

1 Biofuel Production Using Thermochemical Conversion  
2 of Heavy Metal-Contaminated Biomass (HMCB)  
3 Harvested from Phytoextraction Process

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13 **ABSTRACT.** Over the past few decades, bioenergy production from heavy metal-  
14 contaminated biomass (HMCB) has been drawing increasing attention from scientists in  
15 diverse disciplines and countries owing to their potential roles in addressing both energy  
16 crisis and environmental challenges. In this review, bioenergy recovery from HMCBs, i.e.  
17 contaminated plants and energy crops, using thermochemical processes (pyrolysis,  
18 gasification, combustion, and liquefaction) has been scrutinized. Furthermore, the necessity  
19 of the implementation of practical strategies towards sustainable phytoextraction and metal-  
20 free biofuels production has been critically discussed. To meet this aim, the paper firstly  
21 delivers the fundamental concepts regarding phytoremediation approach, and then, reviews

1 recent literature on sustainable phytoextraction of heavy metals from polluted soils.  
2 Thereafter, to find out the possibility of the cost-effective production of metal-free biofuels  
3 from HMCBs using thermochemical methods, the impacts of various influential factors, such  
4 as the type of feedstock and metals, reactor type and operating conditions, and the role of  
5 probable pre-/post-treatment on the fate of heavy metals and the quality of products, have  
6 also been discussed. Finally, based on relevant empirical results and techno-economic  
7 assessment (TEA) studies, the present paper sheds light on pyrolysis as the most promising  
8 thermochemical technique for large-scale electricity and heat recovery from HMCBs.

9 **KEYWORDS:** Biofuel production, Heavy metal-contaminated biomass, Phytoextraction,  
10 Thermochemical conversion, Techno-economic assessment

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# 1 INTRODUCTION

## 2 1.1 Rising bioenergy demands vs. available biofuel feedstocks

3 The energy insecurity and rising environmental issues (i.e. air pollution and GHGs emission,  
4 etc.) resulted from fossil fuels are driving societies to look for sustainable, renewable, clean  
5 and cost-effective energy supply [1-4]. Eminent renewable energy portfolios comprise  
6 biomass, wind energy, solar energy and hydropower. Amongst these options, biomass, as a  
7 sufficiently “green” and carbon neutral energy source, has gained utmost attraction for  
8 biofuel production [3, 5, 6]. Four different feedstock categories can be applied to produce  
9 biofuels, including first generation feedstock (e.g. food crops); second generation feedstock  
10 (e.g. perennial herbaceous and woody plant species, co-called energy crops: willows, poplar,  
11 castor etc.); third and fourth generation feedstock (e.g. macro- and microalgae) [7-11]. Based  
12 on the type of conversion technologies and operating conditions, different biofuel products  
13 can be produced, such as liquid (biodiesel, bioethanol and biobutanol), gaseous (biohydrogen  
14 and biomethane) and solid fuels (pulverized biomass from torrefaction) [7-10, 12].

15 Generally, only 19% of the total energy consumption is supplied from renewable  
16 resources worldwide. However, biomass energy at present contributes up to 9.30% of the  
17 global energy supplies as electricity, heat and transportation fuels [13, 14], and up to 30–50%  
18 of the world’s present energy consumption could potentially be achieved via biomass in 2050  
19 [15]. For instance, the EU and the USA have planned to substitute 10 and 20% of road  
20 transportation fuels with biofuels by 2020 and 2022, respectively [16, 17]. And globally,  
21 current demand of biomass based renewable energy (i.e. 50 EJ y<sup>-1</sup>) is anticipated to become  
22 around double to triple in 2050 [18].

23 On the other hand, ever-growing demand of food with rising population at alarming rate  
24 would limit the availability of arable land for energy crops cultivation, and consequently

1 large-scale biofuel production [14]. Thus, biofuels from arable land based oleaginous or food  
2 crops are not socioeconomically beneficial due to concerns over competing land use, high  
3 food prices and global security [14]. Therefore, contaminated biomass have been widely  
4 investigated as another promising alternative for bioenergy production with a three-fold aim:  
5 (I) producing clean bioenergy and helping global energy demands; (II) mitigating  
6 environmental pollutions towards sustainable phytoextraction process; and (III) solving the  
7 dilemma in food crisis versus biofuel production [19, 20].

## 8 **1.2 Contaminated biomass from phytoextraction processes**

9 Totally, woody biomass or lignocellulosic feedstock has been known as a widely used and  
10 abundantly available source of biomass for biofuel production with yearly supplies of ~200  
11 billion metric tons worldwide [21, 22]. Moreover, biofuels from lignocellulosic biomass  
12 bring various benefits compared to the first generation biomass, such as no competition with  
13 primary food production, higher biofuel yields and lower land requirements [23, 24].

14 Lignocellulosic biomass has been mostly undergone in thermochemical conversion due to  
15 its low ash content and high-quality bio-oil [25]. Yet, plants and crops could be contaminated  
16 owing to their uptake of various pollutants during natural and/or engineered  
17 phytoremediation of polluted environments resulted from diverse anthropogenic activities  
18 [26-29]. Statistically, it has been estimated that more than one-third of the world's terrestrial  
19 resources are contaminated [30] (so-called brownfield sites [31]), however, the real rate of  
20 contaminated lands, plants and crops could be significantly higher even rather than whatever  
21 has been reported so far [32-35]. Recently, it has been reported that the brownfields area is  
22 around 239 M ha<sup>-1</sup> of the world's unexploited soils [36]. For example, heavy metals (HMs),  
23 mineral oils, and polyaromatic hydrocarbons (PAHs) respectively comprise ~35%, 24% and  
24 10% of the total amount of soil contaminants in Europe [37]. Some sources of HMs resulted

1 in contaminating soils are sewage sludge, urban composts, fertilizers, pesticides, car exhausts,  
2 and residues from metalliferous mining or smelting industries [38].

3 Emerging phytoremediation and biosorption techniques are two promising and cost-  
4 effective bioremediation methods over conventional engineering approaches to remediate  
5 contaminated soil and water bodies [39-41]. Phytoremediation technique employs rapidly  
6 growing ligneous/herbaceous plants and energy crops with high HMs accumulation ability in  
7 short rotation coppice [42, 43], while, biosorption uses algae, fungi, etc., for treating  
8 industrial effluent containing high concentrations of HMs [40, 44].

9 So far, phytoremediation has been applied to transfer, degrade, immobilize, or stabilize  
10 different inorganic elements (HMs and alkali-earth-metals) [25, 45, 46], mineral oils,  
11 pathogens (coliforms, fecal coliform), nutrients (nitrogen, phosphorus, sulfur, inorganic  
12 carbon), and organic materials (POPs, PAHs, polychlorinated biphenyls, mineral oils) in both  
13 aqueous and terrestrial environments [47, 48]. Generally, HMs category, including Zn, Cu,  
14 Cd, Pb, Cr, Ni, Fe, etc., refers to naturally occurring or inorganic elements with a high atomic  
15 weight and a density of at least 5 times greater than that of water, plus metalloids bearing  
16 densities  $>5 \text{ g cm}^{-3}$  [49, 50]. The HMs inside plants can possess various forms or molecular  
17 structures including impurities in cellulose, bonds with organic matter, ionic species, defects  
18 in salt or crystal structures, and impurities in sulfate, nitrate, etc. [51]. Inside plants, almost  
19 all HMs, except Fe, Cu, and Al, have been detected along with water-insoluble or cellulosic  
20 structure of biomass, which in turn verifies the accumulation of HMs [51].

21 Phytoextraction is a sub-classification of phytoremediation technique that is used for  
22 transferring inorganic and organic substances from contaminated soil or water body to plants  
23 and partially storing them in the roots and other parts of the plants with various distribution  
24 [42, 52-54]. However, depending on the type of plants and HMs, the distribution of metals  
25 varies significantly among root, shoot and leaves [36, 42, 54]. For willow, as a common

1 example of plant species used for phytoextraction process, Zn and Cd concentrations in  
2 leaves were respectively 5 and 2 times larger than those in stems, while leaves accounted for  
3 approximately 20% of the biomass produced after 3 years [55]. The phytoextraction  
4 processes, i.e. the uptake and accumulation of HMs in plants' body, and bio-waste re-  
5 utilization pathways are shown in **Fig. S1**.

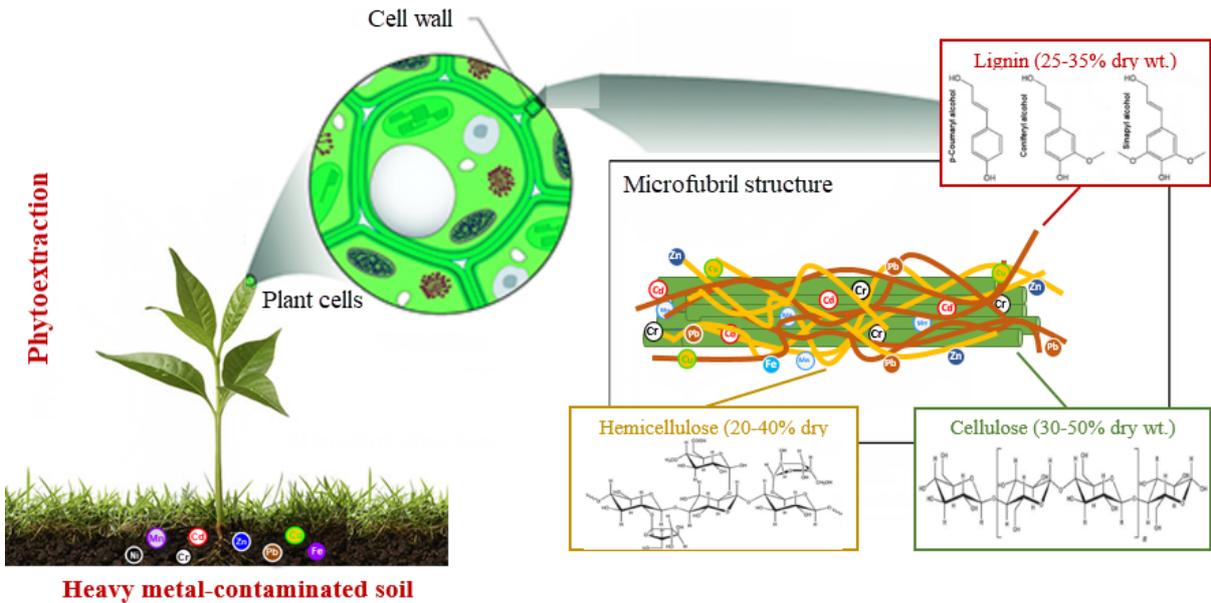
6 Reportedly, highly efficient phytoextraction can be performed by two types of plants such  
7 as hyperaccumulators [56-59] followed by fast-growing species [60]. Hyperaccumulators  
8 characterizes as plants with low biomass production but the high ability of HMs  
9 phytoextraction (1,000 times > typical plants) [61, 62]. Hyperaccumulators are chiefly  
10 herbaceous plants that can take up high amounts of HMs majorly in aboveground tissues  
11 without suffering any damage [56-59]. Some examples of their accumulation abilities are  
12 listed as below: Mn and Zn >10,000 mg kg<sup>-1</sup> dry-wt. [63]; As, Co, Cu, Ni, Se and Pb >1000  
13 mg kg<sup>-1</sup> dry-wt. [64]; and Cd >100 mg kg<sup>-1</sup> dry-wt. [63]. Regarding fast-growing species,  
14 they have lower phytoextraction ability than hyperaccumulators, but their total biomass  
15 production is significantly higher [60]. However, despite the disparity of metal  
16 phytoextraction rate per unit of dry biomass, it has been stated that generally, the total  
17 quantities of metals extracted from soil by these two types of plants to their aboveground  
18 parts are considerably similar [65, 66].

### 19 **1.3 Biomass pretreatment**

20 Generally, lignocellulosic biomass consist of 25–35% lignin, 20–40% hemicellulose and 30–  
21 50% cellulose (dry-wt.) depending on the species [67]. As shown in **Fig. 1**, lignocellulosic  
22 biomass contains three polymeric components, of which hemicellulose and cellulose are  
23 bound together by lignin with a non-biodegradable feature. Such a complex and rigid  
24 structure made cellulose difficult to readily expose to biological and thermochemical reaction

1 media [68, 69]. Besides, the lignin, i.e. the un-fermentable fraction of biomass, has been  
 2 known as one of the main factors for its difficult thermal decomposition in a wide range of  
 3 temperature (160–900 °C) [70]. On the other side, regarding HMCBs, it has been reported  
 4 that cellulose has the potential of binding a wider spectrum of inorganic elements, whilst  
 5 lignin bears the capacity of binding more Fe, Pb and Zn than cellulose (**Fig. 1**) [71-73]. Also,  
 6 the transfer of the aforementioned pollutants, i.e. HMs, POPs, etc., from biomass into the  
 7 products could pose operational, environmental and health risks [74-77]. In terms of  
 8 threatening public health, As, Cd, Cr, Pb, and Hg rank among the priority HMs because of  
 9 their extreme toxicity and carcinogenicity [78].

10



11 **Heavy metal-contaminated soil**

12 **Fig. 1.** Structure and location of the three key fractions of lignocellulosic biomass with an  
 13 approximate speciation of heavy metals. (Based on the explanation of ref. [51, 68, 69, 71-73]  
 14 and a re-arrangement of a figure adopted [79].)

15

16 In order to address the challenges linked to the sophisticated structure of lignocellulosic  
 17 biomass and/or the presence of various contaminants inside biomass, various pretreatment  
 18 methods have been applied, including physical (crushing, milling, drying and torrefaction)

1 [21, 80-82] biological (white-rot fungi, hydrolysis) [83], advanced chemical (acid and  
2 alkaline methods) [84] and hydrochemical pretreatment [85-88]. Furthermore, the application  
3 of novel chemical pretreatment approaches, such as steam explosion, ionic liquids,  
4 eutectic/organic solvents, etc., to fractionate biomass structure (i.e. cellulose from lignin and  
5 hemicellulose) and consequently facilitate the saccharification and/or thermochemical  
6 processes [89-92].

7 The pretreatment techniques can also be implemented with the aim to reduce the transfer  
8 of contaminants (minerals, HMs, POPs, etc.) from feedstocks into the following processes  
9 and/or products, otherwise, the abovementioned contaminants could have poisoned the  
10 conversion/refinery catalysts or degraded the bio-products to some extent [93]. However, few  
11 studies have reported some positive effects of HMs on thermochemical processes, the yield  
12 and quality of biofuels in terms of the distribution of chemical components in the biofuels  
13 [94-98]. Therefore, to enhance the quality and quantity of desired biofuels, the biomass  
14 pretreatments are selected based on the biomass composition and its characteristics, the type  
15 of contaminants, and operating conditions [99, 100]. Advantages and drawbacks of diverse  
16 pretreatment techniques on the quality, yield, stability, and cost of the biofuels produced in  
17 thermochemical and biological processes have been discussed in previous literature [91-93,  
18 101, 102]. For example, Wigley et al. [101] have reported the positive impacts of  
19 pretreatment of a plant using an integrated acid leaching and torrefaction process on the  
20 quantity, quality, stability and total operation costs, respectively, by providing the leaching  
21 reagent, demineralization, and eliminating the further need for biomass rinsing and grinding  
22 costs.

## 1 **2. BROWNFIELDS REMEDIATION TECHNOLOGIES**

### 2 **2.1 Soil remediation and phytoextraction of HMs**

3 Various technologies are applied to remove and/or stabilize HMs from brownfields, including  
4 physical, chemical, biological, and ecological approaches. Physical technologies, such as soil  
5 replacement and thermal desorption approaches [103, 104], which each one has some  
6 limitations, including high workload, costly, and suitable for a small area contaminated soil.  
7 Chemical technologies, including chemical fixation [105, 106], chemical leaching [107],  
8 chemical adsorption [108], electrolytic remediation [108, 109], etc. Chemical technologies  
9 are faster than physical and biological methods (discussed later) in terms of shorter operating  
10 time; however high costs, alteration of soil structure and generation of a number of secondary  
11 pollution deem to be their disadvantages [42]. In contrast, biological technologies, including  
12 microbial remediation, phytoremediation, and integrated approaches, are more  
13 environmentally friendly and cost-effective processes [110-113] that exploit plants and  
14 microorganisms to remove or extract elemental pollutants in various environments including  
15 soils, sediments, wastewater, and sludge, etc. [114-117].

16 Amongst all above-mentioned technologies and approaches, phytoremediation has been  
17 recognized as a green, eco-friendly, safe, effective, and low-cost process for the removal of  
18 HMs with neither adverse effects on the soil structure nor interfering with the ecosystem [118,  
19 119]. As can be seen, **Table 1** shows the removal of HMs from brownfields by  
20 phytoextraction using various plants and the contents of HMs in various matrices involved.  
21 The remediation of brownfields using phytoextraction faces some limitations, including the  
22 long-period cycle, limited use for large-scale applications, as well as instability in term of  
23 species tolerant and treatment efficiency, resulted from the inhibition of the plant growth by  
24 HMs [120, 121], which make it doubtful to be practically commercializable [110, 122]. To  
25 enhance the efficiency and practicability of phytoremediation techniques, more efforts have

1 been made to further develop and promote them as suitable options for the management of  
2 brownfields. For instance, the valorization of biomass produced in phytoremediation in the  
3 form of bioenergy [36, 123] and resource recovery [124, 125], as well as the integration of  
4 phytoextraction with phytostabilization can offer more sustainable and profitable processes  
5 [110, 126]. As an example for the resource recovery and reuse, a pioneering study on the  
6 phytomining of palladium (Pd), using mustard (*Arabidopsis*), *Miscanthus*, and 16 willow  
7 species, demonstrated the promising potential of Pd phytoextracted as nanoparticles and their  
8 comparable catalytic activity achieved to 3% Pd-on-carbon catalysts commercially available;  
9 a subsequent life cycle assessment indicated that such a coupled technology by extracting Pd  
10 for industrial applications got the potential to reduce the overall environmental impacts  
11 associated with the current Pd mining processes [125].

