HEAVY METAL CONTAMINATED BIOMASS COMBUSTION AS TREATMENT AFTER PHOTOREMEDIATION – A REVIEW

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The biomass properties and behaviors are changed in wide range. Technically, the efficiency of biomass combustion depends on fuel composition significantly. The heavy metal contaminated biomass combustion is a special renewable energy source, because the burning process could cause high environmental risk. The biomass with high heavy metal content are coming from phytoremediation, an environment friendly soil remediation technique. Several methods have been developed for the disposal of heavy metal contaminated biomass, for example the liquid extraction, direct disposal, composting or combustion. This review deals with combustion technology as a disposal option of the contaminated biomass, and examines the possibility and circumstances of this process considering environmental aspects. This disposal technique is very complex. If we analyze the economic aspects, we can take notice of the fact, that thanks to this process the energy production is possible. In order to produce energy from the contaminated biomass without environmental pollution, a special technology is required during the disposal (combustion). In case of ordinary biomass combustion, there are several solid and gaseous air pollutants, which have to be considered. If the aim of combustion is disposal, and the fuel is contaminated with heavy metals, certain emissions will probably increase. The problem of volatile and solid heavy metal compounds in flue gas has to be analyzed. The heavy metals and their compounds have various behaviors, thus certain metals are less volatile and concentrate in the ash, and others leave the combustion chamber in a gaseous form. A part of these volatile compounds condensate in the flue gas system, other parts could be detected in solid or gaseous form at the end of the chimney as emission. This is an avoidable environmental pollution. This review deals with the recent reasearches of this complex topic.

Keywords: heavy metal, combustion, temperature, phytoremediation

Introduction

Heavy metals are naturally presented in the environment and are taken up in small amount by living organisms. As trace elements, they provide essential nutrients for plants and herbivores, while at toxic level; they cause harmful effects to the whole ecosystem.

Excessive heavy metal concentrations are regularly encountered at areas of extensive mining spoil and metal processing (mine tailings, plant sites). In any case, measures should be taken to prevent the spread of pollution and to reduce toxic levels of pollutant concentration – whether apparently detectable or not. For the remediation of misused industrial sites, various recovery techniques are known. Biological treatments include bioaccumulation, which is based on the capacity of plants and microorganisms to absorb and store chemical substances in concentrations higher than typical for the original environmental source (soil). The absorbed chemicals are accumulated in the plant cells and tissues.

By extracting large quantities of toxic contaminants (e.g. lead, cadmium, zinc) from soil and groundwater, certain plant species effectively contribute to the remediation of heavy metal contaminated sites [1]. The metals are soaked up by the roots and transported through conductive tissues to the aboveground plant parts (shoots), yielding easily harvestable

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biomass. This vegetal activity effectively improves soil quality and helps restoring the ecological balance [2].

1. Biomass coming from phytoremediation

The plants accumulate nutrients through roots or leaves, but the primary source is the root system. Several factors affect the nutrient uptake from the soil, for example the temperature, the water content of the soil, the soil texture, and the pH. For plants, the pH 6.5 is beneficial; the natural living condition for them is between pH 4–8. Further factors are the temperature and water supply of the soil [3].

When chemical compositions of different biomass (for dry sample) were compared, the results varied in a small interval. The main chemical elements of biomass are (in decreasing order) C, O, H, N, Ca, K, Si, Mg, Al, S, Fe, P, Cl, Na, Mn and Ti [4].

Not only the heavy metal nutrient deficient could give rise to metabolic confusion in plants, but also the extremely high concentration [5]. The chemical balance in living organisms is a primary criterion for growing and developing. This is the main reason, why soil treatments (for example liming) are often necessary for keeping alive a plant organism [6] [7] [8]. The effect of heavy metal concentration change to the plant growth could be described by a kinetic model. This allows the recognition of a heavy metal contaminated soil-plant system. Researches prove, that the heavy metal accumulation in plants depends not only on the properties of heavy metals and plants, but also on the soil type, and on environmental circumstances [9].

The mobility and solubility of pollutants could be decreased with cement or Ca(OH)₂ in a high pH soil environment, but under low pH conditions the mobility of cadmium, cobalt, copper, nickel, lead and zinc increases [10].

