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Theoretical and experimental metals flow calculations during biomass combustion

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HIGHLIGHTS

- The literature was researched and analysed.
- Based on the references, the goal of the investigation was determined.
- Laboratory tests were made to determine the basic behavior of the biomass.
- Theoretical and technical calculation was determined to make the results ready to compare.
- The results were compared, and the metals flow was determined.

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ABSTRACT

All creature of nature needs metals for subsistence. The plants and trees contain this element in a different amount. During biomass combustion and energy production this element could cause environmental and health problems, thus, the cognition of burning and determination of material flow is a very important question. The high amount of metals steps out from the combustion chamber in gaseous form. To determine the metal distribution inside the burning equipment system, we have to get samples from the solid combustion remains and flue gas, and we have to measure the material flows. At the first stage, we made a biomass combustion experiment using ligneous plants with high metal content. The experiment was carried out with a Binder RRK 500 type wood chips-, briquette- and bark-fueled heating system. The fuel was wood chips, and the operational parameters were automatically set by the temperature control so that the circulating water was kept at a constant temperature. The amount of flue gas was calculated based on the theoretical estimate. The analysed metals were Zn, Cu, Cd, Pb, Cr, Ni, Co, and Fe. The metal content of the wood chips, ash and fly ash was determined by ICP spectrometry, and the ash content and fly ash concentration in the flue gas was measured. The material flow was calculated in the matter of metals. The results show that under the experimental circumstances, the solid burning residues (bottom ash, fly ash) contain the following percent of metals referred to the fuel metal concentration: Zn - 17–18%, Cu - 2–7%, Cd - 4–20%, Pb - 14–15%, Cr - 0.5%, Ni - 2%, Co - 10–11%, and Fe - 5–7%. The results proved that the metals are very volatile in the combustion temperature (800 °C) and flue gas temperature (250–300 °C).

1. Introduction

The unequal distribution of fossil energy sources in the world and the environmental problems increase the ambition to use more renewable sources for energy production. Nowadays, there is significant interest in many developing and developed countries in biomass combustion, and co-firing. The energetic utilization technologies are widely known. Several biomass utilization methods are known, and the combustion technology of biomass is a big research topic. The biomass combustion consists the steps of heating-up; drying; devolatilisation to produce char and volatiles, where the volatiles consist of tars and gases; the combustion of the volatiles; and the combustion of the char [1].

In a recent research, it was concluded that the particle size shows most significant impacts on char oxidation, followed by heating and devolatilisation, while fewer impacts of particle size are noticed on drying process [2]. The modes of element structure occurrence in biomass and their content define the behaviors of the

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firing, flue gas and burning residues [3]. The inorganic composition of biomass is variable, and it could have a primary effect of the behavior of a particular fuel during processing [4].

Different biomass types contain different amount of carbon, hydrogen, nitrogen, sulfur, chlorine, and other chemical elements. Carbon and hydrogen are an important, influential factor in point of heat efficiency [5–8]. In ligneous plants, the high Nitrogen and Chlorine content cause significant nitrogen oxides (NO_x) and hydrogen chloride (HCl) emissions [5,7]. Particularly these emissions are responsible for acid rain and corrosion problems in the equipment [5,7,1]. Compared to wood, agricultural materials usually contain less C and H and have higher contents in ash and inorganic elements such as N, S, Cl, K, and Si [3]. Thus, the chemical composition of the biomass and the combustion air is the main components of the material inflow onto the burning system, the chemical composition of fuel must be analysed substantially.

1.1. Metal compounds in the burning system

The elementary biomass composition includes some heavy metals. Many elements classified as metal are important micronutrient for plants. Biomass are commonly enriched in Ca, Cl, H, K, Mg, Mn, Na, O, P, and some trace elements (Ag, Au, B, Be, Cd, Cr, Cu, Mn, Ni, Rb, Se, Zn, others) [6,9].

Furthermore, as a result of human activities, the number of heavy metals are increased in certain soils [10–12]. These areas are called as brownfield lands in the literature [13–15]. The remediation techniques of the soil with plants (phytoremediation) generate heavy metal contaminated biomass [16–18]. In the case of energetic utilization of this biomass, the heavy metal behavior in the burning systems is a very important question [19]. A complete combustion process produces CO_2, NO_x, SO_x, HCl, metal compounds and solid particles [20]. By incomplete combustion, other compounds, like CO, H_2S and solid particles in higher amount can be formed.

