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BEHAVIOUR AND TREATMENT OF METALS IN BURNING SYSTEM DURING BIOMASS COMBUSTION – LITERATURE REVIEW

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Abstract: Biomass is a renewable energy resource and known as an excellent alternative option for the partial replacement of fossil fuels in energy production. Plants, as frequently used biomass energy sources, contain metals in a different amount. During biomass combustion, the emission of certain elements may lead to environmental pollution and health problems even if the biomass comes from a non-contaminated land. Hence, keeping the metals in the combustion system and avoid hazardous emissions is desirable. The same direction can be recognized by noble metals (NMs) and rare earth elements (REEs) as well, however, in these cases, the economic aspects are also considered. This paper briefly reviews the literature on metal contaminated biomass, phytoextraction, polluted biomass combustion, and the behavior of metals in combustion systems. Based on the literature review the fate of NMs and REEs during polluted biomass incineration has not been deeply investigated yet and requires further examination. Furthermore, capturing metals inside the burning system is also a huge challenge because a significant amount of metal compounds leaves the burning system with flue gas in solid and gaseous form. Besides, phytomining is a potential option for the extraction of NMs and REEs from the soil via plants. And, solid remains (bottom ash, fly ash) coming from contaminated biomass is a promising metal resource.

Keywords: metal, phytoextraction, disposal option, biomass combustion

INTRODUCTION

Biomass is a renewable energy resource including plant and animal materials. Its reservations are limitless. Besides that, biomass energy offers various environmental advantages such as reducing climate change, mitigating acid rain, water pollution, soil erosion, etc. Therefore, biomass is a potential energy resource to diversify world fuel supplies and substantially decrease greenhouse gas emissions [1]. According to reported data, biomass made up 64% of renewable energy's contribution [2] and it is anticipated to rise around double to triple in 2050 [3].

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Generally, woody biomass has been known as an extensively used and the most plentiful resource of biomass. Statistically, more than one-third of the global lands are contaminated sites [4], called brownfields [5]. The real number even might be higher than which has been reported so far. According to the received data, mineral oil and metals are the most contaminants contributing 60% to contaminated lands [6]. Soil contamination in general and metals pollution in particular have serious negative effects on the ecosystem, human health, and the environment. Phytoextraction referring to plants accumulating metals (lead, cadmium, zinc, gold, silver, cerium, lanthanum, etc.) from the soil has been proven as an effective, environmentally friendly, safe, and low-cost remediation method to tackle the problem [7], [8]. The production of the phytoextraction process is a large amount of contaminated biomass that needs proper disposal and management. Thus, polluted biomass has been investigated with a dual purpose those are mitigating pollution problems through the phytoextraction process and producing energy.

1. PHYTOEXTRACTION

Phytoextraction is a soil remediation technology. During this process, plants accumulate metals from contaminated soils, transfer, and store them into the roots and above-ground parts of the plants with various distributions [9]. There are two types of plants can be efficiently used for phytoextraction those are hyperaccumulators and fast-growing species. Hyperaccumulators have been defined as plants that can accumulate huge amounts of metals in the soil without suffering [10]. Fast-growing species that have lower metals extracting ability than hyperaccumulators, however, their total biomass production is outstandingly higher such as poplar or willow [11], [12]. The lower limit for hyperaccumulation and studies corresponding to metals accumulated by plants are summarized in *Table 1*.