The connection between the concentration and the toxicity is different in the case of every nutrient. Some microelements important for the plants (B, Cl, Cu, Fe, Mn, Mo, Ni, Zn) are unotoxic in high concentration [11]. In low concentration, other elements, like cadmium, chromium, mercury and lead do not interfere with the plant growth, but in higher concentration, the plant life is risked. It is important to notice, that a certain amount of heavy metals could be piled up in plants without toxicity symptoms (leaf atrophy, plant growth stopping, necrosis). Several researches deal with the effect of heavy metals for plant life, and determine the toxic concentration of heavy metals in plants [12].

During the remediation with phytoextraction, the heavy metal content of soil decreases, thereby the environmental risk caused by the toxic elements is moderated. Through this process, the pollutants are transferred into the plants; this gives rise to another environmental danger. Soil remediation and polluted biomass formation arise simultaneously. The treatment of this contaminate biomass is required. In 2004 a research [13] determined the following disposal options:

- Composting: American researchers have shown the water solubility of bioaccumulated zinc and other metallic components [14], therefore this method is only applicable with strict control requirements. Total heavy metal content should be minimized through mixing the metal-enriched biomass with high proportions of uncontaminated dry matter and other biodegradable substances. The technology requires the close and continuous monitoring of mixture composition. On the other hand, the phytoextracted metals are returned to the soil in small doses to provide for nutrient recovery. Ex-situ composting is proposed as a post-harvest treatment for
biomass by which the disposal of hazardous plant material can be made more effective [15].

- Pyrolysis: Flash pyrolysis can be used for the disposal of heavy metal contaminated biomass [16] [17] [18] [19]. Low-temperature pyrolysis renders liquid fuel, with the metallic substances concentrated in the solid residues and the by-products [18]. Unless it is further processed as recyclables, the produced coke breeze should be treated as hazardous waste.

- Direct disposal: The direct disposal of the harvested biomass waste would cause environmental problems; therefore, it is forbidden [20]. Disposal as hazardous waste is a feasible yet cost-demanding solution, thus, it is less preferred.

- Leaching: this disposal technology is based on the behaviour of soluble metals to percolate from the carrying medium – which is the very property that accounts for the categorization of metal contaminated biomass as hazardous waste. After enrichment, toxic metals are leached with different solvents from the compacted biomass. The leached product (residual biomass matter) can be treated as non-hazardous material [13]. There are viable technologies to recover the metallic components from the leached solution at relatively high costs, though [21]. The leachability (i.e. recovery rate) of toxic metals from biomass is generally determined as a function of time and pH value [22].

- Incineration (smelting): this process is based on the thermal degradation of contaminated woody biomass into manageable volumes of metal-containing ash. By substantially reducing the volume of hazardous waste material, both transport and disposal can be made more cost-effective. Countless descriptions of the technology are known [23], but there is a paucity of data on the efficiency and technical feasibility of the process. Note that the thermal energy obtained from smelting can be utilized for energy purposes, which adds to the benefits of this method.

  The incineration of heavy metal contaminated biomass is a promising yet not fully mature technology. Various combustion systems are currently under development for field-scale application. In the near future, this method is likely to mean an environmentally sound and economically acceptable alternative [13].

  Disposal through incineration is an excellent option to replace the expensive treatment and costly transportation of the harvested biomass to hazardous waste disposal facilities. In this way, up to 99% volume reduction of the contaminated material can be reached, with the pollutants concentrated in the solid combustion residues (ash, fly ash). The final product is easy to mobilize and handle in a controlled, environmentally acceptable manner.

2. Heavy metal contaminated biomass combustion

2.1. Heavy metal behaviors and emissions during biomass combustion

During the combustion of heavy metal contaminated biomass, there are not only regular emissions (CO, NOx, fly ash), but also the problem of the solid and gaseous metal compounds. It would be important to examine these compounds by combustion of ordinary biomass fuels, because certain researches prove, that the heavy metal emission could cause environmental problems, even if the biomass is coming from a non-polluted area [24] [25].

  One of the basic sources of danger is the solubility of heavy metals, which are enriched in the bottom ash after combustion. These leaching behaviors determine the disposal options of ash. The leached heavy metals cause environmental damages in waste yards [26] [27].
Another basic source of danger is, that the heavy metal compounds are volatile at the combustion temperature [28] [29]. During the flue gas flowing across the offtake system, the temperature decreases, and the toxic compounds condensate to the solid parts in its environment [30]. The heavy metal compounds have two types at the end of the chimney (depending on the temperature):

- solid (condensed) form, as fly ash; and
- volatile form.