The metals can be found in the burning system as a chemical element or compound. A lot of research [21–23] deal with the determination of metal physicochemical formations, transformations and reactions during biomass combustion. Based on chemical reactions, these papers summarize that the metal forms are mostly elemental, oxides, chlorides and sulfates during combustion.

Research results show that different elements and their compounds such as Ag, As, Ba, Cd, Cl, Co, Cr, Cu, Hg, Mn, Ni, Pb, Zn and others, are potentially hazardous air pollutant elements [5,8,24,25]. The main problem is that the metal compounds are often more volatile than the metal elements. Table 1 summarizes the melting and boiling point of the analysed metals (Zn, Cu, Cd, Pb, Cr, Ni, Co, Fe) and the most common metal compounds (oxides and chlorides).

As Table 1 shows most of the metal compounds could vaporize in the temperature of combustion. It means that these components probably leave the combustion chamber in volatile form. The metal compound emission is a real risk during combustion, and can cause environmental and health problems through contamination of air, soil and water in the areas surrounding biomass firing equipment.

1.2. Environmental and healthy risk of metal compounds in flue gas and burning residues

Several kinds of research deal with the environmental aspects of biomass combustion [5,24,30–33]. In the case of metal compounds the problem is, that the harmful elements are leachable and mobile in the environment [5,21,34–36]. The biomass combustion could cause local air, water, and soil contamination, which can spread, and increase to a global risk.

Table 1
Melting and boiling points of metals and metal compounds.

Metal	Compound	Normal melting point, °C	Normal boiling point, °C	Reference
Zn	Element	420	907	[26]
	$ZnCl_2$	317–318	732	[27,28]
	ZnO	1975	2000 (sublimation)	
Cu	Element	1085	2560	[26]
	CuCl	451	1212	[27,28]
	Cu_2O	1236	1800 (decomposition)	
Cd	Element	321	767	[26]
	$CdCl_2$	564	960	[29]
	CdO	1540 (sublimation)		
Pb	Element	327	1749	[26]
	$PbCl_2$	501	954	[27,28]
	PbO	886	1470	
	PbO_2	290 (decomposition)		
	PbO_3	370 (decomposition)		
	PbO_4	930 (decomposition)		
Cr	Element	1907	2671	[26]
	$CrCl_2$	815	1300	[27,28]
	$CrCl_3$	631	945	
	Cr_2O_3	1990	4000	
Ni	Element	1455	2913	[26]
	$NiCl_2$	1009	970 (sublimation)	[27,28]
	NiO	1955		
Co	Element	1495	2927	[26]
	$CoCl_2$	740	1049	[29]
	CoO	1805		
Fe	Element	1538	2861	[26]
	$FeCl_2$	677	1012 (sublimation)	[27,28]
	$FeCl_3$	308	319	
	FeO	1370–1378		
	Fe_2O_3	1594		
	Fe_3O_4	1597		

Proved by several papers, a part of the ash-forming compounds leave the combustion chamber in volatile form and become part of the gas phase [1,37,38] (Fig. 1). Metals and metal compounds become an active part of the reactions during the gas phase trough evaporation [39]. The temperature of the flue gas flowing in the combustion system decreases continuously. Some metal aerosols grow and form submicron ash particles by mechanisms that include nucleation, adsorption, condensation, and chemical reaction [40]. At low temperatures, the evaporated compounds will nucleate on the surface of fine particles [38]. This amount of solid particles is called as fly ash.

A part of this fly ash is separated by dust extractor; the separation rate depends on the equipment. When the efficiency of the separator is not good enough, some fine particles could be emitted with the flue gas.

The environmental and health risk of metal compounds during biomass combustion is caused by:

- the metal content of the bottom ash could be hazardous waste, and then a safe disposal treatment is required to prevent the leaching of the metals to the environment [41–44];
- the metal content of fly ash after dust separator is a solid particle emission [45];
- the gaseous metal compounds in the flue gas, which are still volatile at the emitted flue gas temperature.

The issues of the ash and separated solid parts are manageable. Treatment and deposition processes are required for these solid