Table 1

Studies on metals accumulated by plants

Element	The lower limit for Hyperaccumulators (mg/kg)	Plant species	Concentration in plant (mg/kg)	Ref.
REEs	1,000	*Dicranopteris linearis* (fern)	4,438	[13]
		Dicranopteris dichotoma (fern)	2,231	[14]
		Hickory	(in leaves) 2,296	[15]
Silver	1	*Lupinus sp.* (blue lupin) – induced	126.000	[16]
		Amanita species (mushroom)	1,253.000	[17]
		Tobacco – induced	54.300	[18]
Gold	1	*Lupinus sp.* (blue lupin) – induced	6.300	[16]
		B. juncea (indian mustard) – induced	63.000	[19]
		Z. mays (corn) – induced	20.000	[19]

Element	The lower limit for Hyperac-cumulators (mg/kg)	Plant species	Concentration in plant (mg/kg)	Ref.
Platinum	1	*Berkheya coddii* (flowering plant) – induced	0.183	[20]
		Berkheya coddii (flowering plant)	(in leaves) 0.220 (in roots) 0.140	[21]
Palladium	1	*Berkheya coddii* (flowering plant) – induced	7.677	[20]
		Berkheya coddii (flowering plant)	(in leaves) 0.710 (in roots) 0.180	[21]
		Cannabis sativa (hemp)	30.336	[22]
Nickel	1,000	*Berkheya coddii* (flowering plant)	7,880	[23]
		Alssum lesbiacum (flowering plant)	10,000	[23]
Thallium	100	*Iberis intermedia* (herbaceous plant)	4,055	[24]
		Biscutella laevigata (flowering plant)	13,768	[24]
Cobalt	1,000	*Berkheya coddii* (flowering plant)	290	[25]
		Haumaniastrum robertii (flowering plant)	(in leaves) 4,304	[26]
Zinc	10,000	*Thlaspi caerulescens* (alpine pennygrass)	43,710	[27]
		Dichapetalum gelonioides (small semi-evergreen tree)	30,000	[27]
Lead	1,000	*Minuartia verna* (spring sandwort)	20,000	[27]
		Agrostis tenuis (grass)	13,490	[27]
Cadmium	100	*Thlaspi caerulescens* (alpine pennygrass)	2,130	[27]
		Arabidopsis halleri (flowering plant)	267	[28]
Copper	1,000	*Angiopteris sp. nov.* (fern)	3,535	[29]
		Anisopappus davyi (sunflower)	3,504	[29]
Manga-nese	10,000	*Phytolacca acinosa* (herbaceous plant)	(in leaves) 12,180	[30]
		Chengiopanax sciadophylloides (flowering tree)	(in leaves) 23,200	[31]
Chro-mium	300	*Leersia hexandra* (grass)	(in leaves) 2,978	[32]
Arsenic	1,000	*Pteris vittata* (brake fern)	3,280–4,980	[33]
		Pityrogramma calomelanos (fern)	(in leaves) 8,350	[34]

Phytoextraction is not only used for removing metals from contaminated areas but also offers the possibility for exploiting metals from mill tailings, overburdens, low-grade ores, or mineralized soil that is not economic by traditional mining methods [35]. In the economic aspect, NMs are potential candidates for phytomining because of their high value. However, only a few studies can be found in the case of Silver, Gold [35], [36]. While, the information about others like Platinum, Palladium, Rhodium,

Osmium, etc is very limited and even zero. Specifically, the phytoextraction of precious metals in contaminated soils has not been investigated that deserves more attention because of dual advantages including soil remediation and economic benefit.

2. TREATMENT AND DISPOSAL OF BIOMASS USED FOR PHYTOEXTRACTION

Phytoextraction is a soil remediation process that uses plants to uptake pollutants from brownfields and transports them into the plants. Polluted lands remediation and contaminates biomass formation occur simultaneously. It means that the environmental hazard is just transferred from soil to biomass. Hence, the phytoextraction process encounters a serious problem that is the production of large quantities of highly contaminated biomass, it needs proper disposal and management. Several methods of contaminated biomass treatments including composting, compaction, direct disposal, leaching, thermal conversion (pyrolysis, gasification, combustion) have been investigated so far [37], [38]. The pre-treatment step includes composting, compaction, and pyrolysis to decrease biomass volume and remove excess water. This lowers the cost of transportation to the disposal site and enhances the technical parameters. After this step, considerable quantities of polluted material still exist. On the other hand, direct disposal, leaching, incineration (gasification, combustion) known as final disposal methods [39]. The treatment techniques of phytoextraction biomass disposal are shortly described in *Table 2*. Among the aforementioned approaches, combustion has been recognized as the most feasible, economically acceptable, environmentally effective pathway [38], [39].

