ANALYSIS OF THE HEAVY METALS CONCENTRATION IN THE SOLID ALTERNATIVE FUEL ON BIOMASS BASIS

MIROSLAV RIMAR, OLHA KULIKOVA, ANDRII KULIKOV, MARCEL FEDAK, TIBOR KRENICKY

Technical University of Kosice, Faculty of Manufacturing Technologies with a seat in Presov, Presov, Slovak Republic

DOI: 10.17973/MMSJ.2022_10_2022056

e-mail: olha.kulikova@tuke.sk

Sustainable development requires the research on new energy sources that will be safe and at the same time help to solve other societal problems. The paper is focusing on the analysing the heavy metals concentration of biomass and fuel mixtures of biomass and municipal solid waste. Analysis confirmed that the co-combustion of dirty fuels and biomass reduced the risk of releasing minerals and heavy metals from fuel into the natural environment. At a waste concentration of 20%, almost all heavy metals have passed from fuel to ash. Based on the experiment results and measurements, it can be stated that the co-combustion of biomass and municipal solid waste is a possible energy source that will significantly support sustainable energy development, but it is necessary to control the heavy metals concentrations during the whole process.

KEYWORDS

Biomass, municipal solid waste, combustion, heavy metals

1 INTRODUCTION

In recent years, two important problems have been actively discussed in Slovakia and in the world. The first is air protection and reduction of negative effects on the environment by different types of fuel. An integral part of these discussions and ongoing research is the call of the European Parliament to reduce pollution without losing the efficiency of energy equipment. Directive 2009/28/EC of the European Parliament and the Council on the promotion of the use of energy from renewable sources deals with the use of energy-efficient technologies [INVENT 2022]. The second problem is the processing of municipal waste. One approach is to minimize the amount of waste produced and recycle larger fractions of the waste material. However, there is still a significant part of unwanted end products, and it is necessary to find a more suitable solution than landfilling [Biomass 2022].

Biomass - the fourth largest energy source after coal, oil and natural gas - is currently the largest and most important source of renewable energy and can be used to produce various forms of energy. As a result, together with other renewable energy options, biomass is able to provide all the energy services needed in modern society. Renewability and versatility are among the many other important advantages of biomass as an energy source. And unlike other renewable energy sources – such as solar and wind – a biomass heating plant can operate continuously and provide a consistent and reliable flow of energy. In addition, biomass resources are commonly distributed worldwide compared to other renewable resources [Ladani 2009].

Municipal solid waste (MSW) is classified and defined in different ways depending on the country and what waste management practices are used. Eurostat identifies MSW as waste produced by households or from other sources such as commerce, offices and public institutions [Eurostat 2017]. The Environmental Protection Agency (EPA) defines MSW as waste that does not include industrial, hazardous or construction and demolition waste [US EPA 2019].

The choice of waste-to-energy technology will largely depend on the nature and volume of the incoming waste stream. The key factor is the energy content (calorific value) of waste, which determines how much energy can be obtained from it.

We define the simultaneous combustion of two or more fuels in the same energy production device as a co-combustion process. Although this method of combustion has been applied for many years, recently the interest in co-incineration plants has increased, which is evident from the growing number of scientific publications.

Before using each fuel, it is necessary to perform its energy and chemical analyses. Among the important analyzes of solid fuel are analyzes for heavy metals.

Heavy metals (HM) are generally defined as metals with relatively high densities, atomic weights, or atomic numbers. Examples of heavy metals include mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl), and lead (Pb) [Lenntech 2022]. Heavy metals are natural components of the earth's crust. They cannot be degraded or destroyed. To a small extent, they enter our body through food, drinking water and air.

As trace elements, some heavy metals (e.g. copper, selenium, zinc) are essential for maintaining the metabolism of the human body. At higher concentrations, however, they can lead to poisoning. Heavy metal poisoning can be a consequence of, for example, contamination of drinking water, high ambient air concentrations near emission sources or intake through the food chain. The most harmful heavy metals for humans are mercury, cadmium, chromium and lead. An excess of heavy metals in the body produces oxidants, which destroy organic molecules in the body by oxidation [Durackova 1998].