12 As can be seen in **Table 1**, Brunetti et al. [127] have conducted a comparative study  
13 between the phytoremediation potential of frugal *Helichrysum italicum* and mycorrhized  
14 *Helichrysum italicum* by *Septoglomus viscosum* applied for remediation of a land  
15 contaminated by Cd, Cu, Zn, Pb, Cr, Ni, and Co, over a twelve-month period. Results showed  
16 that the non-mycorrhized plant, i.e. *Helichrysum italicum* accumulated greater amounts of  
17 HMs, especially Cr, Cu, Pb, and Zn, in their root system. On the other hand, *Septoglomus*  
18 *viscosum* used in the mycorrhized *H. italicum* study resulted in a better growth of plant in  
19 contaminated soils –likely because of the better soil fertility parameters in the brownfields–,  
20 however, its use decreased the uptake of HMs by the roots, which was possibly resulted from  
21 an exclusion mechanism, thereby reducing the phytoremediation capability of *H. italicum* and  
22 less extraction of the HMs from the contaminated soil (see **Table 1**) [127]. Kocoń and Jurga  
23 [111] studied a three-year micro-plot experiment to investigate the growth possibility and  
24 phytoextraction potential of two energy crops, i.e. *Sida hermaphrodita* and *Miscanthus x*  
25 *giganteus*, cultivated on loamy and sandy soils polluted with Cd, Cu, Ni, Pb, and Zn. In term

1 of the growth possibility, *Miscanthus* demonstrated higher tolerance to concomitant exposure  
2 to HMs and produced around double biomass than *Sida* in all three tested years, irrespective  
3 of soil type. Results revealed that both plants can successfully be grown on moderately  
4 contaminated soil with HMs. Considering the HMs removal potential, *Miscanthus* showed  
5 greater amounts of HMs accumulation (except for Cd), compared to *Sida* (see **Table 1**).  
6 Moreover, both plants absorbed high levels of Zn, lower levels of Pb, Cu and Ni, and  
7 accumulated least Cd. Regarding the effect of the soil type, it was found out that, generally,  
8 in the sandy soil more HMs were taken up (**Table 1**), and plants also showed better yields  
9 [111].

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- 1 **Table 1.** Removal of HMs from brownfields by phytoextraction using various plants and the metal contents in different
- 2 matrices (mg kg<sup>-1</sup> dry wt.)

Soil/sand HMs content			Biomass HMs content			Biomass HMs content			Ref.
Type	Contaminated	Remediated	Type 1	Initial	Accumulated	Type 2	Initial	Accumulated	
Clay-loam soil	Cd 1.40	Cd 0.60	<i>Helichrysum italicum</i>	Cd 1.00	Cd 0.99	Mycorrhized <i>Helichrysum italicum</i>	Cd 1.80	Cd 0.50	Brunetti et al. [127]
	Cu 706.50	Cu 247.80		Cu 12.20	Cu 60.10		Cu 29.80	Cu 48.50	
	Zn 1,999.30	Zn 1,228.80		Zn 35.70	Zn 217.10		Zn 48.50	Zn 129.20	
	Pb 459.70	Pb 251.70		Pb 3.60	Pb 32.70		Pb 6.50	Pb 15.70	
	Cr 4,986	Cr 2,387.50		Cr 13.30	Cr 455.70		Cr 7.80	Cr 109	
	Ni 88.30	Ni 38.50		Ni 10.2	Ni 8.50		Ni 11.60	Ni 6.30	
	Co 18.30	Co 10.60		Co 2.80	Co 1.90		Co 4.80	Co 1.30	
Loam soil	Cd 2.90	–	<i>Miscanthus x giganteus</i>	–	Cd 0.80	<i>Sida hermaphrodita</i>	–	Cd 0.50	Kocoń and Jurga [111]
	Cu 65.70				Cu 8.90			Cu 3.50	
	Zn 1,006.30				Zn 305			Zn 228	
	Pb 592.50				Pb 38.50			Pb 7.80	
Sandy soil	Cd 2.50	–	<i>Miscanthus x giganteus</i>	–	Cd 2.40	<i>Sida hermaphrodita</i>	–	Cd 2.40	Kocoń and Jurga [111]
	Cu 62.30				Cu 12.20			Cu 12.20	
	Zn 845				Zn 937.50			Zn 937.50	
	Pb 427.30				Pb 83.60			Pb 83.60	
Soil	Cd 15.40	–	<i>Miscanthus x giganteus</i> root	–	Cd 1.88	<i>Miscanthus x giganteus</i> aggregate stem and leaves	–	Cd 0.50	Laval-Gilly et al. [36]
	Cu 870				Cu 245.67			Cu 20.81	
	Zn 1,700				Zn 247.33			Zn 145.17	
	Pb 2,200				Pb 214.67			Pb 13.59	
	Cr 410				Cr 44.37			Cr 6.57	
	Ni 71				Ni 12.93			Ni 4.91	
Sediment	Cd 2.40	–	Willow stem	–	Cd 7.30	Willow leaves	–	Cd 11.80	Delplanque et al. [128]
	Cu 33				Cu 3.00			Cu 10.10	
	Zn 228				Zn 285			Zn 412	
	Pb 88				Pb <QL			Pb <QL	
Sandy-loam soil + EDTA	Cd 5.50	–	<i>Sinapis alba</i>	–	Cd 7.93	<i>Trifolium repens</i>	–	Cd 3.27	Kos et al. [129]
	Zn 800				Zn 524.68			Zn 167.99	
	Pb 1,100				Pb 479.71			Pb 434.32	
Sandy-loam soil + EDTA	Cd 5.50	–	<i>Raphanus sativus oleiformis</i>	–	Cd 5.70	<i>Zea Mays cv. Matilda</i>	–	Cd 2.61	Kos et al. [129]
	Zn 800				Zn 402.69			Zn 321.03	
	Pb 1,100				Pb 197.19			Pb 72.80	

3 <QL: below quantification limit

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1 Similarly, a study on the phytoremediation of Cr using young mangrove species, so-  
2 called *Rhizophora apiculata*, revealed the effects of Cr loads, soil composition and presence  
3 of fertilizer on the remediation efficiency. The operation mode of such a complex system was  
4 determined by the following control parameters, including the load of Cr, number of plants,  
5 age of plants, volume of the water, saltness of the water, nutrient level and the mass of the  
6 soil, as well as flow velocity (in the case of a flow reactor). According to empirical and  
7 simulation results, the phytoextraction of Cr using young mangrove trees was feasible, while  
8 the performance of the system was influenced due to 1) the inhabitation of plant growth at  
9 high Cr concentrations; 2) the soil type and their composition, i.e. depending on whether it  
10 was fresh or salty, etc.; and 3) the fertilizer or nutrient content, which increased the system  
11 performance by affecting the plant growth. According to the data, plants showed their  
12 maximum Cr uptake of 326.72 mg kg<sup>-1</sup> Cr at a soil with Cr content of 500 mg L<sup>-1</sup> in the third  
13 month. While for higher Cr loading, an adverse trend was observed for the uptake rate and  
14 plant growth owing to inhibitory effects of Cr on the plants' growth. Besides, at high loads of  
15 Cr, the growth of plant was influenced more at high than at low nutrient levels. Furthermore,  
16 it was observed that the plants' growth in freshwater, sterilized soil, and washed soil had  
17 close and similar curves, whereas, for the salty water and natural soil experiments, the growth  
18 curves demonstrated a more pronounced growth inhibition by Cr [113]. Regarding the impact  
19 of the age of plants, Kocoń and Jurga showed that the concentrations of HMs in plant tissues  
20 decreased annually, so that metal contents usually were the lowest in the oldest plants  
21 harvested at the end of the study [111].

22 Some other researches showed high efficiency of the HMs phytoextraction during seven  
23 years using four conventional energy crops with high biomass production yields, including  
24 *Spartina pectinate* (9.50 Mg ha<sup>-1</sup>), *Sida hermaphrodita* (11.70 Mg ha<sup>-1</sup>), *Panicum virgatum*  
25 (13.30 Mg ha<sup>-1</sup>), and *Miscanthus x giganteus* (15.00 Mg ha<sup>-1</sup> biomass yield) [37, 111, 130-

1 132]. Furthermore, phytoremediation results revealed that *Miscanthus x giganteus* is a more  
2 tolerant species to Zn while *S. hermaphrodita* to Pb [133]. However, in terms of HMs  
3 phytostabilization, *S. pectinata* and *P. virgatum* have been proved as suitable plants [134].  
4 Furthermore, Laval-Gilly et al. [36] showed the capability of *Miscanthus x giganteus* for  
5 efficient phytoextraction of brownfields with considerable accumulation of HMs, like Cd, Cu,  
6 Zn, Pb, and Cr, in roots, compared to their stem and leaves (see **Table 1**). Moreover, willow  
7 (*Salix*) demonstrated a significant performance for the phytoremediation of Zn and Cd from  
8 contaminated sediment, while lower and negligible removals were observed for Cu and Pb,  
9 respectively (see **Table 1**) [128].

10        Nevertheless, as HMs cannot be self-decomposed like organic compounds, hence recently,  
11 the modification of phytoextraction using some suitable methods, namely integrated  
12 phytoremediation, has been proposed to improve the efficiency of the HMs removal process.  
13 Integrated phytoremediation is a technique that applies chelating agents and phytohormones  
14 to intensify the amount of HMs phytoextraction. These novel modifications are some eco-  
15 friendly, time saving and comparatively more effective approaches. To be exact, the  
16 formation of chelates, resulted from the association of HMs ions and chelating agents,  
17 increases the availability of HMs in the soil and enhance the translocation of them to plants.  
18 In fact, integrated phytoremediation is a way to overcome the disadvantages of conventional  
19 phytoremediation by exploiting of chelating agents and phytohormones and/or their  
20 combination, which also supplies nutrients for supporting vegetation growth [120, 126, 129,  
21 135, 136]. Additionally, some other researches have recommended the application of other  
22 methods, such as the addition of organic waste to soil [137, 138], co-planting of different  
23 plant species [139], use of genetically-modified plants [140], etc. However, in order to clarify  
24 and prove the actual potential of integrated phytoextraction methods, the implementation of  
25 large-scale and commercialization studies are required.

## 1 **2.2 Linking phytoextraction and bioenergy recovery**

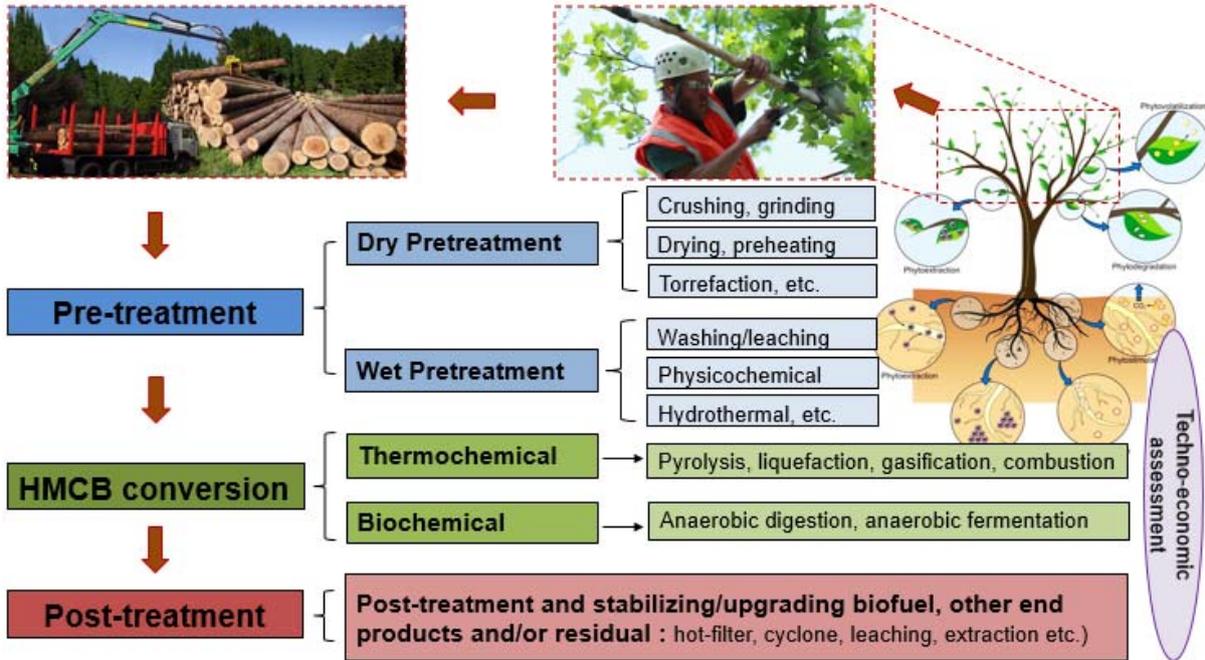
2 The best strategy for remediating a brownfield site via phytoextraction processes is  
3 determined by the extent of soil contamination and the abilities of various plant(s) [43, 54,  
4 141]. However, phytoextraction processes encounter serious issues such as long remediation  
5 periods to clean brownfield sites [43, 141, 142], and production of large amounts of metal  
6 contaminated biomass. The latter is a key challenge in the practice of such approaches, for  
7 which a few types of treatment/reuse processes has been investigated so far [52, 141, 143].

8 Therefore, to cope with used plants rich in accumulated metals, some processes like direct  
9 disposal, biofuel production, combustion, liquid extraction, composting, metals recovery, etc.,  
10 are employed to reuse (metal/energy recovery), treat or dispose the residues originated from  
11 phytoremediation process (**Fig. S1**) [29, 43, 52, 54, 55, 96, 141, 144-148]. However, direct  
12 landfilling and composting of HMxCBs have some inherent drawbacks, including the leaching  
13 and/or transfer of HMs into soil and water bodies, which limit their application [143, 149-  
14 153]. Therefore, in terms of HMxCBs disposal, combustion route has been recognized as the  
15 most environmentally effective compared to other technologies like composting, pyrolysis,  
16 etc. [52, 153]. On the other hand, bioenergy recovery from contaminated plants, as a versatile  
17 alternative of fossil fuels without competing for food security and environment, is globally  
18 more interesting than other phytoextraction-related products including wood, fiber,  
19 bioplastics, charcoal, alkaloids, etc. [141, 154, 155]. Thereby, the growth of energy crops  
20 possessing remarkable HMs phytoextraction ability, such as willow (*Salix ssp.*), switchgrass  
21 (*Panicum virgatum*), poplar (*Populus ssp.*), *Jatropha Miscanthus*, *Dittrichia viscosa* *Silybum*  
22 *marianum*, etc., appears to be the most progressive approach to reach both goals, i.e.  
23 bioremediation and bioenergy production [11, 43, 141]. The novel high-throughput  
24 biotechnological and chemical strategies have unfold a new track in phytoremediation field,

1 by the direct transfer of gene or application of HMs stabilized agents (i.e. algae, fungi, etc.),  
 2 to manipulate the capability of bioenergy crops [156-159].

3 Some potential products extracted from HMCBs comprise sugar via enzymolysis,  
 4 marketable chemicals and fuels, as well as the HMs recovery via thermochemical processes  
 5 [21]. To do so, thermochemical conversion (pyrolysis [160-162], gasification [53, 163, 164],  
 6 liquefaction [94, 165, 166], and combustion [128, 167-169]), and biochemical processes  
 7 (anaerobic digestion [54, 170], and fermentation [147, 171]) have been investigated. In  
 8 addition, some pretreatments, including dry and/or physical [172-174], wet and/or chemical  
 9 [175-177], and physicochemical methods [148] have been examined prior to HMCBs  
 10 conversion to biofuel or to other valuable products, such as char, activated carbons, etc. **Fig.**  
 11 **2** illustrates the detailed HMCBs conversion pathways into various biofuels.

12



13

14

**Fig. 2.** The pathways of HMCBs conversion into various biofuels

15

1 All the aforementioned routes not only could convert contaminated biomass into metal-  
2 free biofuels, but also reduce the waste biomass volume considerably; and the final residue(s)  
3 could undergo further treatment or metal extraction prior to the eventual safe disposal [96].  
4 However, the scale-up of phytoextraction process and energetic valorization of HMCBs are  
5 still challenging on the account of obstacles summarized below:

- 6 • Inorganic elements restrict the entire operation in large-scale cases, mainly owing to  
7 their negative effects such as fouling processing equipment, poisoning catalysts,  
8 contaminating products, etc. [45, 178].
- 9 • The transfer of pollutants into the products could seriously pose health risks [179,  
10 180].
- 11 • The complex involvement of six categories of stakeholders, including local  
12 landowners and farmers, consultants and technology providers, remediation experts,  
13 etc. as the main factors for the successful utilization of HM-contaminated lands  
14 towards scale-up of HMCB-to-bioenergy [141].
- 15 • Management and environmental issues resulted from the processes and final residues,  
16 i.e. the risks of HMs transfer into soil, air and water bodies [74, 75].

17 HMCBs are undoubtedly an inevitable nuisance in today's era and their proper treatment,  
18 reuse, and disposal carry utmost significance. Therefore, more effective control measures and  
19 efficient sophisticated apparatuses are required to counter the aforementioned issues and to  
20 produce clean biofuels with minimum environmental risks.

