Annals of Warsaw University of Life Sciences - SGGW
Forestry and Wood Technology № 92, 2015: 390-394
(Ann. WULS - SGGW, For. and Wood Technol. 92, 2015)

Analysis of selected heavy metals in biomass for preparation of biofuels – Part II. Determination of heavy metals content

EVA RUŽINSKÁ[1)], VLADIMÍR ŠTOLLMANN[2)], VLADIMÍR HAGARA[3)], MAREK JABŁOŃSKI[4)]

[1)]Technical University in Zvolen, Faculty of Environmental and Manufacturing Technology, Zvolen, Slovakia

[2)]Technical University in Zvolen, Faculty of Forestry, Zvolen, Slovakia

[3)]Dubnica Institute of Technology in Dubnica nad Váhom, Slovakia

[4)]Warsaw University of Life Sciences, Faculty of Wood Technology, Warsaw, Poland

Abstract: *Analysis of selected heavy metals in biomassmass for preparation of biofuels – Part II. Determination of heavy metals content.* The second part of the paper is focused on assessment the heavy metals content - as risk elemets in biomass (dendromass) for preparation in biofuels. Presence of trace concentrations of heavy metals (As, Cd, Pb, Ni, Cr) represents risks that is necessary to be acquainted with for consequent assessment of selected fire-technical and ecological characteristics of prepared biofuels from biomass (dendromass).

Keywords: biomass, dendromass, biofuels, heavy metals content, AAS –ETA method, environmental safety, health protection

INTRODUCTION

At present, it is necessary to assess the environmental safety of materials used in the preparation of biofuels from biomass [1- 6]. In addition to the full range of characteristics relating to calorific value, as well as fire safety, it is necessary to pay attention to the chemical (elemental) composition of biomass. The presence of heavy metals in biomass conditional on the subsequent formation of emissions in the process of burning biofuels [1, 9, 10].

The article continues on the issue of heavy metals in biomass utilized in the preparation of biofuels. In the first part of the article (Ružinská et. al. 2015: Toxicological effects of heavy metals) attention was paid to toxic action of heavy metals present in biomass on human health and consequently on the quality of the environment [7 -9].

The second part of the article deals with the determination of heavy metals (As, Cd, Pb, Ni, Cr) content present in biomass (dendromass - beech wood pellets, beech wood briquettes, beech sawdust, beech wood chippings, beech wood shavings) using the atomic absorption spectroscopy (AAS) method [9].

MATERIALS AND METHODS

To assess selected heavy metals (As, Cd, Cr, Ni) in dendromass. Five types of samples were used: wood pellets, briquettes, sawdust, chippings, shavings (Ružinská, E. et. al. 2015: Analysis of selected heavy metals in biomassmass for preparation of biofuels – Part I. Determination of heavy metals content Toxicological effects of heavy metals).

Pellets prepared from beech wood (granules with the circular cross-section 6 mm and length approximately 15 mm), beech wood chippings and the waste product – wooden dust from the beech wood. Pellet granule size of circular diameter is 6 – 8 mm and its length is 30 mm. Pellet are produced exclusively from waste material as sawdust, wood chippings or wooden dust, respectively.

For the determination of selected heavy metals (Cd, Cr, Ni, As) were used commercial wood briquettes (made from beech wood bark shavings) with dimensions of 150 x 70 x 90 mm. The moisture content of wood briquettes should be fixed at 8.2%.

Determination of hazardous elements in biomass (dendromass) by AAS method

Atomic absorption spectroscopy is an instrumental method based on principle of absorption of selected chemical elements in specific electromagnetic radiation. Analyzed elements are released from their compounds and become free atoms by energy delivery in the atomizer [9].

Solution in the atomization equipment gets vaporized immediately and chemical binds in molecules of present compounds are destroyed. During electrothermal atomization (ETA) very small amount of sample (10 - 40 µl) is dosed into special miniature cuvette heated by electrical resistance. Light beam from special discharge tube is radiated in such way that photons are absorbed at targeting atoms of analyzed element and atom of determinated element gets into excited status.