2 MATERIALS AND METHODS

The analysis of HM migration was done for the components of the analyzed fuel (wood chips and MSW) as well as for their combination:

- 50% woodchips and 50% MSW – 50/50,
- 70% woodchips and 30% MSW – 70/30,
- 75% woodchips and 25% MSW – 75/25,
- 80% woodchips and 20% MSW – 80/20.

Wood chips for the experiment were from the north-eastern part of Slovakia min 25 km from the cities and industrial areas. Wood chips were the mix of deciduous and coniferous trees what is typical this area.

During the experiments was used MSW, which belongs to the category of non-hazardous and other combustible waste, according to Decree of the Ministry of the Environment No. 365/2015 Coll. of the Slovak Republic, which is responsible for establishing the Waste Catalogue [European Commission 1998]. Energy analysis of fuels was presented in detail in a previous study [Rimar 2021]. In previous works, the level of possible contamination of wood chips with heavy metals was determined but considering that the analyzes were made based on standards only as a result of the concentration of TK groups, this work is mainly focused on determining the concentration of each element separately.

In order to obtain objective data on HM migration, the analysis of the collected samples was based on STN EN 15 309, which states "Characterization of waste and soil. Determination of elemental composition by X-ray fluorescence" [STN 15309 2011]. To assess the suitability of a given type of fuel for combustion in a biomass boiler, the emission limits listed in Decree 410 of the Ministry of the Environment of the Slovak Republic were used, which was developed on the basis of the standards and requirements of the European Union for reducing emissions and protecting the environment and sets exact emission limits for all sources of environmental pollution [MZPSR 2012].

X-ray fluorescence spectrometry was used for semi-quantitative determination of the elements in the sample with high sensitivity, especially the heavier elements. The technical parameters of the device are as follows:

- focusing using polycapillary optics to a beam with a diameter of 25 µm and an interaction depth of 10–1000 µm;
- a wide-angle camera and two coaxial digital microscopes, 10 × and 100 ×, to scan the test site in the sample;
- mosaic scanning when measuring large objects;
- X-ray tube with target Rh, excitation maximum 50 kV / 600 µA and 5 filters;
- SDD (Silicon Drift Detector) with a resolution of 145 eV and an active area of 30 mm2.

Pollutant concentrations during the processing of the results were converted to normal conditions and reference oxygen content [Tomeczek 2001].

All experimental measurements were carried out in compliance with approved European standards and laws, which made it possible to formulate a methodology for measuring the composition of alternative fuels and demonstrate their suitability as fuel.

The solid fuel that was used during the experiments was not homogeneous, and therefore great attention was paid to the correct sampling method, so that the sample, if possible, best represented the studied unit of measurement of the fuel. Fuel samples were taken according to the STN EN 14778 standard, which is the Slovak equivalent of the European standard EN 14778:2011.

Analytical samples were taken from different parts of the fuel as recommended by the standard. Each fuel sample was made from ten separately mixed smaller samples. The weight of each small sample was 2 to 4 kg.

Biomass and MSW samples were first mixed separately and then mixed again after the necessary mass ratio of the small sample was established. Each experimental fuel mixture was divided into batches. In each sample, the grain size was kept in the same ratio as in the investigated fuel. For each ratio, the weight required for analysis was calculated. After sampling, conditions were provided to ensure that the properties of the samples taken, such as oxidation or drying, did not change

3 RESULTS AND DISCUSION

The results of the analysis of woodchips, MSW and mixtures for heavy metal and metalloid content in the fuel are shown in Table 1.

element		Woodchips	MSW	50/50	70/30	75/25	80/20	Relative
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	eror %
Manganese	Mn	43.139	4.2	26.845	27.02	35.65	35.28	± 12 %
Arsenic	As	0.037	2.05	1.14	0.867	0.783	0.698	± 12 %
Cadmium	Ca	0.004	7.92	3.98	2.438	2.093	1.654	± 12 %
Cobalt	Co	0.058	0.18	3.1	3.554	3.795	4.036	± 12 %
Chrome	Cr	0.101	10.7	5.9	4.75	4.325	3.9	± 12 %
Nickel	Ni	0.203	0.1	0.531	0.66	0.7	0.74	± 12 %
Lead	Pb	0.013	4.9	2.741	1.729	1.502	1.276	± 12 %
Antimony	Sb	0.905	2.9	2.04	1.95	1.525	1.5	± 12 %
Vanadium	V	0.149	1	1	1	1	1	± 12 %
Zinc	Zn	1.244	135	94.4	42.943	36.368	29.792	± 12 %
Thallium	Tl	-	-	-	-	-	-	± 12 %
Mercury	Hg	0.001	0.265	0.512	0.684	0.714	0.595	± 12 %
Copper	Cu	1.193	85	45	25.5	21.25	17	± 12 %