21 Thermochemical conversion pathways, including pyrolysis, gasification, combustion, and  
22 liquefaction, are viable approaches for biomass conversion to bioenergy generally at a high  
23 operating temperature (250–1000 °C). These methods due to significantly faster reaction time  
24 and higher conversion efficiency are much more favorable than biochemical conversion by  
25 microbes and enzymes [181]. Therefore, due to the complex structure of woody biomass,

1 presence of various contaminants and inorganic elements (e.g., HMs, nitrogen, phosphorus,  
2 sulfur, and chlorine) and their complicated behaviors, selecting an efficient thermochemical  
3 process operating with its optimum conditions is required for efficient bioenergy and resource  
4 recovery from HMCBs with less environmental pollution.

5 The present review paper comprehensively encompasses the cutting-edge technologies  
6 closely related to thermochemical processes and the state-of-the-art breakthroughs with  
7 respect to their relevant operating conditions and high-quality/yield biofuels produced from  
8 HMCBs via phytoremediation. The present review has also summarized and discussed the  
9 recent observations and results about the impact of HMs on biomass feedstock conversion  
10 and possible pretreatment options for the betterment of biofuel yield, product distribution,  
11 quality of biofuel, and safe application of products. Finally, there is a brief discussion to  
12 analyze the output obtained from techno-economic assessments on thermochemical processes.

### 13 **3. PYROLYSIS**

14 Pyrolysis process occurs at  $\sim 350\text{--}700\text{ }^{\circ}\text{C}$  in the absence of oxygen to produce vapors or  
15 pyrolytic gases. The vapors need to be condensed through cooling in order to separate the  
16 liquid or bio-oil, leaving behind a solid residue namely char [20, 79]. The bio-oil has a  
17 calorific value of nearly half of conventional fuels ( $40\text{ MJ kg}^{-1}$ ) [182, 183], and is applicable  
18 as fuel in diesel engines [182, 184] or chemical feedstock [21, 185]. Additionally, the char is  
19 used for materials recovery [20], pollutants removal [186], soil applications [187], etc.  
20 Pyrolysis is categorized as slow [188], intermediate [189], fast [96] and flash process [20]  
21 based on operational conditions, i.e. heating rate (HR), gas residence time (GRT) and  
22 temperature.

23 Generally, for the conversion of lignocellulose feedstock, fast pyrolysis with high heating  
24 rate ( $20\text{--}300\text{ }^{\circ}\text{C s}^{-1}$ ) and short GRT of few second ( $5\text{--}10\text{ s}$ ) contributes to high bio-oil yields

1 (40–50 wt.%) [183, 190, 191]. Whilst slow pyrolysis with lower heating rate (4–10 °C min<sup>-1</sup>)  
2 and longer GRT ends up lower bio-oil yield [191]. After pyrolysis, the gaseous phase is  
3 separated from solid matter, and subsequently, that part of the pyrolytic gas is rapidly cooled  
4 down to form bio-oil and the rest as non-condensable gas [192].

5 The recent investigations on the pyrolytic conversion of HMCBs have mainly focused on  
6 the fate of HMs with three goals: (I) to produce metal-free bio-oil; (II) to avoid HMs  
7 emission via gaseous phase (in form of free ions or hydroxide and carbonates); and (III) to  
8 accumulate HMs in the char [45, 96, 173, 188, 193]. It has been reported that a number of  
9 factors (i.e. plants type, pretreatment methods [45, 194], operating conditions and post-  
10 treatment stages [20, 45]) have impacts on the characteristics and quality of bio-oil and char.  
11 **Table 2** shows the operating conditions, bio-oil yields and quality of HMCBs pyrolysis, etc.  
12 in different pyrolytic processes.

13

1 **Table 2.** Pyrolytic conversion of HMCBs and bio-oil production

Feedstock	HMs	Pyrolysis	Temp., °C (Heating rate, °C min <sup>-1</sup> )	Reactor	Biomass feed rates	Pretreatment	Post-treatment	HMs content in bio-oil	Remarks	Ref.
<i>Broussonetia papyrifera</i>	Cd, Cu	Slow	450 (10)	Lab-scale tube furnace	15 g exp. <sup>-1</sup>	Crushed and preheated: PS* < 10 mm	–	Low	<ul style="list-style-type: none"> <li>The pyrolysis of HMCB was affected by the heating rate and alkaline additives, so that appreciably influenced the fate of Cd and Cu, which should be solved.</li> </ul>	Han et al. [123]
<i>Sedum plumbizincicola</i>	Cd, Zn, Pb	Slow and fast	450–750 (10–50)	Lab-scale horizontal quartz tube	15 g exp. <sup>-1</sup>	–	Cyclone	High	<ul style="list-style-type: none"> <li>Bio-oil is not practical for real applications, due to relative high concentration of Cd and Zn.</li> <li>Pyrolysis at 650 °C followed by an efficient cyclone as a post-treatment was able to recover Zn and Cd from char and bio-oil, respectively.</li> </ul>	Zhong et al. [146]
Mixed feedstock (pine and spruce)	Zn, Fe, Al	Fast	750 (Rapid heating, NR**)	Pilot-scale pyrolyzer	20 kg h <sup>-1</sup>	Crushed and preheated: PS** < 1.00 mm	–	Low	<ul style="list-style-type: none"> <li>Pilot scale reactor is useable and efficient to produce high quality and metal-free bio-oil providing introducing feedstock with PS of &lt; 0.50 mm.</li> <li>The appropriate solid residue separation significantly reduce HMs transfer to bio-oil.</li> </ul>	Wiinikka et al. [173]
Willow	Cd	Fast	350–650 (NR)	Full-scale reactor	–	–	–	NR**	<ul style="list-style-type: none"> <li>Fast pyrolysis is promising in compared with gasification and combustion to convert Cd-contaminated willow in heat and power (CHP) system (bio-oil yield 65% and LHV 17 GJ t<sup>-1</sup>). However, the profit depends on the scale of operation.</li> </ul>	Kuppens et al. [182]
Fir sawdust	Cu	Fast	450–600 (300 °C s <sup>-1</sup> )	(Batch) vertical drop fixed bed reactor	15 g exp. <sup>-1</sup>	Crushed and preheated: PS < 0.12 mm	–	Negligible	<ul style="list-style-type: none"> <li>In terms of the total net revenue, 250 °C is the optimal pyrolysis temperature.</li> <li>500 °C is optimum temperature to produce cleaner bio-oil with higher yield.</li> <li>Under optimum operating conditions, only ~0.027% of total Cu (i.e. 1.0 wt.% of feedstock) transferred into the bio-oil and ~95% accumulated in the char.</li> </ul>	Liu et al. [96]
Willow	Cd, Cu, Zn, Pb	Flash	350–550 (Rapid exposure)	Lab-scale, semi-continuous stirred fluidized bed reactor	2.40 kg h <sup>-1</sup>	Crushed and preheated: PS < 0.20 mm	hot-gas filter	Negligible	<ul style="list-style-type: none"> <li>Using a hot-gas filter at 350 °C, the transfer of particles to bio-oil extremely declines, and consequently a cleaner bio-oil with same bio-oil yield (41%).</li> <li>Unlike combustion, flash pyrolysis is an eligible processing method to convert HMCB to metal-free bio-oil with high quality, so that the results were comparable to the pyrolysis of uncontaminated willow presented by Cornelissen et al. [195].</li> </ul>	Stals et al. [20]
Agricultural residues and manure	Cd, Cu, Zn, Pb, Cr, Ni, Co, Mn, Fe, Al	Fast	400–700 (NR)	Fluidized bed reactor	Pilot scale (200 kg h <sup>-1</sup> ) Bench scale (5 kg h <sup>-1</sup> ) Screw (0.50 kg h <sup>-1</sup> )	–	–	Negligible	<ul style="list-style-type: none"> <li>At 400–600 °C, more than 95 wt.% of total inorganic elements is separated from the bio-oil.</li> <li>Completely metal-free bio-oil production seems unlikely owing to the wide variety and forms of inorganic elements present in various feedstocks.</li> <li>Using adequate solid-gas separation technologies before condensation could significantly obstruct the main transferring route of HMs into the bio-oil, resulted from particles.</li> </ul>	Leijenhors et al. [45]
Switchgrass and Timothy grass	Pb	Fast	500 (20 °C ms <sup>-1</sup> )	Micropyrolyzer	–	Crushed, preheated and hydrolyzed using mild acid and enzymes	–	NR	<ul style="list-style-type: none"> <li>Both acidic hydrolysis (4% H<sub>2</sub>SO<sub>4</sub>) and enzymatic hydrolysis pretreatment negligibly affect the chemical distribution of the bio-oil.</li> <li>Switchgrass species with modest levels of Pb uptake is a promising option for both phytoextraction and feedstocks for bio-oil production.</li> <li>Switchgrass showed higher Pb uptake than Timothy grass.</li> </ul>	Balsamo et al. [21]
Switchgrass	Cu, Fe	Fast and Catalytic	450–500 (NR)	Fluidized bed reactor	1.50 kg h <sup>-1</sup>	Crushed and preheated: PS=2.00 mm	–	NR	<ul style="list-style-type: none"> <li>Bio-oil yield decreased (up to 35 wt.%), in compare with non-catalytic process, due to HZSM-5 catalyst poisoning resulting from accumulation of ~42% of Fe and 11% of Cu initial contents on its active surface.</li> <li>Catalyst lead to bio-oil production with lower oxygenates.</li> </ul>	Mullen and Boateng [178]
Willow	Cd, Cu, Zn, Pb	Fast	350 (35)	Quartz horizontal tube reactor	3 g exp. <sup>-1</sup>	Air-dried and crushed: PS=2.00 mm	–	Metal-free	<ul style="list-style-type: none"> <li>Bio-oil is almost metal-free, with small differences in types and amounts of organic compounds.</li> <li>Condensable pyrolysis fraction has only small amount of Zn (5 mg kg<sup>-1</sup> or &lt;1% of total Zn amount), but without any detection of Cd, Cu and Pb.</li> </ul>	Lievens et al. [183]
Birch wood and sunflower	Cd, Cu, Zn, Pb	Fast	400–600 (35)	Quartz horizontal tube reactor	3 g exp. <sup>-1</sup>	Air-dried and crushed: PS=1.00 mm	–	Metal-free	<ul style="list-style-type: none"> <li>Fast pyrolysis at low temperature (~350 °C) is recommended to produce metal-free bio-oil.</li> <li>Metal-free bio-oil is obtained only at temperature of ~350 °C, at which volatilization of highly volatile HMs, like Cd and Zn.</li> </ul>	Lievens et al. [196]
Willow and <i>Thlaspi caerulescens</i>	Cd, Zn	Slow	25–900 (4)	Lab-scale tube furnace	5–10 g exp. <sup>-1</sup>	Crushed and preheated: PS=1.00 mm	–	NR	<ul style="list-style-type: none"> <li>Pyrolysis is a promising technique in compare to incineration to increase the valorization of HMCBs, i.e. for the recovery of Cd and Zn.</li> </ul>	Keller et al. [55]

2 \* PS: Particle size of feedstocks

3 \*\* NR: Not reported

1 Zhong et al. [146] studied slow and fast pyrolysis of a hyperaccumulator (*S.*  
2 *plumbizincicola*) with high concentrations of HMs, including Zn (9,838), Cd (560), Pb  
3 (62.50), Cu (77.60), Cr (45.40), Fe (642) and Al (13,976 mg kg<sup>-1</sup> of HMxCB), in operating  
4 conditions described in **Table 2**. The higher temperatures and heating rates increased the  
5 HMs emission rate into bio-oil with different trends for each element. For example, at 450–  
6 650 °C at least 66.30% of Zn remained in the char while 87.60% of Cd and 73.60% of Pb  
7 transferred into the bio-oil, but no HMs were detected in the gaseous phase. It was concluded  
8 that fast HMxCB pyrolysis at 650 °C could produce bio-oil with highest yield and quality (in  
9 terms of more alkenes with low levels of oxygenated compounds); and it was also suggested  
10 to adopt HMs cleaning technologies (i.e. cyclone and spray tower ) as post-treatment  
11 measures to recover Zn and Cd from char and bio-oil, respectively. However, the bio-oil  
12 produced by such a process may not be suitable for real applications yet due to its high Cd  
13 and Zn content [146].

14 Furthermore, Stals et al. [20] investigated the flash pyrolysis of contaminated willow (a  
15 mixture of stem and leaves based on naturally weight ratio of plant organs) under operating  
16 conditions listed in **Table 2**. The results revealed that by increasing temperature from 350 to  
17 550 °C, a lot more quantity of Cd volatilized to gaseous phase while Zn majorly transferred  
18 into bio-oil. However, negligible level of Pb in bio-oil was detected even at highest testing  
19 temperature. Based on the yields, properties and content of target metals in pyrolysis oil in  
20 this study, 350–450 °C deemed as preferable pyrolysis temperature range at which generally  
21 high yields of bio-oil were achieved and lower amounts of HMs were found in the bio-oil: Zn  
22 <7.80 mg kg<sup>-1</sup>, 1%; Cd <0.80 mg kg<sup>-1</sup>; 13% and Pb <0.60 mg kg<sup>-1</sup>, 7% of initial concentration.  
23 Even though, at the lowest temperature HMs majorly concentrated in the char, the bio-oil did  
24 not meet other optimal indexes, i.e. bio-oil yield (41%), gas yield (38%), char yield (21%),  
25 water content (49%), and high heating value (HHV 21.90 MJ kg<sup>-1</sup>) [20].

1 Likewise, according to Leijenhorst et al. [45] (**Table 2**), using fast pyrolysis process for  
2 agricultural residues in the temperature range of 400–600 °C, over 95 wt.% of total inorganic  
3 elements present in contaminated biomass were separated from the produced bio-oil, and  
4 HMs largely remained in the char. Generally, the easy transfer of HMs to gaseous phase in  
5 thermochemical decomposition of HMxCB is affected by (I) their high volatilization at higher  
6 temperatures (**Table S1**) [20, 146], and (II) the bonding of HMs with initial biomass structure  
7 [71-73] and produced organic vapor [45].

8 Dilks et al. [19] have presented an overall scheme for pyrolysis of HMxCBs (**Fig. S2**)  
9 possessing a cyclone as the post-treatment for phase separation to produce cleaner bio-oil,  
10 whilst, no wet-chemical pretreatment was considered to eliminate the HMs directly from the  
11 feedstock prior to conducting pyrolytic conversion. According some studies, the produced  
12 char obtained from pyrolyzing HMxCBs is mostly not suitable neither for free disposal into the  
13 environment nor for metal extraction/recovery [19, 20].

14 Generally, biomass type, feedstock particle size/distribution, pyrolysis operating  
15 conditions as well as pre- and post-treatments can affect the yield, HHV, and quality of bio-  
16 oil, HMs and solids transfer rate. The effects of aforementioned factors on pyrolytic  
17 conversion of HMxCBs are discussed in the following sections.

### 18 **3.1 Effect of HMxCB type**

19 Generally, the lignocellulosic composition of biomass is one of the factors affecting the  
20 chemical composition of and its distribution in the bio-oil product [21]. Similarly, Lievens et  
21 al. [196] have shown different HMxCBs (i.e. birch and sunflower) end up to pyrolysis  
22 fractions, i.e. bio-oil, char, etc., with different yields, characteristics, and calorific values. The  
23 main reasons can be inferred from the ultimate analysis of birch and sunflower that showed,  
24 in comparison to sunflower, birch wood with a different structure formula (lower H:C (~0.14)

1 and O:C (~0.90) ratios) causes higher bio-oil yield throughout the operation condition.  
2 Therefore, by pyrolysis of birch wood at the optimum temperature of 500 °C, a bio-oil  
3 possessing chemicals with lower H:C (1.41) and O:C (0.51) ratios with higher HHV of  
4 ~21.20 MJ kg<sup>-1</sup> was obtained [196]. Furthermore, the comparison of fast pyrolysis of HM-  
5 contaminated willow and fir sawdust in two different studies under roughly identical  
6 operating conditions reveals the same behavior. In other words, willow with lower H:C and  
7 O:C ratios has resulted in bio-oil yields of 50–80 wt.% per dry feed basis, which was  
8 significantly more than what was obtained from fir sawdust [96, 182].

9 On the other side, it has been reported that different parts of HMCBs, i.e. stems, branches,  
10 and leaves, possess various concentrations of structural organic compounds [71, 183] and  
11 bioaccumulation degrees of inorganic pollutants [72, 73]. Consequently, the difference in  
12 physical structure and composition of HMCB's organs may lead to different yields of bio-oil  
13 products with various HHVs, reactivity, and compositions [183]. For instance, the dominant  
14 bioaccumulation of HMs, such as Cd, Pb, Cu, and Zn, was observed in willow's leaves,  
15 however, the fast pyrolysis of willow's organ at 350 °C showed a higher bio-oil yield of  
16 13.70 MJ kg<sup>-1</sup> and 7% increase of HHV [183]. The same trend was observed by the flash  
17 pyrolysis of willow's branch and leave at 450 °C, from which higher bio-oil yield (49%) and  
18 HHV (15.80 MJ kg<sup>-1</sup>) was obtained. On the contrary, for the flash pyrolysis of the mixture of  
19 leaves and branches under same operating conditions, both bio-oil yield and HHV decreased  
20 to 41% and 13.90 MJ kg<sup>-1</sup>, respectively, which might be attributed to the negative effect of  
21 leaves. However, from practical perspective, the simultaneous pyrolysis of mixed feedstock,  
22 i.e. branches and leaves of HMCBs, was suggested, because mostly nuance differences were  
23 observed between the bio-oils produced from the above two parts in terms of (1) reactivity, (2)  
24 bio-oil yield and composition and (3) heating values [20, 183]. Furthermore, as illustrated in  
25 **Section 1.2**, HMCBs possess various ratios of branch-to-leave with different distributions of

1 HMs due to the different ratios of cellulose to hemicellulose to lignin in various parts of a  
2 plant (**Fig. 1**). Therefore, the pyrolysis of the mixture of HM-contaminated branches and  
3 leave is generally recommended towards easier technical operation (i.e. not to separate leaves  
4 and branches) and safer environmental aspect (i.e. addressing the entire parts of HMCBs).