Along with the increasing flue gas temperature, the gaseous-solid transition (particle formation) is controlled by two mechanisms [31] [32]:

- homogeneous condensation, where new particles are formed; and
- heterogeneous condensation, which takes place on the surface of particles

As soon as the metal vapors reach the super-saturation condition, the condensation begins and it contributes to the formation of ultra-fine particles [33].

The researches in the topic of examining biomass burning remains deal with ash analysis primarily [34] [35]. The expansion of this research topic includes the heavy metal examinations inside the biomass combustion system. The distribution of heavy metals in solid and gaseous burning residues is referred to as partition of metals [36].

The main goal is to treat and dispose of the biomass formed in contaminated lands, thus the accumulation of the contaminants could be considered as an aim. The biggest problem is the volatility of these elements. The material flows of the pollutants are required to know.

In the case of fluid bed combustion, the heavy metals (Cd, Pb, Zn) from the biomass are in volatile form at the temperature of the combustion chamber [37]. These compounds condensate at different temperatures, thus the examination of the volatility behaviors should be considered [38]. After the flue gas cools down (180–200 °C), the heavy metals are detected primarily in solid form, except As, Co and Sb, these could stay in gaseous phase [30]. Table 3 shows the volatility of heavy metals at 1 Pa pressure based on thermochemical calculations (with and without chlorides in the burning system) [36].

### Table 1

<table>
<thead>
<tr>
<th>Heavy Metal</th>
<th>No chlorides</th>
<th>With 10% of chlorides</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volatility</td>
<td>Form</td>
</tr>
<tr>
<td></td>
<td>temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(°C)</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>1613</td>
<td>CrO2/ CrO3</td>
</tr>
<tr>
<td>Ni</td>
<td>1210</td>
<td>Ni(OH)2</td>
</tr>
<tr>
<td>Pb</td>
<td>627</td>
<td>Pb</td>
</tr>
<tr>
<td>Cd</td>
<td>214</td>
<td>Cd</td>
</tr>
</tbody>
</table>

It can be stated based on Table 1, that several metals (Pb, Cd) are volatile at the biomass burning temperature, especially the chlorides [36].

The release of metals depends on many factors, including the volatility, the burning environment and the ash, fly ash treatment [39]. Furthermore, the amount of metals in flue gas depends on the presence of different types of chlorine-, sulfide-, carbon-, nitrogen- and other compounds in the combustion chamber and flue gas. Fly ash samples coming from municipal solid waste burners were analyzed by X-ray scattering technique, and the results
show that the following compounds were detectable in flue gas at 420 °C (the burning temperature was 953 °C).

- oxides: Al₂O₃, MnO, Pb₂SiO₅, Pb₂Sb₂O₇, Pb₂SiO₄, Fe₂O₃, Fe₃O₄,
- others: PbO₂SO₄, Cd₅(AsO₄)₃Cl, CdSO₄, K₂ZnCl₄, ZnCl₂, ZnSO₄ [39].

The fluid bed combustion experiments of biomass with high heavy metal content show that the Pb, Zn and Cd compounds leave the combustion chamber at 700–800 °C especially quickly. The Pb, Zn and Cd contents of flue gas depending on time are shown in Figure 1 [40].

Three different exit ways should be studied in reference to heavy metals entering the combustion chamber: the solid remains in the combustion chamber (bottom ash); the solid particles in the flue gas (fly ash); and the exhausted gas (flue gas). Based on this fact a research determined, that the metals distribute very differently in the combustion system. Almost all of the Hg is exhausted; contrarily the Cu stays in the bottom ash mostly. The Cd and the Pb distribution was more uniform [36].

In every respect, the solubility of metals is a very important fact. The metals could be solubilized with chemicals from the solid remains (bottom ash, fly ash), but the solubility is influenced by the combustion technology [36] [42] [43], the metal compounds properties and other circumstances [44].

The change of heavy metal content depending on the pH of hydrochloric acid solvent was determined in fly ash [41]. Based on Figure 2, it can be stated, that the solubility of heavy metals is the highest in undiluted hydrochloric acid environment.