Tab. 1 Results of the fuel HM analysis

The results of the analysis of woodchips, MSW and mixtures for heavy metal and metalloid content in the ash are shown in Table 2.

The content of heavy metals in wood chips was within the permitted limits according to Decree 410. However, the concentration of HM and metalloids can vary significantly depending on the species and origin [Ciolkosz 2019].

Experimental measurements were carried out using a biomass boiler with a stepped sliding grate with a nominal output of 83 kW. The device consists of boiler body, intermediate fuel tank, divided 2-zone combustion chamber made of fire-resistant concrete, standing pipe heat exchanger and regulation. The properties of the boiler are listed in table 3. Primary and secondary air in the combustion process is sucked in by the vacuum of the spline fan, which achieves uniform combustion over the entire surface of the fuel on the grate. The lambda probe checks the values of the sputum gases and based on these values, the boiler automatically corrects the required amount of transported fuel and secondary air. Comparing to the results [Nicewicz 2008] of the HM concentration in healthy and damaged wood it can be concluded that for the energy purpose was used woodchips from damaged wood. The HM concentrations were at the lower border of the typical HM concentrations of the region.

element		Woodchips	50/50	70/30	75/25	80/20	Relative
		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	eror %
Manganese	Mn	32.384	12.662	23.549	32.698	± 12 %	± 12 %
Arsenic	As	0.306	0.536	0.404	0.301	± 12 %	± 12 %
Cadmium	Ca	0.1	2.437	1.801	1.301	± 12 %	± 12 %
Cobalt	Co	3.25	0.074	0.072	0.073	± 12 %	± 12 %
Chrome	Cr	1.936	4.359	3.253	2.284	2.196	± 12 %
Nickel	Ni	0.792	0.173	0.165	0.173	0.145821	± 12 %
Lead	Pb	0.326	1.542	1.182	0.849	0.741374	± 12 %
Antimony	Sb	2.112	0.673	1.439	2.336	2.397686	± 12 %
Vanadium	V	0.88	0.093	0.568	0.603	0.07621	± 12 %
Zinc	Zn	3.49	61.199	21.238	41.318	32.12475	± 12 %
Thallium	Tl	-	-	-	-	-	-
Mercury	Hg	0.69	-	0.0005	0.001	0.001034	± 12 %
Copper	Cu	0	0.763	6.235	11.863	11.52878	± 12 %

Tab. 2 Results of the ash HM analysis

The combustion equipment was represented by the automatic woodchip 83 kW boiler with fuel storage.

However, analysis of the concentration of HM in the ash showed that about 55% of HM was set in the ash. The concentration of HM in the flue gases, even in the case of average contamination, was in the range of 0.4 mg/m^3, which is 20% below the permitted limits. Nevertheless, the higher concentration of Zn in TAP leads to a possible risk of human health due to the contact with ash. Comparing the results with a healthy wood has a higher HM concentration as damaged not appropriate fuel for the co-combustion with dirty fuels without an appropriate HM concentration analysis [Nicewicz 2008, Pazalja 2021].

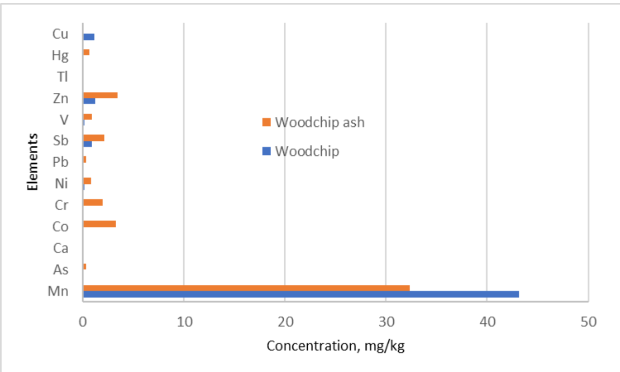

Figure 1. Concentration of the HM in woodchips and its ash

To understand the possible influence from the combustion equipment were compared the concentration of the HM in woodchips and its ash (Figure 1). The main HM in the fuel was Mn (92% of total HM concentration). According to the results almost 75% of Mn were transferred to ash. The higher concentrations of the Co, Cr, Sb, Zn in the ash is a result of contamination of the fuel in the combustion equipment and/or fuel storage.