5 Based on the literature reviewed in this report (**Table 2**), willow and switchgrass have  
6 been predominant plant species used for twofold aims such as phytoremediation and bio-oil  
7 production. Meanwhile, Cd, Cu, Zn and Pb have been the most phytoextracted HMs from  
8 brownfields [20, 21, 178, 183]. Regardless of the effect of pyrolysis operating conditions,  
9 more research on different HMCBs for bioaccumulation of the same group of contaminants  
10 are required to compare and correlate the structural type of various HMCBs –in terms of  
11 cellulose, hemicellulose and lignin fractions– with (I) their phytoextraction ability and (II)  
12 bioenergy recovery potential in terms of metal-free and high yield and quality bio-oil  
13 production.

### 14 **3.2 Effect of HMCBs pretreatment**

15 The effect of dry pretreatment (i.e. crushing, preheating and torrefaction) and wet  
16 pretreatment (using various acids, solvents, etc.) on HMCBs have been investigated to  
17 explore their effects on bio-oil yield and HMs content. As seen in **Table 2**, mostly crushed  
18 feedstock with the particle size (PS) of <2.00 mm was introduced to different reactors [96,  
19 173, 183]. For example, Wiinikka et al. [173] demonstrated that feedstock with PS <0.25 mm  
20 had a higher conversion, whilst the product converted from feedstock with PS of 0.50–1.00  
21 mm had a lower conversion rate with a high amount of volatiles that was almost comparable  
22 to the raw material. However, according to Park et al., the bio-oil yield reduced with  
23 decreasing feedstock particle size due to overheating resulted during fast pyrolysis of  
24 Japanese larch using a bubbling fluidized bed reactor [197]. Therefore, PS <0.50 mm was

1 suggested as optimum size for suitable operation with a reasonable accumulation of  
2 refractory and volatiles in the char resulting in metal-free bio-oil production [173].

3 On the other hand, Balsamo et al. [21] investigated the effect of wet pretreatment  
4 (hydrolyzing with 4% H<sub>3</sub>PO<sub>4</sub> solution) and biological pretreatment (hydrolyzing by three  
5 cellulose-producing fungi) on fast pyrolysis conversion of switchgrass with a higher  
6 capability of Pb uptake (compared to Timothy grass) (**Table 2**). According to the results,  
7 neither enzymatic nor acid hydrolysis pretreatment of examined HMxCB affected the products  
8 yield, i.e. bio-oil and sugar. However, both acid and enzymatic hydrolysis treatments  
9 influenced the distribution of chemical products in the bio-oil obtained from both clean and  
10 Pb-contaminated switchgrass. They concluded that switchgrass species with modest levels of  
11 Pb content can serve as both promising phytoextraction agent and biofuel feedstock [21].  
12 Furthermore, Raveendran et al. [198] showed that using a two-stage demineralization  
13 pretreatment of thirteen types of woody biomass, the bio-oil yield mostly elevated with  
14 higher heating values at 500 °C in a packed bed reactor. In the first stage, biomass samples  
15 (PS of 100-250 mm) were treated with 10% HCl at 60 °C for 48 h with constant stirring. In  
16 the second stage, biomass containing higher silica content was further treated with aqueous  
17 5% NaOH for 1 h at 90 °C, and finally, samples were washed with distilled water, filtered,  
18 dried and stored. In fact, demineralization intensifies the devolatilization rate and the initial  
19 decomposition temperature. However, a decrease of volatiles yield after the removal of the  
20 mineral matters was observed for some biomass, such as coir pith, groundnut shell and rice  
21 husk, which was attributed to their high lignin content; in fact, lignin gives a higher char yield  
22 than cellulose and hemicellulose [198]. Therefore, demineralization of HMxCBs is anticipated  
23 to cause the increase of bio-oil yield and quality, however, it is been reported that the  
24 presence of HMs, like Zn, Cu, etc. in biomass could also perform as an efficient catalyst to  
25 promote the gas yield and char formation while reducing the liquid production [73, 198, 199].

1 Moreover, according to Wigley et al., an integrated acid leaching and torrefaction  
2 pretreatment led to a demineralized and stabilized biomass, which consequently limited the  
3 catalysis of pyrolysis vapors using water, organic acids and inorganics present in the biomass  
4 [101]. In fact, demineralization and dewatering lead to controlling secondary reactions in  
5 pyrolysis that reduces reactions towards the production of oxygenated compounds, high  
6 molecular weight compounds, pyrolytic water, and coke [200]. Therefore, the reduction of  
7 catalytic secondary reactions of pyrolysis vapors results in the production of bio-oils with  
8 higher quantity, quality and stability [101].

9 Moreover, Lievens et al. [196] showed that, unlike sand, the presence of fumed silica as  
10 heat harrier in HMCBs fast pyrolysis at operating temperature of 400 °C (**Table 2**) decreased  
11 evaporation and/or transfer of Cu and Pb into total pyrolysis products by 17% and 12%,  
12 respectively, through increasing the retention of HM compounds. This observation could not  
13 be explained clearly by the original study; it was indicated that the surface functionality or  
14 molecular build-up might be the reasons for the difference in retention behavior of HMs. In  
15 other words, the reason might be because the SiO<sub>2</sub> promoted binding of HMs onto silica  
16 towards the formation of HMs silicate, which is more thermodynamically favored compared  
17 to the formation of simple oxides, and consequently, minimized the probability of HMs  
18 transfer into the liquid, and gas fractions [196].

19 Recently it has been reported that, compared to direct pyrolysis, the phosphate-assisted  
20 pyrolysis of Pb-contaminated water hyacinth at low temperatures (300 and 400 °C) led to the  
21 decrease of the bioavailability and leaching potential of Pb to <5% and 7%, respectively. The  
22 reported conditions enhanced the recovery and stability of Pb in the char, resulting from the  
23 formation of Pb phosphate minerals such as pyromorphite and lead-substituted  
24 hydroxyapatite [201]. However, it has also been demonstrated that the catalytic pyrolysis of  
25 wood using phosphate could dramatically lower the yield of bio-oil [202]. In other words,

1 after direct pyrolysis or application of phosphate-assisted approach, HMs may reduce their  
2 harm to the environment by probable transferring from the toxic state of ions into some  
3 amorphous state in the char [203, 204], in the form of phosphate minerals [201, 205], or  
4 being stabilized with external materials including  $\text{Al}_2\text{O}_3$ ,  $\text{FeCl}_3$ ,  $\text{CaCO}_3$  and  $\text{NaOH}$  [206].  
5 Therefore, it can be inferred that pyrolysis assisted by phosphate and/or other materials can  
6 be mainly recommended for the safe disposal of HMCBs rather than bio-oil recovery.

### 7 **3.3 Optimum pyrolysis temperature and HMs behavior**

8 Generally for lignocellulosic biomass structure [67], the decomposition temperature of  
9 cellulose, which has the potential of binding a wider spectrum of inorganic elements, is  
10 around 300–430 °C; whilst the decomposition temperature for lignin is in the range of  
11 300–550 °C, which possesses the capacity of binding more Fe, Pb, and Zn than cellulose [71-  
12 73]. Given the above-mentioned properties and characteristics, an approximate correlation  
13 can be anticipated between the operating temperature for the further decomposition of  
14 biomass fractions, and the rising risk of HMs release attached to each part, i.e. cellulose,  
15 hemicellulose, and lignin. Furthermore, it has been reported that the bio-oil yield, HHV, HM  
16 contents, and quality in terms of chemical composition and distribution in bio-oil vary  
17 depending on the lignocellulosic composition of biomass, the impact of minerals, operating  
18 temperature, gas residence time, and reactor configuration [21]. Therefore, to find optimum  
19 operating conditions for the pyrolysis of HMBC, all aspects and facts should be considered  
20 towards higher yield and cleaner bio-oil production.

21 In terms of yield, the bio-oil yield was higher by fast pyrolysis of HMCB at 650 °C than  
22 those at both 450 °C and 750 °C, because at the former more biomass to char conversion  
23 occurred and at the latter more cracking of bio-oil was converted to gas products [146].  
24 According to Wiinikka et al. [173] fast pyrolysis of HMCBs (75 wt.% pine and 25 wt.%

1 spruce) in a cyclone pyrolyzer at 500 °C with the feedstock particles size of <0.50 mm  
2 resulted in high yield (54.60 wt.%) and relatively metal-free bio-oil product (Zn = 0.99, Fe =  
3 2.43 and Al = 0.36 mg kg<sup>-1</sup> bio-oil). In addition, the quality of bio-oil was good with respect  
4 to the homogeneous oil phase, HHV (21.10 MJ kg<sup>-1</sup>), LHV (17.50 MJ kg<sup>-1</sup>), and low water  
5 content. Similarly, Liu et al. [96] have reported fast pyrolytic conversion of sawdust at  
6 500 °C (**Table 2**) as optimum conditions for higher bio-oil yield and HHV with negligible  
7 transfer of Cu to the bio-oil (~4.60–7.60 mg kg<sup>-1</sup>, i.e. 0.03% of initial Cu content) because the  
8 Cu was predominantly enriched in the char (~95%). Interestingly, Cu played a catalytic role  
9 in promoting bio-oil yield (to ~54%) and HHV (to ~14 MJ kg<sup>-1</sup>) at 500 °C. Furthermore,  
10 using fast pyrolysis process at 400–600 °C, more than 95 wt.% of total inorganic elements  
11 present in biomass was separated from the bio-oil and accumulated in the solid phase [45]. In  
12 addition, Liu et al. [96] have demonstrated 500 °C would be the optimum temperature for fast  
13 pyrolysis of Cu-contaminated biomass (Cu 1.00 wt.% of feedstock) in a fixed bed reactor.

14 Furthermore, Koppolu et al. [145] showed that the fluidized bed reactors allow the  
15 utilization of higher pyrolysis temperatures up to 600 °C without compromising the  
16 sequestration of the HMs in the char. On the contrary, Stals et al. [20] have suggested a lower  
17 temperature, i.e. ~350 °C, for flash pyrolysis of HMxCB in a fluidized bed reactor equipped  
18 with a hot-gas filter. Additionally, based on the type, melting/boiling points and content of  
19 HMs in the HMxCB, the appropriate operating temperature could be determined according to  
20 **Table S1** and following classification: 1) Hg, As, Cd and Pb as highly volatile metals  
21 partitioning into the gas phase [207], 2) Cu, Mo, Ni and Zn as semi-volatile elements [208],  
22 and 3) Co, Cr, Mn, and V as non-volatile elements [209]. For example, the temperature of  
23 350 °C was favorable to avoid volatilization of highly volatile elements, like Cd and Zn,  
24 while Cu and Pb could even remain immobilized at 350–600 °C (**Table S1**) [196].

1 On one hand, the higher temperatures of pyrolysis process by 700 °C lead to further tar  
2 cracking and higher oxygen content resulted from increased oxygen functionality of bio-oil  
3 structure [79, 196], and consequently, resulting in lower heating values (LHV) of bio-oil  
4 (~16.80 – 19 MJ kg<sup>-1</sup>) that is less than desired HHV of conventional fossil fuels (40 – 45 MJ  
5 kg<sup>-1</sup>) [196, 210, 211]. A promising way to deoxygenate the bio-oil is the application of  
6 catalytic pyrolysis, through which the catalyst depresses the operating temperature, thereby  
7 decreases oxygen functionalities of the bio-oil structures by dehydration, decarbonylation and  
8 decarboxylation reactions [212]. On the other hand, pyrolysis at lower temperatures produces  
9 cleaner bio-oil [20, 96], but leads to more char formation [146, 189]. Meanwhile, as operating  
10 temperature can influence the contingency of HMs leaching from a contaminated char,  
11 350–450 °C has been stated as optimum operating temperature to produce a char with  
12 maximum metal retention capacity from HMCBs particularly containing high contents of Cd  
13 and Pb [20, 213]. Briefly, fast pyrolysis at 350 °C is suggested towards economical  
14 valorization of HMCBs [183]. However, according to a techno-economic assessment study,  
15 250 °C has been determined as the optimal pyrolysis temperature in terms of the total net  
16 revenue [182]. Considering all aforementioned factors, optimum operating temperature for  
17 HMCBs pyrolysis is 350–450 °C in terms of maximum HMs removal and acceptable bio-oil  
18 yield, which can be extended by 150–250 °C (i.e. threshold up to 600 °C), mainly depending  
19 on the type and concentration of HMs inside plants' organs, reactor configuration and  
20 pre/post-treatment techniques. On the other hand, Sun et al. [214] showed that operating  
21 conditions, including temperature, processing method, and feedstock type, influence the  
22 physicochemical and biological properties of bio-chars and hydro-chars obtained from  
23 pyrolysis of biomass. Results indicated that if the target is the production of bio-char for land  
24 use, different properties can be acquired depending on the operating conditions, for example,  
25 higher pyrolysis temperatures (>250 °C) led to the decrease of bio-char production rate but

1 increased its carbon content and thermal stability; dry-pyrolysis bio-chars had lower pH  
2 values and higher carbon contents; in addition, the type of biomass also affects the quality of  
3 bio-chars. Therefore, bio-chars with different properties can be produced by manipulating  
4 production conditions to better satisfy their environmental applications [214]. Considering  
5 the likely leakage of HMs from bio-char, the selection of optimum operating temperatures  
6 would be more critical if the quality of both bio-oil and bio-char needs to be considered.

7 Overall, for pyrolytic decomposition of HMCBs, fast pyrolysis appears to be promising in  
8 terms of low metals content, high yield and HHV of the resultant bio-oil. Contrarily, slow  
9 pyrolysis of HMCBs has shown lower bio-oil yield, less diversity and lower content of  
10 organic components, as well as higher transfer rate of HMs to bio-oil [189, 215].

### 11 **3.4 Usability of bio-oil and the necessity of post-treatment**

12 Generally, the bio-oils are unstable due to possessing chemically dissolved oxygen and HMs,  
13 thus they require upgrading and likely the removal of water and contaminants such as HMs,  
14 etc. [192, 216-218]. Even though, typical concentrations of total metal content in bio-oil even  
15 for non-contaminated biomass can reach up to 500 mg kg<sup>-1</sup> [219]. To the date, no general  
16 benchmark values has been set for the maximum acceptable level of inorganic content,  
17 including HMs in biofuels neither bio-oil [45, 97, 173].

18 To minimize environmental and operational issues resulting from particles and HMs in  
19 bio-oils, the concentration of <0.10 wt.% for particles and that for HMs as low as possible  
20 have been recommended [220]. Some issues related to solid particles and metals in bio-oil are  
21 particle emissions, particle deposits on surfaces of heating equipment, high temperature  
22 corrosion [220], as well as increment of bio-oil instability and contamination [217] and high  
23 heating value [96]. Noticeably, in some pyrolytic operations, the high, scattered, or inaccurate  
24 amounts of HMs (like Cu, Ni, Zn, Cr, Al, Mn) in the bio-oil or other phase have been

1 attributed to biomass harvesting systems [45], reactor construction materials [20, 45], heating  
2 carrier material [20] or bio-oil collecting system [173].

3 Some studies reported the feasibility of bio-oil production with negligible amounts of  
4 HMs using fast pyrolysis of various HMCBs even though without implementing any wet  
5 pretreatment and/or post-treatment [96, 183, 196]. For example, using fast pyrolysis of an  
6 HMCB under optimum operating conditions (500 °C) only resulted in ~0.03% of total Cu  
7 transferred into the bio-oil [96]. In addition, without running any post-treatment process,  
8 Lievens et al. reported only small amounts of Zn (5 mg kg<sup>-1</sup>, i.e. equal to <1.00 wt.% of  
9 initial Zn) were found in the condensable pyrolysis fraction, and even without any detection  
10 of Cd, Cu and Pb [183]. Moreover, results of the slow pyrolysis of HMs-impregnated and real  
11 HMCBs, containing Cd, Cu and Pb, also showed the accumulation of more than 67.76% of  
12 the HMs in the solid phase, and their uniform distribution in the pore structure, indicating the  
13 interesting role of pyrolysis to process HMCBs [123, 160]. Furthermore, Wiinikka et al.  
14 showed the feasibility of fast pyrolysis for the production of almost metal-free bio-oil in a  
15 pilot-scale reactor, while HMs majorly concentrated in the solid residue [173].

16 However, some other studies do not recommend the real applications of the bio-oil  
17 produced from the pyrolytic conversion of HMCBs, due to its high metals content, including  
18 Cd and Zn [146]. To cope with this issue, they have emphasized the necessity of post-  
19 treatment to avoid, separate, or remove HMs from bio-oil towards cleaner product. For  
20 example, in pyrolysis process, the transfer of HMs from solid phase to condensable phase has  
21 been introduced as the main migration route [45, 173]. Therefore, using adequate  
22 technologies for solid-gas/liquid separation before condensation has been recommended for  
23 the effective obstruction of the HMs migration from char into bio-oil [45, 173]. For instance,  
24 the effective and successful application of cyclone as the post-treatment of pyrolytic  
25 conversion of HMCBs at 650 °C for both metal-free bio-oil production and metals recovery

1 [146]. For example, Stals et al. showed the negligible transfer of metals in the produced bio-  
2 oil (Cu and Zn <5 mg kg<sup>-1</sup>; Cd and Pb <1 mg kg<sup>-1</sup>) in the case of using hot-gas filter at 350 °C  
3 [20]; The HMs content of bio-oil was even comparable to what was obtained from pyrolysis  
4 of uncontaminated willow [195]. Although for an uncontaminated plant, Park et al., reported  
5 that using a two-staged bio-char removal system, high-quality bio-oil could be produced,  
6 which consists of low concentrations of alkali and alkaline earth metals, <0.005 wt% solid,  
7 and no ash [197].

