J. Simulation and Life Cycle Assessment of Biofuel Production via Fast Pyrolysis and Hydroupgrading. *Fuel* **2015**, *139*, 441–456, doi:10.1016/j.fuel.2014.09.014.
33. Han, D.; Yang, X.; Li, R.; Wu, Y. Environmental Impact Comparison of Typical and Resource-Efficient Biomass Fast Pyrolysis Systems Based on LCA and Aspen Plus Simulation. *J Clean Prod* **2019**, *231*, 254–267, doi:10.1016/j.jclepro.2019.05.094.
34. Asad, M.; Menana, Z.; Ziegler-Devin, I.; Bert, V.; Chalot, M.; Herzig, R.; Mench, M.; Brosse, N. Pretreatment of Trace Element-Enriched Biomasses Grown on Phytomanaged Soils for Bioethanol Production. *Ind Crops Prod* **2017**, *107*, 63–72, doi:10.1016/j.indcrop.2017.05.028.
35. Yu, C.; Thy, P.; Wang, L.; Anderson, S.N.; Vandergheynst, J.S.; Upadhyaya, S.K.; Jenkins, B.M. Influence of Leaching Pretreatment on Fuel Properties of Biomass. *Fuel Processing Technology* **2014**, *128*, 43–53, doi:10.1016/j.fuproc.2014.06.030.
36. Han, Z.; Guo, Z.; Zhang, Y.; Xiao, X.; Peng, C. *Metals Recovery from Biomass*; 2018; Vol. 13;.
37. Zhong, D.; Zhong, Z.; Wu, L.; Ding, K.; Luo, Y.; Christie, P. Pyrolysis of Sedum Plumbizincicola, a Zinc and Cadmium Hyperaccumulator: Pyrolysis Kinetics, Heavy Metal Behaviour and Bio-Oil Production. *Clean Technol Environ Policy* **2016**, *18*, 2315–2323, doi:10.1007/s10098-016-1150-y.
38. Liu, W.J.; Tian, K.; Jiang, H.; Zhang, X.S.; Ding, H.S.; Yu, H.Q. Selectively Improving the Bio-Oil Quality by Catalytic Fast Pyrolysis of Heavy-Metal-Polluted Biomass: Take Copper (Cu) as an Example. *Environ Sci Technol* **2012**, *46*, 7849–7856, doi:10.1021/es204681y.
39. Mullen, C.A.; Boateng, A.A. Accumulation of Inorganic Impurities on HZSM-5 Zeolites during Catalytic Fast Pyrolysis of Switchgrass. *Ind Eng Chem Res* **2013**, *52*, 17156–17161, doi:10.1021/ie4030209.
40. CERTH *CERESiS: ContaminatEd Land Remediation through Energy Crops for Soil Improvement to Liquid Fuel Strategies D1.2: Decontamination and Separation Requirements*;
41. Arévalo, J.; Ruiz, L.M.; Pérez, J.; Moreno, B.; Gómez, M.Á. Removal Performance of Heavy Metals in MBR Systems and Their Influence in Water Reuse. *Water Science and Technology* **2013**, *67*, 894–900, doi:10.2166/wst.2012.620.
42. Liu, X.; Jiang, B.; Yin, X.; Ma, H.; Hsiao, B.S. Highly Permeable Nanofibrous Composite Microfiltration Membranes for Removal of Nanoparticles and Heavy Metal Ions. *Sep Purif Technol* **2020**, *233*, doi:10.1016/j.seppur.2019.115976.

43. Behroozi, A.H.; Ataabadi, M.R. Improvement in Microfiltration Process of Oily Wastewater: A Comprehensive Review over Two Decades. *J Environ Chem Eng* 2021, 9.
44. EPA *Air Pollution Control Technology Fact Sheet EPA-CICA Fact Sheet Cyclones*;
45. Stals, M.; Thijssen, E.; Vangronsveld, J.; Carleer, R.; Schreurs, S.; Yperman, J. Flash Pyrolysis of Heavy Metal Contaminated Biomass from Phytoremediation: Influence of Temperature, Entrained Flow and Wood/Leaves Blended Pyrolysis on the Behaviour of Heavy Metals. *J Anal Appl Pyrolysis* **2010**, *87*, 1–7, doi:10.1016/j.jaap.2009.09.003.
46. Agblevor, F.A.; Besler, S. *Inorganic Compounds in Biomass Feedstocks. 1. Effect on the Quality of Fast Pyrolysis Oils*; 1996;
47. NTUA *CERESiS: ContaminatEd Land Remediation through Energy Crops for Soil Improvement to Liquid Biofuel Strategies D1.3: Assessment of Clean Liquid Biofuel Value Chains*; 2021;
48. Ma, W.; Jacobs, G.; Sparks, D.E.; Todic, B.; Bukur, D.B.; Davis, B.H. Quantitative Comparison of Iron and Cobalt Based Catalysts for the Fischer-Tropsch Synthesis under Clean and Poisoning Conditions. *Catal Today* 2020, *343*, 125–136.
49. Pudasainee, D.; Paur, H.R.; Fleck, S.; Seifert, H. Trace Metals Emission in Syngas from Biomass Gasification. *Fuel Processing Technology* **2014**, *120*, 54–60, doi:10.1016/j.fuproc.2013.12.010.

50. Zevenhoven and Kilpinen. Control of Pollutants in Flue Gases and Fuel Gases. The Nordic Energy Research Programme. 2001. Available at: http://large.stanford.edu/publications/power/references/leep/