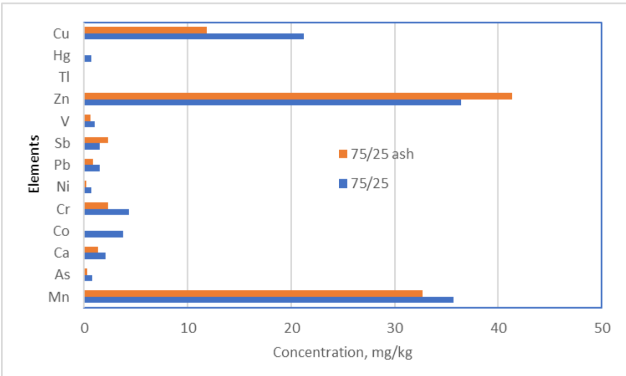

Figure 2. concentration of the HM in the fuel mixture of 75% of woodchips and 25% of solid alternative fuel

The same analysis of the fuel and ash were made for the fuel mixture of 75% of woodchips and 25% of MSW (solid alternative fuel - SAF) (Figure 2). Co-combustion of the woodchips and SAF shows even better migration of Mn to ash. Migration of the Cu to ash was approximately 60%. Nevertheless, the higher concentration of Zn and Sb shows that the source of the contamination is mainly combustion equipment. The possible place of contamination is shown at the Figure 3.

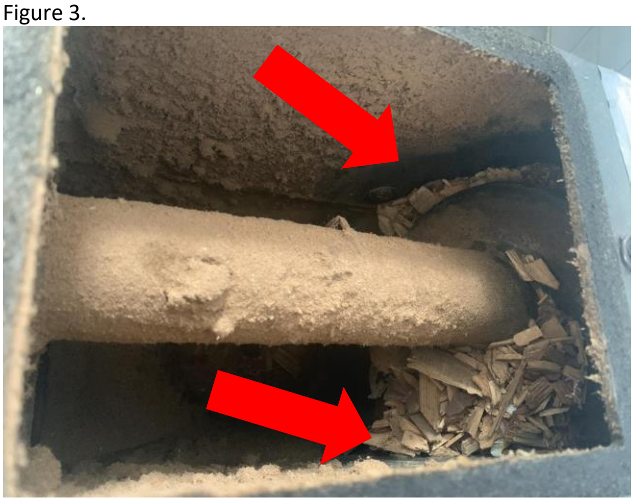

Figure 3. Detail of boiler dispenser

The contamination is possible at the part of storage equipment where woodchips are scratches the construction parts due to it movement to the combustion chamber.

4 CONCLUSIONS

Experimental measurements have confirmed that the co-combustion of polluted fuels and biomass reduces the amount of released minerals and heavy metals from the fuel into the natural environment. At a 20% concentration of municipal solid waste in a mixture almost 99% heavy metals migrate to the ash. But at 50% concentration, only 45% of heavy metals remain in the ash. However, the concentration of heavy metals in the flue gas was still below the permitted emission limits, which only confirms the positive impact of biomass. Also, a possible source of HM contamination is a combustion and storage equipment.

ACKNOWLEDGMENTS

The authors would like to thank the KEGA grant agency for supporting research work and co-financing the project KEGA 023TUKE-4/2021.

REFERENCES

[Biomass 2022] Biomass explained: Biomass – renewable energy from plants and animals. 2018, Available from <www.eia.gov/energyexplained/biomass/>.

[Ciolkosz 2019] Ciolkosz, D. Introduction to Biomass Combustion. Farm Energy, 2019. Available from: <https://farm-energy.extension.org/introduction-to-biomass-combustion/>.