A result of this process is decreasing of transmitted light intensity; this decreasing is quoted by Lambet-Beer law expressed in the form:

$$I = I_0.e^{-(k.n.l)} \quad (1)$$

where: I_0 – is intensity of excited light;

I – intensity of light after passing through absorbing layer;

k – atomic absorption coefficient for given absorption line;

n – number of atoms of analyzed elements in the volume unit;

l – length of absorbing layer (length of burner).

In practice, a variable logarithm of luminous energy decreasing called absorbance (A) is measured. For absorbance, a linear dependence on concentration of measured element atoms is valid. Samples shall to be in a liquid form.

$$A = log\ (I0/I) = 2{,}303.k.n.l \quad (2)$$

Quantitative total amount of selected hazardous elements (As, Cu, Cd, Pb, Cr) in tested samples as mineralized yields were measured by AAS-ETA method by AAS THERMO iCE 3000 apparatus according to ISO 11047 methodology. Measured results were calculated to final value on 100 % dried material (dry basis).

Microwave decomposition MARS X-press

Tested samples were dried freely spread in a drying chamber at 55 °C temperature. Being dried, samples were grinded in the ball mill Fritsch into powder form. Consequently, samples undergo microwave decomposition. This method is suitable for decomposition of organic biomass samples (waste from wood – chippings, sawdust, or pellets, respectively) [9].

Amount of 0.5 g (± 0.0005 g) of grinded homogenized organic sample is weighted on analytical balances into clean dry Teflon vessel. Then there is added 2 ml of deionised water, 5 ml of nitric acid (concentrated w = 65 %, I_{20} = 1.4 kg.dm^{-3} according to STN 68 5002) and 1 ml of hydrogen peroxide (H_2O_2, w = 30%). Teflon vessel is closed, placed into circle stand and into the microwave furnace MARS X-press.

After finishing of mineralization and cooling, the vessel with sample is carefully opened (in fume cupboard/ fume hood), vessel stopper is sluiced by deionised water and mineralized yield is quantitatively transferred into graduated flask (50 ml) through funnel. Final results obtained by AAS-ETA measurement shall by multiplied by the factor 100 (due to the sample weight 0.5 g into 50 ml volume with dilution).

RESULTS AND DISCUSSION

The results obtained from quantitative analysis of selected heavy metals content by AAS-ETA method [9] in tested samples of biomass are shown in the Table 1.

Tab. 1.Result values of quantitative analysis of heavy metals (As, Cd, Pb, Cr, Ni) content by AAS-ETA method in tested samples of biomass

Sample	As total	Cd ** total	Pb total	Cr total	Ni total
	(µg/kg) (dry basis)	(µg/kg) (dry basis)	(µg/kg) (dry basis)	(µg/kg) (dry basis)	(µg/kg) (dry basis)
Wood pellets	216*	112*	<251*	509*	129*
Sawdust	372*	118*	<251*	661*	378*
Wood chippings	252*	72,5*	1130*	175*	458*
Wood shavings	247	91	306	412	298
Wood briquettes	204	84	<251	397	117

Notes: *Results published in Ružinská, E. et al., 2014 [9]

**Expanded measurement uncertainty of measurement U (k=2) for determination of Cd total is 33 %.

Evaluation of quantitative heavy metals content (As, Cd, Cr, Pb, Ni) by atomic absorption spectrometry with electrothermal atomization (AAS-ETA) is shown in the Table 1 according to ISO 11047. Due to fact that there is neither in any standard nor in any legislative regulation stipulated summary content of hazardous heavy metals in virgin biomass, evaluation was carried out by mutual correlation of produced beech wood pellets, briquettes and of components from which the final product (pellets) was prepared.