8        Nevertheless, bio-oils derived from the pyrolysis of lignocellulosic biomass consist of a  
9 considerable amount of water and a heterogeneous mixtures of aromatics and aliphatics  
10 oxygenated compounds [221], including phenolics and alkylated (poly-) phenols, relatively  
11 small amounts of phenol, eugenol, cresols and xylenols [222], carbohydrates, alcohol,  
12 aldehydes, ketones and carboxylic acids [223]. The oxygenated compounds orchestrate low  
13 H/C and high O/C ratios that make the bio-oil to have lower heating value compared to  
14 petroleum fuels [224]. Correspondingly, the bio-oil faces aging and instability during storage  
15 that is caused by the oxygenates [225, 226]. Therefore, regardless of the type of  
16 lignocellulosic biomass, i.e. HMCBs or uncontaminated woody biomass, it is required to  
17 upgrade the bio-oil produced using in-situ or ex-situ catalytic reactions [227-229]. Various  
18 zeolite, acid, base, and transition metals-based catalysts, like ZSM-5, HZSM-5, MgO,  
19 Na<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, Pt/Al<sub>2</sub>O<sub>3</sub>, Al-MCM-42, low-cost base catalysts (mineral clay), etc., have  
20 been examined to upgrade the bio-oil derived from woody biomass pyrolysis [228, 230-233].  
21 For example, the hydro-pyrolysis of woody biomass at 500 °C and 1 atm in a dual bed system  
22 packed with Na<sub>2</sub>CO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> catalysts in two consecutive beds showed a  
23 promising performance resulting in high quality bio-oil with oxygen content of 5.60 wt.%  
24 and HHV of 42 MJ kg<sup>-1</sup>, which was close to the characteristics of conventional fuels [230].  
25 Generally, the bio-oil upgrade possesses reaction mechanisms that require C-C cleavage,

1 reforming, water-gas shift and methanation reactions [234], and the removal of oxygen  
2 molecules from the functionalities of the bio-oil [235, 236]. According to the literatures,  
3 using the catalytic pyrolysis of various woody biomass, the oxygenated compounds can be  
4 converted to an upgraded bio-oil with more stable structures, higher molecular weight  
5 compounds, increased phenols and aromatics compounds, thereby producing a bio-oil with  
6 higher calorific value and acidity, compared to non-catalytic pyrolysis oil [224, 227-230,  
7 237].

### 8 **3.5 Dual behavior of HMs and catalyst poisoning**

9 A number of studies have investigated and reported the catalytic roles of HMs  
10 (particularly Cu, Zn, Cr, etc.) present in contaminated biomass. Some studies indicated the  
11 positive roles of HMs towards improving activation energy and thermo-decomposition of  
12 biomass components, and consequently bio-oil yield and HHV [96, 98, 125, 238, 239]. Lin et  
13 al. [203] showed the catalytic function of chromium during the fast pyrolysis of Cr-  
14 contaminated water hyacinth on the quantity and quality of bio-oil produced. Reportedly, the  
15 maximum bio-oil reached up to 63.10 wt.% at 500 °C, and the amount of nitrogenous  
16 compounds, alcohols and phenols increased, while the number of acids and esters reduced  
17 which revealed that Cr promoted bond rupture of lignin and switched the degradation process  
18 of protein [203]. The pyrolysis of *Arundo donax* and *Broussonetia papyrifera* impregnated  
19 with Cd, Cu and Pb also confirmed the complete pyrolysis of HMCBs. According to the  
20 results, more than 60% of the mass was lost after decomposition stage occurred from 200 to  
21 450 °C. In addition, due to catalytic effect of HMs, the activation energies of *A. donax*  
22 pyrolyzed and *B. papyrifera* were reduced by around 1.85–3.84 kJ mol<sup>-1</sup> and 0.93–13.28 kJ  
23 mol<sup>-1</sup>, respectively [160]. Han et al. also reported that due to the presence of HMs in biomass  
24 the activation energy reduced by around 10% in the main decomposition stage during the  
25 slow pyrolysis of contaminated *Broussonetia papyrifera* (**Table 2**) [123].

1       Conversely, Zhong et al. showed the adverse effect of HMs on activation energy (from  
2 150 to 186 kJ mol<sup>-1</sup>) [146], and justified this kinetic behavior based on previous studies  
3 indicating that it might be due to the function of the chemical composition of individual  
4 species or possibly be linked with the presence and absence of mineral content in various  
5 biomass [240, 241]. Moreover, Mullen and Boateng [178] revealed the considerable  
6 accumulation of Fe and Cu on HZSM-5 catalysts during catalytic pyrolysis of switchgrass  
7 (containing 604.40 and 17.19 mg kg<sup>-1</sup> of Fe and Cu, respectively) in a fluidized bed reactor  
8 (**Table 2**). As a result, more exposure of catalyst to higher amount of switchgrass led to more  
9 HMs accumulation on HZSM-5, resulting in further catalyst deactivation. The bio-oil yield  
10 of catalytic process reached up to 35 wt.%, which was considerably lower than that of non-  
11 catalytic process (49 wt.%) [178].

12       The catalytic upgradation of bio-oils derived from HMCBs pyrolysis –using commercial  
13 catalysts– faces some obstacles such as the deactivation and/or poisoning of catalysts by  
14 different factors, which considerably affects the yield and the efficiency of the process  
15 technically, environmentally and economically. To be exact, those affecting factors during  
16 the biomass pyrolysis generally include the high concentration of HMs, water content and  
17 coke formation that can reduce the catalytic activity significantly [45, 178, 223, 242]. Mullen  
18 and Boateng [178] have indicated the increased concentration of two metals, i.e. Fe and Cu,  
19 on the HZSM-5 catalyst while other metals with a high concentration in HMCBs also can  
20 poison the active sites in different catalysts. Therefore, it is expected that the catalytic  
21 pyrolysis of HMCBs might be economically feasible only after some post-treatment of  
22 products, like adsorption, filtration, etc., to remove HMs, then ex-situ catalytic upgradation of  
23 bio-oil can be conducted. Such a process will reduce the catalyst deactivation so as to avoid  
24 the reduction of bio-oil yield/quality during in-situ catalytic pyrolysis of HMCBs in presence  
25 of catalysts [178].

1       The coke formation during pyrolysis process and its accumulation on the catalyst surface  
2 poisons the active site(s), and varies the catalyst topology and textural characteristics, thereby  
3 reducing the total liquid and organic fraction yields, as well as inhibiting the production of  
4 aromatics [67, 243]. In other words, during pyrolysis conversion of biomass, coke deposits in  
5 the catalyst pores to limit the capillary and diffusion flow of reactants leading to low  
6 selectivity and yield of the desired products [244]. On the other side, some catalysts, like  
7  $ZrO_2$ , behave unusually in deoxygenating of pyrolysis oil because it inhibits the poisoning of  
8 its active site by carbon dioxide and water [245]. Furthermore, the Al-MCM-41 catalyst  
9 elucidated the capability of expelling water from the bio-oil, thereby displaying its innate  
10 dehydration potential owing to the presence of moderate acid sites. However, the alumina  
11 catalyst hardly demonstrated any catalytic function in improving the properties of the bio-oil  
12 [210].

#### 13 **4. GASIFICATION**

14 Gasification is a versatile and clean technology to produce environmentally sustainable  
15 biofuels compared with other conventional technologies such as landfilling, incineration, etc.  
16 In fact, gasification augments the value of waste biomass via transforming them into  
17 marketable bio-fuels and products [246]. It converts the biomass virtually into any organic  
18 material and/or syngas ( $H_2$ ,  $CO$ ,  $CH_4$ , etc.) at elevated temperatures (700–1000 °C) via partial  
19 oxidation of compounds using steam, air or oxygen. In addition, gasification process causes  
20 the decrease of adverse climate change via  $CO_2$  mitigation, however some unwanted products  
21 such as tar (mainly oxygenated hydrocarbons), ash, etc. are also formed [79, 246, 247].

22       The main process parameters relating to syngas, are gas yield, LHV, and composition  
23 [97]. The yield and characteristics of the desired product depend on the feedstock properties,  
24 reactor design, temperature, heating rate, pressure, gasifying medium, catalyst, and biomass

1 pretreatment stage(s) [248-250]. Ultimately, syngas can be upgraded by means of the  
2 Fischer–Tropsch process into methanol, dimethyl ether, etc., or combusted directly for power  
3 generation and gas engines [246, 247]. On the other hand, the occurrence of tar (sometimes  
4 containing HMs) in biomass gasification lead to serious problems such as piping or filter  
5 blockage, corrosion and engine failure [246, 251]. Recently, gasification of HMCBs has been  
6 investigated for energy recovery and/or bio-waste volume reduction with considering the  
7 impacts of various gasification conditions on transferring and distribution of metal (loid)  
8 compounds into particle and gas phase (**Table 3**) [97, 163, 252, 253].

1 **Table 3.** Gasification conversion of HMCBs and syngas production

Feedstock	HMs	Gasifier	Temp. (°C)	Pres. (atm)	Gasification agent	Biomass feed rates	Pretreatment	Post-treatment	HMs content of syngas	Remarks	Ref.
Willow	Cd, Zn, Cu, Pb, Cr, Ni, Co, Al, Fe, Mg, Mn, Sn	Lab-scale fixed bed gasifier	450–950	NR	CO <sub>2</sub> 5.40 L h <sup>-1</sup>	5 g exp. <sup>-1</sup>	Dried and crushed: PS* 0.50–1.00 mm	–	High	<ul style="list-style-type: none"> <li>The thermochemical results are in a good agreement with the solid residue composition obtained in an experimental fixed-bed reactor (the open system methodology).</li> <li>HMCB gasification at temperature of 750 °C in presence of CO<sub>2</sub> leads to complete transfer of Cd, Pb and Zn into gas phase.</li> </ul>	Said et al. [254]
Five HMCBs (wild plants)	As, Cd, Zn, Cu, Pb, Cr, Ni, M, Co, Al, Fe, Mg	Gasifier modeling	0–1800	1–40	Steam: oxygen (2:1)	NR	Crushed and air-dried: PS <0.50 mm	–	–	<ul style="list-style-type: none"> <li>HMCBs gasification at temperature &lt;1000 °C and higher pressure up to 30 atm is feasible to produce efficient and clean syngas.</li> <li>Even at pressure of 1 atm and from temperature of &gt;600 °C, As, Cd, Zn and Pb tend to volatilize rapidly.</li> </ul>	Jiang et al. [53]
<i>Leucaena leucocephala</i> and <i>Saccharum officinarum</i>	Cd, Zn, Pb, Cu, Ni, Fe, Al, Co, Ti, Cr, Mo, V, Mn	Bench-scale fluidized bed gasifier reactor	800	NR	Steam ~2 kg h <sup>-1</sup>	1 kg h <sup>-1</sup>	Dried and crushed: PS=3.00 mm	Heated, silicon carbide(SiC) filter	Low	<ul style="list-style-type: none"> <li>Regardless of Al and Fe, other HMs, particularly Pb and Zn, majorly accumulate in the syngas.</li> <li>~70% of HMs content in the syngas samples is resulting from fuel, and ~25% from gasifier system.</li> <li>Using the adequate hot-gas filtration, HMs transferring rate to the syngas decreases, however still some of volatile metallic elements (such as Pb, Zn, Cd and Mo) can pass through the filter.</li> </ul>	Cui et al. [164]
Mixed feedstock (flax, oak and beech)	Cd, Zn, Cu, Pb, Ni, Fe, Mn, Ti	Atmospheric fluidized bed gasifier	855	1	Steam 1.01 kg kg-biomass <sup>-1</sup>	1.08 kg h <sup>-1</sup>	NR	Cyclone	High	<ul style="list-style-type: none"> <li>HMs concentrations in the syngas (nitrogen free, dry gas) is in the range of 0.37–4.20 mg m<sup>-3</sup>.</li> <li>Efficient cleaning procedures must be applied to produce clean syngas with high quality.</li> </ul>	Šyn et al. [97]
Commercially wood pellets	Cd, Zn, Cu, Pb, Cr, Ni, Co, As, Hg, Fe, Al, Mn	Pilot scale (fixed bed) autothermal downdraft system	900–1250	NR	NR	122.50 kg h <sup>-1</sup>	Preheated at 85 °C and flash pyrolysis in the presence of preheated air at 620 °C	Two cyclones, electrostatic filter, cartridge filter	NR	<ul style="list-style-type: none"> <li>The produced syngas (N<sub>2</sub>-free, dry gas) contains 18.30% of H<sub>2</sub>, 28.30% of CH<sub>4</sub>, 27.50% of CO, 25% of CO<sub>2</sub>, with a LHV of ~9.21 MJ Nm<sup>-3</sup>.</li> <li>Cd, Zn, Pb, Cr and Ni accumulates in the fly residue due to their high volatility at the operating temperature of the pyro-gasifier (&gt;900 °C).</li> </ul>	Tafur-Marinos et al. [247]
Straw char and glycol	As, Cd, Pb, Cr, Hg, Ni, V	60 kW pilot-scale atmospheric entrained flow gasifier REGA	1700	1	enriched air (41.82 vol.% O <sub>2</sub> )	10 kg h <sup>-1</sup>	NR	Syngas cleaning devices	Negligible	<ul style="list-style-type: none"> <li>The HMs concentration in the syngas are in the order of Ni (53.20 µg Nm<sup>-3</sup>) &gt;Cr &gt;Pb &gt;As &gt;V &gt;Cd &gt;Hg (2.40 µg Nm<sup>-3</sup>).</li> <li>Increase in fly ash content in syngas causes increase of HMs emission into gas phase.</li> <li>HMs tendency to volatilize is more in reducing gasification environment.</li> </ul>	Pudasainee et al. [163]
Four energy-crops ( <i>M. x giganteus</i> , <i>S. hermaphrodita</i> , <i>S. pectinatus</i> , <i>P. virgatum</i> )	Cd, Zn, Pb	Lab-scale tube furnace	1500	1	Nitrogen ~80 ml min <sup>-1</sup>	10 mg exp. <sup>-1</sup>	Crushed: PS<1 mm	Cooler gas cell	NR	<ul style="list-style-type: none"> <li>Using gasification at &lt;800 °C, HMs almost concentrate in the ash fraction and mostly in the form of a carbonates, silicates and sulphates.</li> <li><i>Miscanthus x giganteus</i>, followed by <i>S. pectinatus</i> appear most attractive species for phytoremediation coupled with thermal utilization of HMCBs.</li> </ul>	Werle et al. [37]
Rice straw, wheat straw, corn stover, switchgrass, Miscanthus, Jose tall wheatgrass, and Douglas fir wood	Cd, Cu, Zn, Pb, Cr, Ni, etc.	furnace	950	1	NR	15 g exp. <sup>-1</sup>	Crushed, preheated and undergone leaching pretreatment	–	–	<ul style="list-style-type: none"> <li>Leaching pretreatment, due of possible changes in the composition of residual solids, contributes to products with more complex properties.</li> <li>After leaching, the heating values of rice straw, wheat straw, switchgrass, and Miscanthus remain quite fix whilst ash concentrations declines 15–39%.</li> <li>The produced leachates is safe for downstream application or disposal.</li> </ul>	Yu et al. [255]
Willow	Cd	Full-scale reactor	850	NR	NR	NR	–	–	–	<ul style="list-style-type: none"> <li>Fast pyrolysis is promising in compared with gasification and combustion to convert Cd-contaminated willow in heat and power (CHP) system (bio-oil yield 65% and LHV 17 GJ t<sup>-1</sup>). However, the profit depends on the scale of operation.</li> </ul>	Kuppens et al. [182]
Willow and <i>Thlaspi caerulescens</i>	Cd, Zn	Lab-scale tube furnace	25–900	1	NR	5–10 g exp. <sup>-1</sup>	Crushed and preheated: PS=1.00 mm	–	NR	<ul style="list-style-type: none"> <li>Gasification (reducing environment) is better than combustion (oxidizing environment) when striving for metal valorization, i.e. HMs recovery.</li> </ul>	Keller et al. [55]

2 \* PS: Particle size of feedstocks; \*\* NR: Not reported

1 Jiang et al. [53] conducted a thermodynamic modelling to demonstrate the solid-to-  
2 gaseous phase transformation of 12 metal (loid) compounds during the gasification of  
3 HMCBs under the operating conditions presented in **Table 3**. Results showed that the  
4 temperature, pressure and initial HMs content to be the major parameters influencing the  
5 behavior of metals during gasification. For example, when the operational pressure was 1 atm:  
6 (1) As, Cd, Zn and Pb tended to rapidly volatilize at temperature  $>600$  °C, and (2) Ni, Cu, Mn  
7 and Co thoroughly transferred into gaseous phase in the temperature range of 1000–1200 °C;  
8 whilst (3) Cr, Al, Fe and Mg remained immobile in solid phase even at temperature  $>1200$  °C.  
9 The gasification simulation revealed that increasing the pressure of gasification process from  
10 1 to 30 atm not only significantly enhances the product yield and reaction rate, but also  
11 elevates the phase transition temperature of HMs from solid to gas by 100–200 °C [53]. Such  
12 a trend had also been proven empirically by Liu et al. [256].