Table 2

Treatment techniques of phytoextraction biomass disposal, based on [38], [39]

Process	Step	Advantages	Disadvantages
Composting	Pretreatment	• Reduce volume and water content, decreases the costs of handling and transportation	• Time-consuming (2-3 months) • End-product needs to be treated as hazardous waste • In laboratory scale
Compaction	Pretreatment	• Volume reduction leads to cost transportation reduction • Shorter time compared to composting • Recovery of metals	• Special equipment is required • End-products (remaining biomass, leachates) should be treated as hazardous waste
Direct disposal	Final disposal	• Simple and time effectiveness	• Expensive and limited dumping sites • Slow reduction of polluted material • Serious environmental problems • This method has been forbidden
Leaching	Final disposal	• Recovery of metals	• No technology
Pyrolysis	Pretreatment	• High volume reduction, increases the energy density of biomass and decreases the	• Solid product fraction needs to be treated as hazardous waste

Process	Step	Advantages	Disadvantages
		costs of handling and transportation • Useful end-product	
Gasification	Final disposal	• High volume reduction, toxic metals enriched in solid residual • Lowering harmful climate change via CO_2 mitigation	• Undesired products such as tar, ash, etc., are formed • Technical and environmental problems during the utilization of syngas produced from contaminated biomass
Combustion	Final disposal	• High volume reduction, toxic metals enriched in solid residual • Produce energy	• Undesirable emissions of CO, NO_x, fly ash and solid, gaseous metal compounds

3. BIOMASS COMBUSTION

Combustion is a thermal conversion process and recognized as the best way for contaminated biomass final disposal. Combustion degradates material in the presence of excess oxygen/air at high temperatures over 900 °C [40]. The benefits of combustion technology are more than 90% volume reduction and toxic metals enriched in solid residual. Additionally, combustion is not only a disposal method for polluted biomass but also a promising energy producing solution. Nonetheless, the combustion of polluted biomass results in diverse environmental issues such as undesirable emissions of CO, NOx, fly ash, and solid, gaseous metal compounds. Where solid and gaseous metal compounds are the main concern of polluted biomass combustion, further investigations of these compounds during the combustion of biomass fuels (polluted and unpolluted) would be imperative, because many studies have proven than metals emission could arise even if the biomass feedstock comes from a non-contaminated land [41], [42].

Metals enter the combustion chamber subsequently exit in one of the three following forms: solid residues in the combustor (bottom ash); solid particles in the flue gas (fly ash); and the exhausted gas (flue gas). The fate of metals during combustion in ashes reported by different studies is presented in *Table 3*, which shows that most of the metals were detected in bottom ash and cyclone ash. Nonetheless, in another work, Vassilev et al [43] concluded that more than 90% of Cd, Hg, Sb, Se, and V are volatilized during biomass combustion, and higher than 50% volatilization in case of As, Cr, Pb, or Zn.

Table 3

Distribution of metals in some boiler ashes mg/kg, based on [44]

Metal	Bottom ash			Cyclone ash		Filter ash			Flue dust
	[45]	[46]	[47]	[45]	[47]	[45]	[46]	[47]	[47]
As	9.2	<3.0	3.0	25.6	1.9	5.1	16.0	0.7	0.2
Ba	534.9	330.0	–	671.4	–	206.4	2000.0	–	–
Cd	1.1	<0.3	1.2	2.3	8.6	1.9	3.0	6.6	1.9
Co	6.7	2.5	9.7	11.5	3.7	6.4	8.0	0.6	0.2