During the combustion of metal contaminated biomass, it is required to analyze the hazard risk of solid remains (bottom ash, fly ash). Based on researches the volatile, toxic metals mean risk primarily to the environment [45] [37]. To determine the amount of metals in flue gas in volatile form is a higher technological challenge, and the technology of minimizing or ceasing the metal emission is the biggest environmental task. The dust (and condensed metal) extractor of flue gas is an obvious solution, but not perfect. The dust extractor could solve the metal emission problem only if the temperature of flue gas is low enough, and the condensation of metal compounds ends before the separator. If this condition is not fulfilled, than the efficiency of the extractor system is not fit for metal separation. In this case additional flue gas cleaning technology is required.
2.2. Particle removal systems

The particle removal technologies are very important in the case of biomass combustion especially if the fuel contains a high amount of metals.

The amount of solid particles in flue gas depends on fuel properties [46] and combustion technology [47]. Usually two types of fly ash are discerned: rough and fine dust particles [48]. In the cooling zones of the burning system, the metals are condensed with two different methods; fine particles are formed with homogeneous condensation [49], and on the surface of fine dust heterogeneous condensation takes place [50].

Several different particle separator systems exist, but to select and form the correct, efficient and sufficient technology is an engineering task. Particle removal from flue gas can be divided into categories (Figure 3) [51].

![Classification of particle separators](image)

**Figure 3**

*Particle removal system categories [51]*

Figure 4 shows, that these technologies are applicable for the separation of specific solid particle diameter intervals efficiently.

![The dust extractor types regarding the efficient particle size separating](image)

**Figure 4**

*The dust extractor types regarding the efficient particle size separating [52]*
Multi-cyclone equipment is often used by small industrial biomass furnaces, but the solid particle emission could exceed the emission limit value [53]. With filters or electrostatic precipitators the solid particle emission could decrease under 10 mg/Nm³, but these equipments increase the operational costs significantly [53]. The fly ash needs to be bigger than 5 µm to separate with cyclones, but to separate the particles smaller than 1 µm electrostatic precipitators or filters are required [45]. The efficiency data of different particle separators are summarized in Table 2 [51].

<table>
<thead>
<tr>
<th>Technology</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclone</td>
<td>90–99</td>
<td>80–90</td>
<td>&lt;80</td>
<td>Less effective for small particles</td>
</tr>
<tr>
<td>Multi-cyclone</td>
<td>90–99</td>
<td>90–99</td>
<td>&lt;80</td>
<td>Less effective for small particles</td>
</tr>
<tr>
<td>Electrostatic Precipitator</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>80–90</td>
<td>Removal efficiency and emission may be low for small plant</td>
</tr>
<tr>
<td>Fabric Filter</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>Final emission should be much less than 5 g/GJ</td>
</tr>
<tr>
<td>Ceramic Filter</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>Final emission should be much less than 5 g/GJ</td>
</tr>
<tr>
<td>Mop Fan</td>
<td>&gt; 95</td>
<td>&gt; 95</td>
<td>&gt; 95</td>
<td>Technology needs to be tested more for validity, also removes water soluble gas</td>
</tr>
<tr>
<td>Hybrid</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>&gt; 99</td>
<td>Novel technology, more niche and problem specific</td>
</tr>
</tbody>
</table>

*a: Effectiveness (coarse particles) (%), b: Removal efficiency (PM10) (%), c: Removal efficiency (PM2.5) (%)

It can be stated that the cleaning of flue gas from biomass combustion is a complex task, and it is difficult to obtain high efficiency for a smaller particle range. The particle removal efficiency especially for PM 2.5 is usually low.

**Conclusion**

The environmental problems of solid particle emission are a seeded area in air cleaning protection goals. Solid particles are produced during every solid fuel combustion process, accordingly by biomass firing. The compounds of solid particles are composed by the fuel composition. It is evident, that every biomass contains a certain amount of metal compounds, but in the last decade, the metal contaminated biomass achieved increasing attention. Several researches deal with this topic including the biomass based remediation techniques, the metal accumulation process of biomass and the disposal options of biomass. The combustion, as a disposal option is a known process, but experiments dealing with emissions were performed only in the last few years. This research area is also important concerning energy production, as in these energy-hungry times every potential energy source should be analyzed. Regarding the literature it can be stated, that the combustion of contaminated biomass is not an ordinary biomass firing process. The particles in flue gas contain metal compounds, thus an efficient air cleaning system is crucial. The particle separation efficiency depends mainly on the cleaning equipment and on the temperature of flue gas. The flue gas temperature must be
under the temperature, where the condensation of metal compounds is finished. For particle separation, filters or an effective hybrid technology is required.

Acknowledgements

This research was carried out in the framework of the Center of Excellence of Sustainable Resource Management at the University of Miskolc.

References