13 Cui et al. [164] sampled and analyzed several HMs in the filter char, bed material and  
14 product gas stream during the gasification of two different HMCBs under operating  
15 conditions listed in **Table 3**. According to their results, regardless of biomass type, Pb and Zn  
16 were mostly found in the gaseous stream. For *Leucaena* the Pb and Zn content in the gas  
17 were  $1690.30 \mu\text{g m}^{-3}$  and  $1151.90 \mu\text{g m}^{-3}$  in the dry  $\text{N}_2$ -free gas, respectively; and for  
18 *Saccharum* they were  $447.90 \mu\text{g m}^{-3}$  and  $144.10 \mu\text{g m}^{-3}$  in the dry  $\text{N}_2$ -free gas, respectively.  
19 Generally, except for the major elements, i.e. Al and Fe, most other HMs mainly volatilized  
20 into the gaseous phase rather remained in the solid residues. Noticeably, the application of  
21 hot-gas filtration, e.g. silicon carbide (SiC) filter could significantly reduce the high transition  
22 of HMs into the gaseous stream.

23 Furthermore, Šyn et al. [97] studied the HMs distribution during co-gasification of a  
24 homogenized mixture of three HM-contaminated energy crops, including 40 wt.% of flax  
25 (*Linum usitatissimum L.*) and 60 wt.% of mixed hardwood (oak and beech) under operating

1 conditions listed in **Table 3**. The initial HMs concentrations in blended feedstock were  
2 approximately Cd = 0.33, Cu = 15.20, Ni = 8.03, Pb = 10.60, Zn = 44.90, Fe = 871, Mn =  
3 67.40 and Ti = 33.70 mg kg<sup>-1</sup> feedstock. According to their observations over co-gasification,  
4 Cd, Zn, Pb, Ni, and Cu ended up in the different downstream sections, such as bed ash,  
5 cyclone ash, and downstream syngas. Moreover, the volatilities of HMs were as follows: Cd  
6 (90% in syngas) >Pb >Zn >Cu >Ni. Totally, HMs concentrations in the syngas (nitrogen free,  
7 dry gas) were in the range of 0.37–4.20 mg m<sup>-3</sup>. Meanwhile, due to the catalytic role of  
8 metals accumulated in ash material and on heat carrier of the fluidized bed (silica sand), the  
9 equilibrium of water gas reaction was shifted to the right, resulting in higher concentration of  
10 H<sub>2</sub> and CO<sub>2</sub> and lower concentration of CO [97].

11 In another work, Pudasainee et al. [163] investigated the emission and distribution of  
12 HMs in both particles and gas phase in syngas from gasification of a slurry (glycol + straw  
13 char 10 wt.%) in a 60 kW pilot-scale atmospheric entrained flow gasifier REGA (Research  
14 Entrained Flow Gasifier) (**Table S2**). It was found that HMs distributed among the different  
15 sections of gasifier (boiler, cooler, syngas cleaning devices) and the remaining entered the  
16 chemical synthesis process (in case of using bioliq®). On average, the fly ash particles and  
17 unburned carbon content in syngas were 1511.70 mg Nm<sup>-3</sup> and 1950 to 2200 mg C Nm<sup>-3</sup>,  
18 respectively. Generally, increase in fly ash content increased HMs emission into gaseous  
19 phase. In other words, tendency of HMs to partitioning into particles enhanced owing to the  
20 increase of fly ash particle concentration and unburned carbon content in syngas. As shown  
21 in **Table S2**, for the gasification of the slurry, the total concentrations of HMs in the gas and  
22 particulate were in the order of Ni (53.20 µg Nm<sup>-3</sup>) >Cr >Pb >As >V >Cd >Hg (2.40 µg Nm<sup>-3</sup>).  
23 Noticeably, from the distribution of HMs shown in **Fig. S3**, it can be seen that Cd, Hg, and  
24 Ni mostly transferred into the gas phase, however, there was not a constant trend for all

1 elements, which might be resulting from their evaporation characteristics and/or various  
2 chemical bonds within particulate [163].

3 Generally, the distribution of HMs and quality of syngas produced from HMCBs are  
4 influenced by several factors including 1) the chemical speciation of metals and dynamics of  
5 fluidization [97, 257], 2) operating conditions (temperature, pressure) [53, 97], 3) nature of  
6 HMCBs [37, 163, 247], 4) implementation of pre- and/or post-treatment processes [164, 247,  
7 255], 5) type of gasifier system (fluidized bed, fixed bed, entrained bed reactors, etc.) [97,  
8 163, 247, 258], 6) impact of fluidized bed materials [20, 252], and 7) the type of gasification  
9 agent [97, 253].

10 The impacts of the last three factors (5–7) could be evident from the following  
11 observations. It was reported that the emissions of HMs containing solid particles from a  
12 countercurrent downdraft fixed bed gasifier were almost one order of magnitude lower than  
13 those from a fluidized bed gasifier [97, 258]. This may explain why in the case of using  
14 fluidized bed gasifier, the emissions of solid particles are more significant which lead to  
15 higher distributions of Cu and Ni through more partitioning on particles of various sizes.  
16 Furthermore, as for gasification agent type, the volatilization of HMs over the steam fluidized  
17 bed gasification of blend feedstock [97] was not as high as had reported for the air fluidized  
18 bed gasification of woody biomass [253, 259]. The slight decrease of CH<sub>4</sub> and higher  
19 concentrations of organic compounds in the syngas have been attributed to the catalytically  
20 enhanced steam reforming reaction in the gasification process [260, 261]. Therefore,  
21 compared to (enriched-) air as gasification agent, the application of steam is preferred due to  
22 the reduction of HMs emission, catalytic role, and production of syngas with higher LHV,  
23 with higher process cost though. However, according to Nzihou and Stanmore [262], the type  
24 of gasification agent (i.e. H<sub>2</sub>O, O<sub>2</sub> or CO<sub>2</sub>) does not significantly affect the HMs transfer, so  
25 that the application of syngas, ash and tar produced may increase serious human and the

1 environmental risks due to the accumulation of HMs along with other inorganics. The  
2 negligible effects of gasification agents can be also concluded by the comparison of Keller et  
3 al. [55] and Said et al. [254] studies on the gasification of willow under same operating  
4 conditions, respectively with air and carbon dioxide as gasification agents, for which, the  
5 total evaporation of Cd and Zn happened at the same temperature range of <750 °C. The rest  
6 factors (1–4) are discussed in the following sub-sections.

#### 7 **4.1 Effect of HMxCB type**

8 Using thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR),  
9 Werle et al. [37] investigated the product distribution, yield and quality of the gas phase  
10 obtained from the gasification of four different types of HM-contaminated energy crops  
11 under operating conditions listed in **Table 3**. The TGA results demonstrated the highest peak  
12 for all four samples at ~350 °C, indicating all samples contained clusters of wooden structure  
13 like uncontaminated biomass with approximately equal amounts of cellulose reported in  
14 another literature [263]. In addition, over the gasification process in the temperature range  
15 <800 °C, most of HMs concentrated in the ash fraction in the forms of carbonates, silicates,  
16 and sulphates. It was concluded that among all four species, *Miscanthus x giganteus*,  
17 followed by *S. pectinata* appear to be most attractive species for phytoremediation coupled  
18 with thermal utilization of HMxCBs; however, these two species have higher amounts of  
19 lignin compared to other two samples [37]. On the other hand, Cui et al. [164] specifically  
20 indicated the negligible impact of the type of two biomass, i.e. *Leucaena leucocephal* or  
21 *Saccharum officinarum*, so that regardless of biomass type, Pb and Zn were observed as two  
22 most abundant HMs in the gas samples. According to thermodynamic modeling, significant  
23 energy can be recovered from wild plants if appropriate conversion facilities could be  
24 provided [53].

1        Regarding the effect of HMCB type on syngas characteristics, Šyn et al. [97] reported that  
2 relatively stable composition and yield of syngas could be achieved; it was found that the dry  
3 gas yield of the blended fuel gasification was  $1.19 \text{ m}^3 \text{ kg}^{-1}$  with the LHV of  $14.60 \text{ MJ m}^{-3}$ ,  
4 and around 90% of feedstock carbon converted to syngas. In addition, the average gas  
5 composition ( $\text{N}_2$ -free, dry gas) was as follows:  $\text{H}_2 = 39.30 \text{ vol}\%$ ,  $\text{CO} = 27.70 \text{ vol}\%$ ,  $\text{CO}_2 =$   
6  $18.10 \text{ vol}\%$ ,  $\text{CH}_4 = 10.20 \text{ vol}\%$ , sum of the C2–C7 hydrocarbons =  $4.70 \text{ vol}\%$ , and tar =  
7  $11.40 \text{ g m}^{-3}$  [97]. However, lower  $\text{H}_2$  concentration and LHV were reported by Tafur-Marinos  
8 et al. [247] in the syngas converted via gasification of commercially wood pellets (**Table 3**),  
9 which the  $\text{N}_2$ -free, dry syngas was, in fact, a mixture of  $\text{H}_2$  (18.30%),  $\text{CO}$  (28.30%),  $\text{CH}_4$   
10 (27.50%) and  $\text{CO}_2$  (25%) with an LHV of  $9.21 \text{ MJ Nm}^{-3}$ . The similar composition was also  
11 observed in the syngas produced from gasification of slurry (glycol + straw char 10 wt.%)  
12 containing  $\text{H}_2$  (18.80%) and  $\text{CO}$  (21.57%) [163].

## 13 **4.2 Effect of HMCBs pretreatment**

14 Dry pretreatments, including preheating and crushing (PS 0.50–3.00 mm), have been  
15 practiced on HMCBs feedstock in most previous studies, but none of them has reported their  
16 effects on the yield and syngas quality, as well as HMs distribution in solid-gaseous phases  
17 [37, 53, 55, 164, 247].

18        However, Yu et al. [255] examined the effect of wet pretreatment (leaching with distilled  
19 deionized water) on the thermochemical conversion of various woody biomass (**Table 3**). For  
20 each leaching pretreatment assay, 20 g of air-dried milled sample was batch-leached at room  
21 temperature ( $22 \text{ }^\circ\text{C}$ ) with distilled deionized water in a sufficient amount to yield a  $20 \text{ L kg}^{-1}$   
22 dry matter-leaching ratio. Firstly, it was found that ash contents were significantly reduced in  
23 all cases though it does not mean it always accompanied by increasing heating value or  
24 improving initial ash melting temperatures; secondly, simultaneous extraction of both

1 inorganic and organic material led to the products possessing more complex properties  
2 because of possible changes in the composition of residual solids. As an example, after  
3 leaching rice straw, wheat straw, switchgrass, and *Miscanthus*, the heating value remained  
4 unchanged whilst ash concentrations declined 15–39%. Additionally, considering the HMs  
5 content of leaching effluent, it met the environmental safety criteria for downstream  
6 application or direct disposal [255].

7 Nonetheless, Li et al. [85] studied the treatment of *Pteris vittata L.*, a hyperaccumulator  
8 contaminated with Cd, Zn, Pb and As, using supercritical water gasification (SCWG) method  
9 in a bench-scale batch reactor conducted under main operating parameters in the following  
10 ranges: reaction temperature of 395–445 °C, pressure of 21–27 MPa and residence time of 0–  
11 40 min. The obtained results indicated that even although HMs, particularly Pb and Zn,  
12 tended to stock in solid residues with a maximal increment of around 50% in the aggregate  
13 content, they were mostly converted to more stable oxidizable and residual fractions, and thus  
14 the ecotoxicity and bioavailability were greatly mitigated with no obvious increase in direct  
15 toxicity fractions. After treatments of contaminated biomass using SCWG method, it was  
16 concluded that each tested HM exposed no or low risk to the environments, meaning that  
17 SCWG has a remarkable ability for the stabilization of HMs after conversion [85].

### 18 **4.3 Optimum gasification conditions and HMs behavior**

19 According to thermodynamic model presented by Jiang et al. [53] increasing pressure  
20 from 1 to 30 atm not only enhanced the product yield and reaction rate considerably, but also  
21 augmented the volatilization temperature of HMs emission to gaseous phase by 100–200 °C.  
22 As a result, temperature <1000 °C and higher pressure up to 30 atm were introduced as  
23 optimum gasification conditions to minimize the transfer of most volatile HMs, including Cd,  
24 Zn and Pd, towards cleaner syngas production [53]. Likewise, the empirical results on

1 optimum gasification temperature (855 °C) and HMs behavior [97] validated the theoretical  
2 outcomes predicted by models employed for different HMCBs [53, 208]; however under that  
3 operating conditions Cd and Pb were almost completely volatilized and transferred into the  
4 syngas. Yet, at the same time, only 20% of Zn was concentrated in the ash (20%), and  $\geq 80\%$   
5 of Cu and Ni remained in the bed and cyclone ash [97], which were in the agreement with  
6 Verweeke et al. [258]. Furthermore, Said et al. [254] investigated the thermodynamic and  
7 experimental gasification of willow under the operating conditions listed in **Table 3** with  
8 adding a fixed amount of CO<sub>2</sub> at each temperature step (every 10 °C from 350 to 1000 °C).  
9 Reportedly, both experimental results and thermodynamic calculations showed that the  
10 behavior of the some HMs (Cd, Sn, Sb, Pb) was remarkably well reproduced by an  
11 calculations open system, however, there was more divergence for Cu, Co and Fe. According  
12 to the results representing the open system methodology, complete evaporation of Cd into gas  
13 phase happened at the temperature of 550 °C and Pb and Zn at 750 °C.

14 According to the previous theoretical and empirical studies on the gasification of HMCBs,  
15 the volatilization temperature of HMs varies significantly from one element to another. From  
16 that point of view they are classified as follows: (I) some HMs may be totally condensed in  
17 gasification gas under cleaning and emission conditions (like Mn); (II) some may get mainly  
18 enriched in the gas phase (e.g., Hg, Cd); (III) element like Co could be totally or partially in  
19 the gas phase at the temperature of hot-gas cleaning systems (500–800 °C), while (IV) other  
20 elements (e.g. As, Zn, Cd, Pb, Cr, Ni, Sb and V) would be present in the gas phase at  
21 temperature <500 °C (**Table S1**) [163, 264, 265].

22 Generally, in spite of operating temperature of thermochemical processes and the  
23 presence of other compounds or elements, to provide less volatility of Cu and Ni, reductive  
24 environment is preferred [257]; however, the environment should be oxidative for less  
25 volatility of Zn [97]. Equilibrium calculations predicted that at ~850 °C and under reducing

1 conditions, no significant volatilization of Cu and Ni occurred [208]. Noticeably, unlike Cd  
2 and Pb which have not been affected by the presence of other elements, the volatility of Zn is  
3 sensitive to sulfur and chlorine content, S/Cl ratio, and the content of alkali metals [257].

4 To study the catalytic effect of HMs present in the HMCBs on the gasification process,  
5 some willow samples, containing 0.01 to 5 wt% Ni, were heated from 20 to 1000 °C (heating  
6 rate of 5 °C min<sup>-1</sup>) in a fixed bed reactor under atmospheric pressure in the presence of N<sub>2</sub> (2  
7 L h<sup>-1</sup>) and CO<sub>2</sub> (6 L h<sup>-1</sup>). The results demonstrated that a maximum efficiency and catalytic  
8 performance was observed during char gasification of willow samples containing 1.60 wt%  
9 Ni, between 450 and 600 °C. An increase in the syngas production and a decrease in the char  
10 gasification temperature by 100 °C confirmed the results obtained [95].

#### 11 **4.4 Usability of syngas and the necessity of post-treatment**

12 Based on the operating conditions and presence of other compounds/elements within  
13 feedstock or hot gas paths, HMs can react to form particles, or the vapor species can  
14 condense to form particles [163, 266, 267]. Consequently, the increasing rate of HMs  
15 emission into gas phase could result from carrying the role of fly ash [163]. From previous  
16 literature, it can be deduced that with the exception of Cd, all other HMs studied (Cu, Ni, Pb,  
17 and Zn) could be dominantly transferred to the solid phase in a gasifier equipped with  
18 cyclone working in the range of 500–600 °C. The average HMs contents in the syngas were,  
19 Zn (4.20), Cu (1.20), Pb (1.20), Ni (0.80) and Cd (0.37 mg m<sup>-3</sup>) [97]. However, sometimes  
20 unexpected high concentrations of some HMs (Cr, Ni, Cu, Fe, and Mo) were observed in  
21 syngas, which has been attributed to their release from gasifier system, including construction  
22 material of reactor [164], lubricants applied [247], cooling system or tubes, etc. [97, 258].

23 As mentioned in pyrolysis of HMCBs the main concern of bio-oil is mostly Cd [146],  
24 however, in gasification, Cd, Pb, and Zn have been found as the most abundant HMs in

1 gaseous stream [97]. Therefore, syngas obtained from HMCBs gasification requires  
2 conditioning and clean-up prior to further usage [97, 164] or catalytic syngas upgrading [163,  
3 246], although, because of its HMs content, there has not been any benchmark or decisive  
4 limits for such sort of syngas valorization yet [97]. Despite products, high emission of HMs  
5 contributes to corrosion, fouling, abrasion, and erosion of gasification facilities and catalyst  
6 deactivation in syngas upgrading facilities [53, 163, 178].