Nzihou, A., 2013; Demibras, 2005 and Fereira, P. T. et al., 2014 present different content of heavy metals in biomass ashes surveys, content that does not exceed < 0,05 $mg.kg^{-1}$ (converted on dry basis samples) for all monitored heavy metals. The authors state in their contributions that increased representation of heavy metal content in the biomass is conditional upon the site from which the biomass comes. When sawdust was observed variable incidence of heavy metals caused by pollutants from technological processes of machining wood [1-3, 6].

Mutual comparison of total As content in biomass samples (Table 1) proves quotation that arsenic content is in the range (204 - 372 µg/kg), while the lowest value was measured for beech wood pellets and the highest one for sawdust; by dust processing into more compact form more significant decrease of total As content takes place.

When evaluation total Cd content, interesting fact is that the lowest measured value (72.5 µg/kg) was found for wood chippings; and pellets (112 µg/kg) and sawdust (118 µg/kg) contain almost identical values of this hazardous element. Lower Cd content than other biomass samples was measured in samples of wood shavings and briquettes.

Total Pb content was identified lower than detectable value (<251 µg/kg) for wood pellets and also for sawdust but wood chippings was found value not until 1130 µg/kg), what is probably caused by pollution of chippings during wood processing process (pollutants at planning cause by technological equipment punishment; for example breaking of layer of safety surface finishing of equipment that contains pigments with lead content).

Evaluated total Cr content was the lowest for beech wood chippings (175 µg/kg), while in pellets was 509 µg/kg and in wood dust not until 661 µg/kg.

Total Ni content was the lowest one for prepared pellets (129 µg/kg) compared with wooden dust (378 µg/kg) and the highest one for beech wood chippings (458 µg/kg). Increasing of Ni content values for sawdust and chippings was probably caused by technological equipment punishment during planning or abrading processes when punishment of such equipment takes place and Ni traces penetrate sawdust and chippings. Pressing and consequent compacting process of wooden dust leads to decreasing of this hazardous element

CONCLUSION

From measured and discussed results of heavy metals content in biomass by AAS-ETA method follows that it is necessary to determination the quantitative content of these hazardous elements also in prepared ecological fuels (where wood pellets and briquettes be prepared from chippings, sawdust, shavings or wooden dust where traces of heavy metals can be present because of punishment or mechanical damage of technological equipment, intended for abrading, planning, milling of wood).

It would be suitable to refer besides qualitative characteristics of biofuels also determination of heavy metals as hazardous elements for prediction environmental safety purposes of complex assessment of these biofuels.

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Streszczenie: *Analiza zawartości wybranych metali ciężkich w biomasie do produkcji biopaliw - Część II. Oznaczenie zawartości metali ciężkich.* W ramach drugiej części pracy przedstawiono badania zawartości metali ciężkich w biomasie (dendromasie) stosowanej w

produkcji biopaliw. Obecność nawet śladowych ilości metali ciężkich (As, Cd, Pb, Ni, Cr) wymaga konieczności ich oznaczenia w celu charakterystyki biopaliw wytworzonych z biomasy w aspekcie paramterów tchnicznych ich palności i ekologiczności.

***ACKNOWLEDGEMENTS*:**–This *paper was processed within the VEGA project* The Ministry of Education, Science, Education and Sports of the Slovak Republic*, No. 1/0931/13: „Basic research of new principles cable system equipment for trucks RELAZ".*

Corresponding authors:

Eva Ružinská
Faculty of Environmental and Manufacturing Technology,
Technical University in Zvolen
Študentská 26
960 53 Zvolen,
Slovak Republic
eva.ruzinska@tuzvo.sk

Vladimír Štollmann
Faculty of Forestry
Technical University in Zvolen
T.G. Masaryka 24
960 53 Zvolen,
Slovak Republic
stollmann.vladimir@tuzvo.sk

Vladimír Hagara
Dubnica Institute of Technology
Sládkovičova str. 533/20
018 41 Dubnica nad Váhom
Slovak Republic
hagara.vladimir@gmail.com

Marek Jabłoński
Faculty of Wood Technology
Warsaw University of Life Sciences – SGGW
02-776 Warsaw
159 Nowoursynowska
Poland
marek_jablonski@sggw.pl