Metal	Bottom ash			Cyclone ash		Filter ash			Flue dust
	[45]	[46]	[47]	[45]	[47]	[45]	[46]	[47]	[47]
Cr	24.6	15.0	187.0	128.1	50.7	10.1	24.0	15.2	4.6
Cu	12.8	<10.0	147.1	31.6	51.6	18.9	60.0	29.9	8.8
Fe	5230.9	–	11756.8	8136.0	4442.2	1988.3	–	384.1	116.9
Mn	4864.0	–	12293.0	7144.0	5700.0	5020.0	–	779.0	228.0
Ni	28.5	19.0	27.1	68.3	14.6	24.5	67.0	3.5	1.1
Pb	29.0	<3.0	43.4	36.1	22.5	23.4	49.0	27.5	8.2
Ti	160.0	–	–	179.0	–	982.0	–	–	–
V	–	95.0	32.2	–	10.3	–	140.0	2.0	0.6
Zn	99.2	160.0	485.9	252.0	946.7	61.7	480.0	511.1	150.8
Hg	0.005	<0.030	0.003	0.007	0.030	0.014	<0.300	0.283	0.084

Several studies have been carried out corresponding to the metals flow calculations [48] and the distribution of metals during woody biomass combustion [43], [49]–[51]. Besides, the fate of metals during combustion of different feedstocks like waste [52], [53], sludge [54], [55], poultry litter [56], [57], contaminated oil [58], co-combustion [59], [60] also have been investigated.

The volatilization of metals is one of the major factors influencing the distribution of metals in biomass combustion [43]. It is dependent on the boiling point, the lower boiling point leads to the higher volatilization of metal.

The combustion temperature has been proven as the main parameter influencing the fate of metals during biomass combustion. Jimenez et al [61] combusted olive residue *(orujillo)* and analyzed the concentrations of Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, and Pb in sub-micrometer aerosols at different furnace temperatures (1,100, 1,300, and 1,450 °C) in an entrained flow reactor. The results revealed that almost metals (except Co, Ga, and Mn) were enriched in fine particles by increasing combustor temperature. Hu et al [62] investigated the impact of the combustion temperature, moisture content, chlorine on metals (Zn, Pb, Cu, Mn, and Cd) transferring into flue gas of sewage sludge combustion. According to the results, the higher burning temperature caused the higher selected metals content in the flue gas. It was also found that a higher moisture content decreased the transfer Cd, Zn, and Pb into the flue gas, but it had a slight effect on Cu and Mn. Furthermore, added chlorine during sewage sludge combustion promoted to release Cs, Zn, and Pb into the flue gas, but it had little influence on Cu and Mn. Likewise, Belevi and Langmeier [63] studied the evaporation behavior of Zn, Sn, Cu, Sb, Cd, and Pb during municipal solid waste combustion in a furnace temperature range of 500−900 °C. It was indicated that higher burning temperature caused an increase in transfers of target metals into the gaseous phase, except Sb. The authors also revealed, the residence time increase (from 10 to 120 min) resulted in higher evaporation of Zn, Cu, Cd, Pb, and it showed a slight effect in the case of Sb. Likewise, several studies investigated the influence of combustor temperature on the behavior of metals during the combustion of different kinds of feedstocks such as contaminated woody biomass [64], sewage sludge

[65], waste [66], [67], poultry litter, co-combustion [68]. These results showed the same connection between the burning temperature and distribution of metals.

Besides that, the effect of flue gas temperature on the behavior of metals during biomass combustion has been rarely investigated. Polluted biomass *(Populus tremula)* was combusted to analyze the impact of flue gas temperature [69]. According to the results, more metals (Ag, Co, Cr, Cu, Fe, Ga, Mg, Mn, Ni, Pb, Si, Sn, Ti, V, and Zr) could be condensed on fly ash particles and captured inside the combustion system by decreasing flue gas temperature from 250 to 150 °C. The study also revealed that more than 50% of the total metals input (except Ni) could not be detected in bottom ash and fly ash as seen in *Figure 1*. This means that, during contaminated biomass combustion, these metals likely were volatized and exited the combustion system in gaseous form.