7 In previous investigations, there were some failures even in the case of using gasifier  
8 equipped with post-treatment systems, such as hot-gas filter, candle filter, cooler gas cell, etc.  
9 In fact, increasing operating temperature in gasification not only could affect rising  
10 volatilization rate of HMs but also significantly affects the capability of applied filters to  
11 capture elements associated with fine particulates in syngas [37, 164, 268]. Moreover, Tafur-  
12 Marinos et al. [247] examined several post-treatment sections in their pilot-scale gasifier  
13 reactor (**Fig. S4**), but some of HMs (Cd, Zn, Pb, and Cu) could pass the first filtration phase  
14 (cyclones) due to their high volatilization and high temperature of the syngas in the cyclones.  
15 While, after the cyclone filters, the syngas was successfully purified, cooled, and sent to the  
16 engine [247]. The comparison of the results obtained by Cui et al. [164] and Syc et al. [97]  
17 studies –with same operating conditions (i.e. temperature, pressure, gasification agent, reactor  
18 type) and different HMCBs though– also confirms a better performance of the hot-gas filter  
19 to significantly reduce the transfer of HMs into the syngas, compared to the cyclone.  
20 However, due to using different post-treatment technologies, it was not possible to roughly  
21 compare the direct effect of the type of HMCBs on the emission rates of HMs.

22 Furthermore, Poskas et al. [269] showed the high efficiency of widely-used electrostatic  
23 precipitators (ESPs) for the collection of solid particles from gaseous phase of a large-scale  
24 gasifier (100 kW) and a boiler (50 kW) used for wood pellet conversion to energy. According  
25 to results, EPS showed a collection efficiency of ~98-99% for the flue gas with solid particles

1 concentration of  $13 \text{ mg.m}^{-3}$  and diameters of  $0.30\text{--}20 \text{ }\mu\text{m}$ . On the other hand, EPS  
2 demonstrated a lower efficiency of  $\sim 75\%$  for the syngas produced by the gasifier, which  
3 possessed different particle size of  $4\text{--}400 \text{ }\mu\text{m}$ ,  $1.80\text{--}390 \text{ }\mu\text{m}$  and  $3.90\text{--}375 \text{ }\mu\text{m}$  in various part  
4 of the system, i.e. in cyclone downstream of the gasifier, in the cyclone upstream of the ESP  
5 and in the ESP, respectively. The data revealed that HMs, such as Cu, Zn, Cr, and Ni, did not  
6 accumulate in the cyclone downstream of the gasifier, whilst, they were detected in the  
7 cyclone upstream of the ESP and the ESP, which confirms the transfer of HMs by solid  
8 particles through the gas phase and their partial collection using EPS. The reason for the  
9 lower efficiency of EPS in gasifier was attributed to the challenging working conditions and a  
10 big difference in the concentrations of particles between syngas and flue gas. According to  
11 their observation, by voltage increase of EPS system, a slight but gradual decrease in particle  
12 quantity was obtained, however, still, the worst collection was for the particles with the  
13 smallest diameters [269].

14 Various condensation points of common HMs obtained from different thermodynamic  
15 models and experimental researches have been listed in **Table S3** which is helpful for  
16 efficient running cyclone or other cooling gas cells as post-treatment stage of contaminated  
17 feedstock: among them Hg has been predicted to bear the lower condensation point of  
18  $<200 \text{ }^\circ\text{C}$  [264, 270]. Noticeably, all databases presented for the thermodynamic model of  
19 HMs are limited and different due to the variety of dissimilar compounds and significant  
20 variation of thermodynamic data for some species, which greatly influences predictions for  
21 the speciation of the elements [271]. This fact discloses that limited or insufficient databases  
22 or equilibrium calculation software can contribute to a risk of misleading conclusions, due to  
23 which experimental validation of the modeling results and scale up the results will not be  
24 precise and valid as well [272]. Therefore, a fully consistent thermodynamic database is  
25 required to develop and tackle major limitation of thermodynamic equilibrium modeling.

1 Eventually, owing to the considerable concentration of HMs in the ash by factors of 10–  
2 20, appropriate management and disposal of the ash resulted from gasification process has to  
3 be considered [53, 97]. In case of impossibility of using ashes remained from the gasification  
4 process, landfilling looks to be an undeniable disposal method after leachability tests as a  
5 decisive factor to designate the dump type [97].

## 6 **5. COMBUSTION**

7 Combustion is another thermochemical pathway for the thermal degradation of in presence of  
8 excess oxygen/air at elevated temperatures over 900 °C [273]. Recently, combustion has been  
9 also used for the conversion of HMCBs into wieldy amounts of metal-containing ash, and  
10 simultaneously energy harvesting [169, 274]. The combustion of HMCBs leads to diverse  
11 undesirable emissions of CO, NO<sub>x</sub>, fly ash, solid and gaseous metal compounds [275, 276].  
12 Moreover, the study of aforementioned compounds through combustion of uncontaminated  
13 biomass fuels would be imperative, because some studies have also proven that,  
14 environmental drawbacks triggered via HM emission could arise even if the biomass comes  
15 from an unpolluted area [262, 277].

16 The main concerns about the combustion of HMCBs is not only the volatilization of HMs  
17 and other pollutants but also the management of produced residuals [52]. **Fig. S5** elucidates  
18 the distribution of HMs over the combustion of HMCBs. As seen, HMs enter into the  
19 combustion zone and subsequently exit in three categories: (i) solid residue in the combustor  
20 (bed ash); (ii) solid particles in the fly ash; and (iii) the exhausted gas (flue gas) [278].  
21 Typically, HMs are supplemented in the bottom ash after the combustion due to their  
22 solubility, which certainly restricts the ash disposal opportunities. The leached HMs could be  
23 one of the problems causing environmental damage at waste yards [279, 280]. **Table S4**  
24 shows the distribution of ashes during combustion reported by different studies. The ash

1 distributed into the cyclone ash, the bottom ash, the filter ash (where present), and the rest  
2 was within the flue gas. Most of the HMs signified are found either in the cyclone ash or in  
3 the bottom ash.

4 Moreover, HM compounds depending on their boiling points are volatile at the certain  
5 combustion temperatures (**Table S1**) [52], and their partitioning also depends on the type of  
6 furnace [55, 97, 281]. As the flue gas travels through the stack, the gas stream temperature  
7 declines, and due to which the toxic compounds condensate on neighboring solid particles  
8 [52]. The HM compounds can be noticed as submicron ash and vapor form at the end of the  
9 chimney (depending on the temperature).

10 Several studies have been conducted corresponding to the metals flow calculations [168],  
11 the fate of metals and process viability [128, 169], biosorption performance [282], HMs  
12 content of bottom and fly ash during biomass combustion [193, 262, 278, 283-287]. **Table 4**  
13 presents the experimental approaches applied for the combustion of HMCBs.

1 **Table 4.** Applied combustion processes for the conversion or disposal of HMCBs

Feedstock	HMs	Reactor	Temp. (°C)	Time	Air flow	Biomass feed rates	Pretreatment	Post-treatment	Remarks	Ref.
<i>S. plumbizincicola</i> and sewage sludge	Cd, Pb, Zn, Al	Large-scale fluidized bed reactor	500–1100	NR*	Air 14 m <sup>3</sup> h <sup>-1</sup>	NR Mixing ratio 7:3	Dried and crushed: PS**<5 mm	–	<ul style="list-style-type: none"> <li>• A standard level of Cd, Zn, and Pb concentrations are observed in flue gas.</li> <li>• The medium and low risk of Cd and Zn as well as Pb to environment resulted from fly ash and bottom ash indicates the possibility of co-combustion of <i>S. plumbizincicola</i> and sludge for the safe disposal in China.</li> </ul>	Guo and Zhong [288]
<i>S. plumbizincicola</i> and coal	Cd, Cu, Pb, Zn, Cr, Mg, Mn, Al, Fe	Quartz glass tube furnace	650–950	NR	Air O <sub>2</sub> content (0, 7, 14 and 21%)	2 gr Mixing ratio: 9:1, 7:3, 5:5, 3:7, 1:9	Pre-washed by distilled water, then dried and crushed	Gas absorption system	<ul style="list-style-type: none"> <li>• Mixing ratio of 1:9 can control the total amount of HMs, which is instructive for engineering application.</li> <li>• Increasing temperature significantly increases the volatilization of Cd and Pb in the form of Cd (g) and PbO, and anaerobic conditions increases the volatilization of Zn in the form of Zn (g).</li> </ul>	Guo et al. [289]
Willow ( <i>Salix viminalis</i> and commercial <i>S. Tora</i> )	Cd, Zn, Cu, Cr, Co, Ni, Mn	Industrial scale boiler (40 kW)	900–1000	NR	Excess air	54 kg exp. <sup>-1</sup>	Crushed and then digested by aqua regia and HNO <sub>3</sub> solution (65%).	–	<ul style="list-style-type: none"> <li>• The application of boilers equipped with an efficient filtration system could minimize air pollution resulted from highly volatile HMs, like Cd and Zn.</li> <li>• Obtained ashes are not appropriate as the soil fertilizer.</li> </ul>	Delplanque et al. [128]
Poplar	Cd, Zn, Cu, Pb, Cr, Ni	Industrial scale boiler (200 kW)	509–940	4.70 h	NR	172 kg exp. <sup>-1</sup> , i.e. ~36 kg h <sup>-1</sup>	Crushed and air-dried: PS<40–60 mm	Fabric filter	<ul style="list-style-type: none"> <li>• The application of incinerators equipped with sophisticated pollution-control devices such as cyclone, filter-fly and electrostatic precipitators are suggested to mitigated or eliminated the emission of highly volatile HMs.</li> </ul>	Chalot et al. [169]
<i>S. plumbizincicola</i> and <i>Sedum alfredii</i>	Cd, Zn, Cu, Pb	Entrained flow tube furnace & Horizontal tube furnace	650–950	15 min	1.40 m <sup>3</sup> h <sup>-1</sup>	0.50 g exp. <sup>-1</sup>	Pre-washed by distilled water, then crushed and dried at 85 °C	Stainless steel mesh	<ul style="list-style-type: none"> <li>• Unlike the horizontal tube furnace, incineration in the entrained flow tube furnace causes further fluctuation or accumulation of HMs like Cu and Cd.</li> </ul>	Lu et al. [281]
Willow ( <i>Salix caprea</i> )	Cd, Zn, Cu, Pb	Stainless steel fluidized bed reactor	850	8 h	Air	0.33 kg h <sup>-1</sup> Equivalence ration: 1.30–1.60	NR	Cyclone and glass wool filter	<ul style="list-style-type: none"> <li>• Phytoextraction seems to be a suitable technique to eliminate some negative effects connected with increasing usage of food feedstock-to-bioenergy.</li> <li>• The incineration of HMCBs is the best disposal approach and no ash agglomeration is observed at operating temperature of 85 °C.</li> <li>• The ashes are not appropriate for land usage (soil fertilizer).</li> </ul>	Šyn et al. [274]
Willow ( <i>Salix leaves</i> )	Cd, Zn	Quartz glass tube reactor	25–90	22 min	Air 1040 N L <sup>-1</sup>	5–10 g exp. <sup>-1</sup>	NR	–	<ul style="list-style-type: none"> <li>• Incineration is a feasible choice for treating and safe disposal of HMCBs.</li> <li>• Pyrolysis is a better method than incineration for valorization of HMCBs, i.e. Cd and Zn recovery.</li> <li>• Gasification (reducing environment) is better than combustion (oxidizing environment) when striving for metal volatilization.</li> </ul>	Keller et al. [55]
Biomass char (willow)	Cd, Zn, Cu, Fe	TGA–MS/DSC	25–900	45 min	50 cm <sup>3</sup> min <sup>-1</sup>	5 g exp. <sup>-1</sup>	Crushed and pre-dried: PS<1 mm with mesh size of 80–20	–	<ul style="list-style-type: none"> <li>• Added metals support char combustion and enhance the ignition capability of char.</li> </ul>	Mayer et al. [73]

2 \* NR: Not reported

3 \*\* PS: Particle size of feedstocks

1 Delplanque et al. [128] analyzed the combustion of contaminated willow species in an  
2 industrial scale boiler (40 kW) at operating conditions listed in **Table 4**. According to the  
3 observations, the high temperature inside the boiler (900–1000 °C) led to the high  
4 volatilization of target HMs particularly Cd. Bottom ash included only 0.80% of Cd and  
5 5.30% of Zn of the initial willow stems content, and the rest were mostly found in the flue  
6 gas. Yet, bottom ashes were enriched in Cu, Cr, Co, Ni and Mn because of their lower  
7 volatilization rate resulted from their high boiling points (**Table S1**). Also, Chalot et al. [169]  
8 tested another industrial scale boiler (200 KW) equipped with a fabric filter for the  
9 combustion of contaminated poplar obtained from a polluted agricultural field (**Table 4**).  
10 According to the results, HMs such as Cr, Ni, and Cu were distributed across furnace ash,  
11 followed by heat exchanger ash, and bottom ash. On the contrary, Cd, Zn, and Pb were  
12 mainly present in the particulate and gas fractions that came out of the cyclone in the absence  
13 of the fabric filter. In average >99% of HMs have been accumulated in the ash, and <1%  
14 transfer to the particulate and gas phase [169].

15 Lu et al. [281] compared the suitability of pyrolysis and combustion processes of  
16 hyperaccumulator plants in the range of 450–650 °C, and 550–950 °C, respectively (**Table 4**).  
17 The results showed that incineration diminished the biomass matrix from 13 to 17% of the  
18 initial mass, whilst pyrolysis generated ash content of about three times higher (30–44% ash).  
19 Moreover, it was inferred that incineration in a horizontal tube furnace enhances the  
20 volatilization of Cu and Cd. The amounts of HMs retained in residues after incineration were  
21 lower than those after pyrolysis, particularly for Cd, Pb, and Zn [281], indicating that  
22 oxidizing atmosphere supports the transfer of aforementioned HMs to gaseous phase as  
23 noticed in MSW incineration [290]. Similarly, Keller et al. [55] revealed that the pyrolysis of  
24 HMCBs under a reducing environment is in favor of the stabilization of HMs, like Zn, Cd,  
25 and Cu in ash, as well as their subsequent valorization. Nevertheless, in an entrained tube

1 furnace, increase in furnace temperature enhanced Zn concentration in flue gas, however Cu  
2 and Cd concentrations were fluctuated depending upon experimental conditions [281].  
3 Therefore, in terms of accumulating HMs in the residues, pyrolysis seems a better option in  
4 compare with gasification and combustion.

5 Şyc et al. [274] conducted the combustion of HM-enriched *Salix caprea* in a fluidized bed  
6 reactor to study the distribution of HMs and the energetic utilization of solid residual as  
7 fertilizer (**Table 4**). Accordingly, most of the Cu and Zn (>90%) were found in the ashes  
8 (bottom ash and bed material) followed by Pb (~80%), whilst ~40% of Cd was found in  
9 cyclone and fly ashes and partly volatilized in flue gas either accumulated on submicron ash.  
10 On the other side, different trends were observed in the combustion experiment done by  
11 Keller et al. [55] in a quartz glass tube reactor on Cd and Zn enriched *Salix* leaves. According  
12 to the results, Zn was retained in the bottom ash, whilst Cd was volatilized during combustion  
13 process. After comparison with legal thresholds, Keller et al. [55] and Şyc et al. [274]  
14 inferred that obtained ashes are not appropriate to be employed as the soil fertilizer due to  
15 relatively high content of HMs.

16 Furthermore, Mayer et al. [73] studied the combustion of biomass char, the solid co-  
17 product of the metal enriched wood (willow) pyrolysis, to investigate the influence of various  
18 metals on char combustion and gaseous profile (**Table 4**). According to observations, the rate  
19 of mass loss and heat flow as a function of temperature and time were recorded and  
20 combustion properties of char were estimated by characterization methods introduced by  
21 Sahu et al. [291] and Smith et al. [292] The TGA combustion profile exhibited two  
22 consecutive combustion zones. The first zone (I) was related to release and combustion of  
23 volatiles within the temperature range of 25–270 °C, and the second zone (II) was attributed  
24 to the combustion of fixed carbon within the temperature range of 270–637 °C with a total  
25 carbon conversion of 88–97%. The presence of inorganic compounds affected the first zone

1 combustion; however, marginally boosted combustion reactivity (rate of mass loss) during  
2 second zone combustion. Moreover, both ash and added metals supported char combustion  
3 and enhanced the ignition capability of char. In terms of evolved gas formation, the first zone  
4 of BC combustion was characterized by a slower reaction corresponding to release of  
5 hydrocarbons. Whilst, the second reaction represents the actual combustion of the carbon rich  
6 char, evidenced by the combustion of the released CO<sub>2</sub>, water formation and detected  
7 exothermic heat flow.

## 8 **5.1 Practicability of combustion of HMCBs**

9 The fate of HMs (i.e. Cr, Cu, Cd, Zn, Pb, and Ni) and the suitability for biofuel production  
10 was focused via various thermochemical pathways [169]. Considering such constraint, the  
11 usability of contaminated wood originated from phytoextraction process has to be endorsed  
12 prior to their application as feedstock for bioenergy production [169, 281]. In addition,  
13 according to the French regulations, the combustion of HMCBs produced during  
14 phytoextraction should be taken into account as waste, not as a legal commercial fuel or  
15 viable source for clean bioenergy recovery [128].

16 In the previous studies majorly contaminated Willow or Salix species have been  
17 combusted [73, 128, 274], but there is not enough data to compare either the effect of the type  
18 of HMCBs on HMs distribution, or the effect of pretreatment techniques on combustion of  
19 HMCBs. However, Leaval-Gilly et al. have recommended the application of bioenergy plants,  
20 such as *Miscanthus x giganteus*, for effective phytoextraction of the HMs, like Cd, Cu, Zn, Pb  
21 and Cr; and subsequently, the low accumulation of HMs in aboveground biomass, i.e. stem  
22 and leaves, can facilitate its application in combustion units [36]. Generally speaking,  
23 regardless of the wood source, the applications of industrial scale boilers equipped with  
24 efficient filtration systems was suggested to minimize air pollution resulted from volatile

1 HMs especially Cd [128]. In fact, the high vaporization of the elements contributes their  
2 enrichment in the fly ash, subsequently developing fine particles in the flue gases [293].  
3 Therefore, the application of efficient filtration systems could be practical in order to  
4 minimize air pollution resulted from considerable emission of highly-volatile HMs, such as  
5 Cd, Zn, etc., through the gas phase [128, 169]. Nonetheless, effect of the incinerator type,  
6 horizontal tube furnace causes higher volatilization rate of HMs rather than entrained tube  
7 furnace [281].