[Durackova 1998] Durackova, Z. Free radicals and antioxidants in medicine. Slovak Academic Press, Bratislava, 1998. 285 p. ISBN 8088908116.

[European Commission 1998] European Commission: Report from the commission to the European parliament, the council, the European economic and social committee and the Committee of the regions. 2020 report on the State of the Energy Union pursuant to Regulation (EU) 2018/1999 on Governance of the Energy Union and Climate Action, 2020, Available from: <https://eur-lex.europa.eu/legal-content/GA/TXT/?uri=CELEX:52020DC0950>.

[Eurostat 2017] Guidance on municipal waste data collection: Eurostat – Unit E2 – Environmental statistics and accounts; sustainable development. [online]. European commission. Eurostat, 2017, Available from: <https://ec.europa.eu/eurostat/documents/342366/351811/Municipal+Waste+guidance/bd38a449-7d30-44b6-a39f-8a20a9e67af2>.

[INVENT 2022] INVENT – Final Meetings, Biomass combustion. Biomass combustion processes, 2022, Available from <http://www.invent.hs-bremen.de/e-learning_Dateien/Presentations/Biomass%20Combustion%20Processes.pdf>.

[Ladani 2009] Ladani, S. and Vinterbaeck, J. Global Potential for Sustainable Biomass for Energy: Report 013. Department of Energy and Technology. Swedish University of Agricultural Sciences, Uppsala, 2009, Available from: <http://pub.epsilon.slu.se/4523/1/ladanai_et_al_100211.pdf>. ISSN 1654-9406.

[Lenntech 2022] Heavy Metals. Lenntech, 2022, Available from: <https://www.lenntech.com/processes/heavy/heavy-metals/heavy-metals.htm>.

[MZPSR 2012] Ministry of the Environment of the Slovak Republic. Decree of the Ministry of the Environment of the Slovak Republic no. 410/2012, which implements some provisions of the Act on Air, as amended. Ministry of the Environment of the Slovak Republic; Bratislava, Slovakia, 2012.

[Nicewicz 2008] Nicewicz, D. and Szczepkowski, A. The content of heavy metals in the wood of healthy and dying beech trees. Acta Sci. Pol., 2008, Vol. 7, No. 4, pp. 35-44.

[Pazalja 2021] Pazalja, M., et. al. Heavy metals content in ashes of wood pellets and the health risk assessment related to their presence in the environment. Scientific Reports, 2021, Vol. 11, No. 17952, pp. 1-9.

[Rimar 2021] Rimar, M., et. al. Energy Treatment of Solid Municipal Waste in Combination with Biomass by Decentralized Method with the Respect to the Negative Effects on the Environment. Sustainability, 2021, Vol. 13, No. 4405.

[STN 15309 2011] European Committee for Standardization. Slovak technical standard STN EN 15309. Characterization of waste and soil. Determination of elemental composition by X-ray fluorescence. 2011.

[Tomeczek 2001] Tomeczek, J. and Gil, S. Influence of pressure on the rate of nitric oxide reduction by char. Combustion and Flame, 2001, Vol. 126, Issue 1-2, pp. 1602-1606.

[US EPA 2019] United States Environmental Protection Agency. Report on the Environment. Municipal Solid Waste. 2019, Available from: <https://cfpub.epa.gov/roe/indicator.cfm?i=53>.

CONTACTS:

Prof. Ing. Miroslav Rimar, CSc.

Ing. Olha Kulikova PhD.

Ing. Andrii Kulikov PhD.

Assoc. Prof. Ing. Marcel Fedak, PhD.

Technical University of Kosice

Faculty of Manufacturing Technologies with a seat in Presov

Department of Process Technique

Sturova 31, 080 01 Presov, Slovak Republic

+421-55-602-6341

miroslav.rimar@tuke.sk, olha.kulikova@tuke.sk, andrii.kulikov@tuke.sk, marcel.fedak@tuke.sk,

Assoc. Prof. RNDr. Tibor Krenicky, PhD.

Technical University of Kosice

Faculty of Manufacturing Technologies with a seat in Presov

Department of Technical Systems Design and Monitoring

Sturova 31, 080 01 Presov, Slovak Republic

tibor.krenicky@tuke.sk