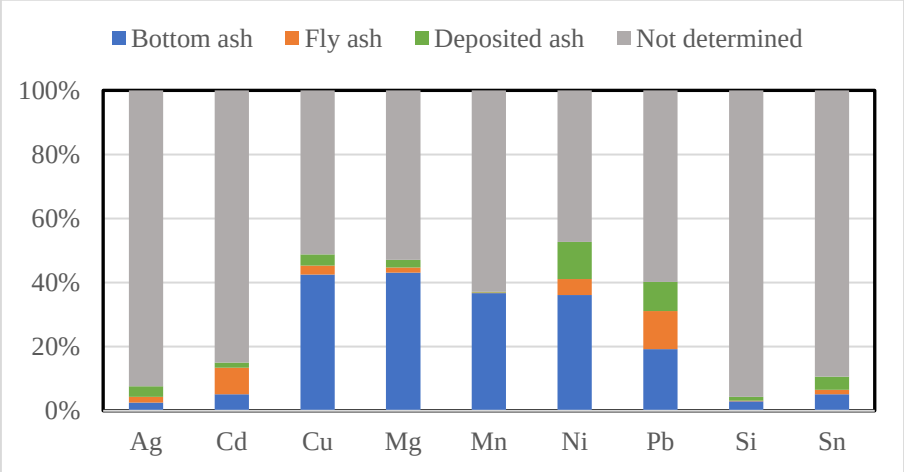

Figure 1
Metal flow in contaminated biomass combustion, based on [69]

Residence time and moisture content are recognized as the secondary influencing factors on the fate of metals during combustion. It has been reported that longer reaction time leads to more volatilization of metals while, an increase of moisture content in feedstocks may decrease the emissions of metals [62], [70].

The distribution of metals during combustion also influenced by the presence of chlorine. It was found that the increase of chlorine content in the combustion chamber results in a higher concentration of metals in flue gas [62], [70]. That can be explained by decreasing volatility temperature [71].

It has been indicated that the lack of oxygen accelerates metals volatilization due to the less formation of metal oxides that have higher volatility temperature than metal elements [72], [73].

The partitioning of metals in biomass combustion also depends on the type of furnace. Lu et al. [74] stated that in terms of the influence of the combustor type, the

horizontal tube furnace resulted in a higher metals volatilization compared to the entrained tube furnace.

Generally, the distribution of metals during biomass combustion depends on various factors such as feedstock properties, reactors, operating conditions (combustion temperature, flue gas temperature, pressure, oxygen, residence time), the boiling point of metals, presence of chlorine, etc. It can be said that the fate of NMs and REEs during contaminated biomass combustion has not been investigated yet. Moreover, the capture of metals inside the combustion system is a huge challenge because more than 50 percent of metals emit in the gaseous phase according to recent research. These tasks need further investigation so far. Additionally, during combustion process metals are enriched in bottom ash, especially in fly ash. Thus, the concentration of metals in the ash might be high enough for extraction and the solid remains coming from contaminated biomass is a promising metal resource.

CONCLUSIONS

Based on the literature review it can be stated that various studies are corresponding to the behavior of heavy metals during contaminated combustion. However, the investigation of NMs and REEs in the burning system is extremely limited and requires further examination.

Furthermore, developing a technique to capture (and possibly recover) metals is also the potential gap of knowledge. Since, according to several recent studies, a significant amount of metal compounds is leaving the burning system with flue gas in solid and gaseous form without ensuring their capture and treatment. It can be said that capturing metals inside the burning system is challenging and it has not been fully solved yet as well.

Additionally, phytomining is a potential option for the extraction of NMs and REEs from the soil via plants. And, solid remains coming from contaminated biomass is a promising metal resource.

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