8       Among thermochemical processes even though, pyrolysis has been introduced as the best  
9 option for clean bioenergy production [20, 195], according to Keller et al. [55] and Kovacs  
10 and Szemmelveisz [52] combustion has been claimed as the best HMCBs disposal pathway.  
11 Likewise, as previously reported by Lu et al. [281], incineration of HMCBs reduced the  
12 biomass amount from 13 to 17% of the initial mass, in a way that the ash content generated  
13 by combustion was around three times lower than that by pyrolysis, however, the oxidizing  
14 environment of combustion unfavorably led to more volatilization of HMs to the gaseous  
15 phase. On the other hand, Kuppens et al. [182] by implementation of a novel dynamic techno-  
16 economic assessment demonstrated that, pyrolysis of HMxCB was the best option in terms of  
17 heat and energy recovery, compared to gasification and combustion. Nevertheless, Laval-  
18 Gilly et al. [36], regardless of HMs content, have emphasized the limiting concerns resulting  
19 from the increase of K content of HMxCB in brownfield cultures owing to its critical problems  
20 of fouling and slagging in combustion units, which Ljung and Nordin [294] and Keller et al.  
21 [55] attributed that to the formation of inorganic carbon in an oxidative environment, like  
22 potassium carbonate. Therefore, in case of linking brownfield culture to standardize  
23 engineering practices for bioenergy recovery, the regulation of K associated to exclusion of  
24 metal by plant is required.

## 1 **5.2 Necessity of post-treatment**

2 As mentioned, Lu et al. [281] explored the suitability of the combustion process for the  
3 disposal of hyperaccumulator plants contaminated with HMs via phytoextraction process.  
4 The higher volatilization of Cd, Zn, and Pb allowed the further enrichment of these elements  
5 in the fraction at downstream the cyclone. The application of efficient fabric filters,  
6 particularly for highly volatile HMs, will permit the amounts of these last three HMs in the  
7 ashes collected below the filter, therefore fulfilling with entire existing thresholds sanctioned  
8 by EU directive for large combustion plants [169].

9 The absence of fabric filter caused 10–30 times higher concentration of Cd and Zn than  
10 emissions limits. Thus, modern waste-to-energy incinerators equipped with sophisticated  
11 pollution-control devices such as cyclone, filter-fly and electrostatic precipitators as a sink for  
12 Cd, Zn, and Pb could eliminate considerable amounts of HMs and fly ashes from an  
13 incinerator's air emission [169]. It is noteworthy that a recent research has reported the  
14 capability of natural and modified limestone for the capture of HMs, including Cu, Pb, Zn,  
15 and Cr, during the wood sawdust combustion in an atmosphere of 80% CO<sub>2</sub> and 20% O<sub>2</sub>  
16 from 600 to 900 °C. Results revealed a considerable performance of natural limestone at  
17 temperatures >700 °C to capture Cu and Pb, but not for Cr and Zn. The limestone modified  
18 with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> enhanced the capture performance for all studied HMs (i.e. Cu, Pb, Zn, and Cr)  
19 [295]. The modifications removed impurities in inner pores of limestone, resulting in the  
20 increase of the pore size and specific surface area, and consequently the enhancement of  
21 dominant physical and chemical adsorption abilities at 700 and 900 °C, respectively [295].  
22 The application of recent technique seems a potential method for *in-situ* control of HMs in  
23 thermochemical biomass conversion in presence of limestone modified by reasonable  
24 inorganic modification method based on specific targeted HMs.

1 The combustion of *Sedum plumbizincicola* containing high concentrations of Cd, Cu, and  
2 Pb with sewage sludge and coal were conducted in a large-scale fluidized bed and a tube  
3 furnace at different temperatures by Guo and Zhong [288], and Guo et al. [289], respectively  
4 (**Table 4**). According to Guo and Zhong [288], results showed that in the flue gas, the  
5 emission concentrations of Cd, Zn, and Pb were below the standard. The dominant phase in  
6 Zn and Pb is the residual fraction, and by increasing temperature from 700 to 1000 °C, the  
7 proportion of residual fraction in Cd for bottom ash also increased from 16.82 to 44.03%. Cd  
8 and Zn show medium risk to the environment in fly ash and bottom ash. Pb presents no risk  
9 to the ecosystem in fly ash and low risk in bottom ash, indicating that the co-combustion is a  
10 suitable pathway for the safe disposal of *S. plumbizincicola* and sludge in China. Moreover,  
11 according to Guo et al. [289], the results indicated that high temperature was beneficial to the  
12 volatilization of HMs with the order of  $Pb > Cd > Zn$ , in the form of Cd (g), PbO (g). In the  
13 oxygen atmosphere, Zn exists in the form of heavy metal oxides, not easy to volatilize. With  
14 increasing oxygen content, the distribution of Zn and Cd in bottom ash is more, while Pb  
15 concentration is initially increased and then decreases. Under anaerobic condition, Zn begins  
16 to volatilize as Zn (g) and oxygen which are not conducive to the volatilization of Zn.  
17 Therefore, the co-combustion in air condition appears to be beneficial to the disposal of HMs.

## 18 **6. LIQUEFACTION**

19 To the date, various types of biomass, such as plants, algae, etc., have been effectively  
20 converted to the liquid by means of liquefaction techniques, i.e. solvent- and hydrothermal  
21 liquefaction (HTL) [296-298]. In HTL, wet biomass slurries are heated (200–500 °C) under  
22 high pressure (5–20 Mpa) to produce a mixture of products (e.g. bio-oil, 15–75%; gaseous  
23 products, 10–20%; and a negligible amount of solids) [299, 300]. Liquefied products resulted  
24 from a process with high content of both nutrients and organics are suitable for various  
25 applications as biofuel, chemical industries feedstock, polyurethane, etc. [301-303]. The

1 chemical extraction and separation of bio-oil and HMs from HMCBs could be conducted by  
2 HTL process efficiently, and the possibility of both safe disposal and reuse of final solid  
3 residue as fertilizer [304].

4 The solvent liquefaction process is the combination of (1) the direct dissolving of low  
5 molecular content and hemicellulose, (2) the catalyzed degradation of polymer celluloses and  
6 lignose into smaller fragment and also (3) the degradation of the micellar-like resulted from  
7 hydrolysis, to smaller compounds by means of dehydration, dehydrogenation, deoxygenation  
8 or decarboxylation process [215]. Under solvent-based liquefaction, the type of solvent is the  
9 major parameter that affects the process rate and the yield and quality of products [305, 306].

10 The liquefaction of giant reed shoots, containing As (7.53), Cd (9.05), Zn (135.26) and Pb  
11 (17.16 mg kg<sup>-1</sup> dried biomass), was examined in the presence of ethylene glycol system with  
12 sulfuric acid as the catalyst for the precursors of valuable products like polyurethane  
13 compounds [165]. The impacts of operational parameters including solvent/biomass ratio (1:1  
14 – 7:1), temperature (110–190 °C), liquefaction time (20–80 min) and sulfuric acid content  
15 (1–9%) were investigated. According to results, optimum biomass liquefaction rate of  
16 85.20% was achieved at a temperature of 170 °C, 60 min, 3% sulfuric acid, solvent/biomass  
17 ratio of 5:1, and proper pretreatment (i.e. preheating and crushing feedstock (<0.25 mm) in  
18 acidified ethylene glycol system). However, the results demonstrated the major transfer of  
19 HMs to liquefied products high amount of HMs content in the products: As 8.06, Cd 10.33,  
20 Pb 19.55 and Zn 151.16 mg kg<sup>-1</sup> oil [165].

21 Qian et al. [94] investigated the recycling of a Zn-contaminated *Sedum plumbizincicola*  
22 via the subcritical HTL reaction into value-added products, such as bio-oil, hydro-char,  
23 carboxylic acids and other chemicals. To determine the influence of operating temperatures  
24 on Zn distribution and bio-oil products in each subcritical HTL experiment, 15 g of mixed  
25 biomass with and without 150 mL of diluted hydrogen chloride (HCl) solution introduced to

1 a 250 mL autoclave and heated to different temperature from 190 to 310 °C for 2 h. The  
2 results showed that the minimum transfer of Zn into bio-oil (~15%) happened in the presence  
3 of water (i.e. without HCl) at the temperature of 250 °C and the rest accumulated in the  
4 hydro-char. In addition, by increasing HTL temperature, the decomposition of biomass and  
5 the production of acetic acid increased, whereas furans dramatically decreased. More  
6 importantly, at temperatures >280 °C, the favorable depolymerization, deoxygenation and  
7 aromatization reactions of large molecules and the formation of compounds with lower  
8 molecular weight towards a more stable bio-oil were confirmed [94].

9 Furthermore, Yang [304] developed a chemical extraction of HMs and crude bio-oil from  
10 *Sedum plumbizincicola* (contaminated by Zn, Pb and Cu), through hydrothermal upgrading  
11 process in an stainless iron type autoclave (500 mL). The influences of temperature (270–  
12 421 °C), pressure (18.00–25.40 MPa), time (10–120 s) and PS (1.00–4.75 mm) on the  
13 separation efficiency and yield of bio-oil were investigated. For each assay 20 gr of crushed  
14 feedstock with PS of 1.00 mm was introduced to a stainless iron type autoclave (500 mL).  
15 The results showed that the bio-oil yield and gaseous products continuously augmented with  
16 intensifying temperature and pressure due to further decomposition of the feedstock.  
17 However, the efficiency of HMs removal and liquid roughly retained constant in higher  
18 temperature and pressure. Accordingly, maximum HMs removal efficiency of >99% and high  
19 bio-oil yield of >63% were obtained at optimal condition of 370 °C; 22.10 MPa; PS 1.00 mm;  
20 60 s and in the presence of 10 mg L<sup>-1</sup> additives. It was incurred that the HTL is a feasible and  
21 efficient approach for both producing clean crude bio-oil and coping with HMs-polluted  
22 hyperaccumulators [304].

23 According to Guo et al. [165], the solvent liquefaction verified as a potential approach to  
24 dispose HMCBs, whilst further treatment of the liquefied products was strongly  
25 recommended to tackle the potential pollutions and thus further applications of products as

1 appropriate pioneer for polyurethane compounds [165]. It was also indicated that  
2 hemicellulose and lignin are liquefied prior to cellulose, and the final results from  
3 liquefaction of metal-contaminated biomass in optimized conditions was potential and similar  
4 to the bamboo liquefied products [307]. Conversely in Yang [304] study, not only all  
5 components, i.e. oil phase, water raffinate phase, gaseous phase and char-like solid phase,  
6 satisfied the criteria set by China biosolids disposal legislation but also the solid residue can  
7 be reused as fertilizer. Furthermore, according to Qian et al. [94], in the case of using a  
8 reaction containing  $0.24 \text{ mol L}^{-1}$  of HCl at temperature of  $250 \text{ }^\circ\text{C}$  up to 72% of Zn transferred  
9 to the bio-oil. Therefore, it can be inferred for the safe disposal and/or use hydrochar product  
10 from HMCBs, the acidic environment (with  $0.24 \text{ mol L}^{-1}$  of HCl) is favorable with decreasing  
11 rate of Zn transferred into the bio-oil at higher temperature from 220 to  $310 \text{ }^\circ\text{C}$ . Moreover, a  
12 catalytic effect of released  $\text{Zn}^{2+}$  was observed in favor of the bio-oil and acetic acid  
13 production via the oxidation of furfural and 5-(hydroxymethyl)-furfural [94].

## 14 **7. TECHNO-ECONOMIC ASSESSMENT**

15 From a techno-economic point of view, the major barrier for the commercialization of the  
16 technology reviewed in this report appears to lie in 1) the long-time consumption for  
17 phytoextraction of contaminated soil; 2) experimentation and cost to obtain an optimum  
18 thermochemical process towards valorization of a mixture of specific type of HMCBs for  
19 clean production of biofuel and other valuable-end products. In other words, in these cases, to  
20 make phytoextraction of HM-contaminated soil economically viable for farmers, additional  
21 benefits should be provided by bioenergy production [308] or selling metals extracted [309].

22 A techno-economic assessment (TEA) is often linked to biomass and/or carried out on  
23 new technologies that are designed for environmental purposes. In addition, techno-economic  
24 modeling tools are more often required to assess the valorization potential of emerging  
25 technologies towards giving clear insights of key uncertainties to decision makers [310], and

1 funding prospective regional, national and transnational programs [311-314]. However, some  
2 of barriers towards TEA of pyrolysis and almost other thermochemical processes are: 1)  
3 thermochemical treatments of HMCBs are quite new technologies, therefore, there are not a  
4 lot of cost data available [315]; 2) there are significant variations of cost data for pyrolysis,  
5 etc., plants [316]; 3) no large datasets or historical data are available for the uncertainties  
6 [317]; 4) there is a considerable uncertainty for the capital cost of processes that have not  
7 been put into practice yet [318].

8 Kuppens et al. [182] developed a dynamic TEA and cost recovery study on  
9 thermochemical conversions of Cd-contaminated willow harvested from Campine soil (**Table**  
10 **2 and 3**) with respect to positive net present value (NPV), which is an indicator of the  
11 technology's profitability. In their study [182], willow had been selected due to its formerly  
12 established efficiency [319] and economic [320, 321] for Cd removal from contaminated  
13 lands over a short rotation and realistic crop life cycle. According to the results, among  
14 thermochemical conversion processes, only fast pyrolysis for the combined production of  
15 heat and power (CHP) showed more profitability than gasification and combustion (**Table**  
16 **S5**). Whilst, none of three thermochemical conversion technologies showed a positive NPV  
17 for electricity production (**Table S5**).

18 Additionally, it has been pointed out that the profit depends on the operation scale, the  
19 policy support (subsidies) and the oil yield. Regarding the reduction of the economic risk,  
20 following items have been suggested, (I) operation scale-up using complementing  
21 feedstock(s), and (II) valorization of the char byproduct by subsequent processing to  
22 activated carbon, fertilizer, etc. [182]. Meanwhile, companies can decrease risk by reducing  
23 operational risk through co-pyrolysis of various proper biomass [322], increasing the scale of  
24 operation [190], outputs optimization/upgrading [323], etc.

## 1 **8. OUTLOOK**

2 The concept of linking phytoextraction process and thermochemical biofuel production is a  
3 potential and promising pathway towards sustainable phytoremediation process via metal-  
4 free bioenergy production and HMs recovery from HMCBs. The life cycle analysis on  
5 bioenergy from various clean biomass and its lower environmental impact, compared with  
6 fossil fuels has been verified [324]. However, any life cycle analysis of bioenergy or resource  
7 recovery from HMCBs has not been explored yet to the best of our knowledge. However,  
8 according to previous studies, the economic reliability aspect (or TEA) of linking  
9 phytoextraction technique to bioenergy recovery mostly depends on vast areas and sufficient  
10 numbers of farmers, even although soils only moderately polluted with metals.

11 To the date, among thermochemical approaches on HMCBs mostly over last decade, fast  
12 pyrolysis with the operating temperature of 300–450 °C has been determined as the most  
13 promising method, based on thermodynamic/empirical results and TEAs with respect to  
14 usable metal-free bio-oils production without secondary pollution. Generally, the optimum  
15 temperature and pyrolysis operating conditions depend on the inorganic content of HMCBs,  
16 type and content of HMs/metalloid pollutants, pre- and post-treatment technologies,  
17 pyrolyzer reactor, target quality and application of bio-oil, HMs recovery, etc. However, the  
18 effect of HMCBs ash and moisture content on process yield and operating conditions have  
19 been rarely explored.

20 Although, the thermochemical conversions of HMCBs with the emphasize on fast  
21 pyrolysis has been verified a promising pathway to metal-free bio-oil production, still, they  
22 are in infancy stages, because many potential pretreatments, post-treatment or technical  
23 processes towards clean energy recovery and minimized HMs transfer to products has not  
24 been investigated yet. Further opportunities for future research:

- 1 1- Some potential sorbents, including zeolites, char, activated carbon, etc., or  
2 demineralization and leaching techniques due to their effective performance to  
3 immobilize or remove dissolved HMs from HMCBs, condensable and/or liquid  
4 phase, could be examined in processes or pre-/post-treatment stages to minimize the  
5 negative effects of HMs on the reaction performance and the final products. By doing  
6 so, more opportunities are anticipated to promulgate yield and quality of bio-oil plus  
7 HM recovery.
- 8 2- Implementing appropriate post-treatment with respect to the type and risk of HMs  
9 discharged from the reactor or the biofuel produced, and finally precise measurement  
10 of HMs and other potential contaminants levels prior to re-utilization of products and  
11 by-products according to probable relevant national or international environmental  
12 regulations.
- 13 3- Further TEA and technical uncertainties of HMCBs fast pyrolysis are required to be  
14 validated using experimental research, such as (I) checking the quality of bio-oil and  
15 char produced at different temperatures, (II) the moisture content of bio-oil at  
16 different temperatures, resulting in changes on heating values and economic  
17 profitability and (III) other impactful quality parameters, such as bio-oil viscosity,  
18 bio-char fixed carbon, etc.
- 19 4- Further researches and TEAs on other potential biological, chemical and  
20 physicochemical HMCBs conversion routes or pretreatment techniques are required.  
21 Those technologies might be resulted in different net energy productions, cleaner  
22 biofuel production, and consequently better outcomes in terms of CO<sub>2</sub>-equivalents.

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