

## Analysis of selected heavy metals in biomass for preparation of biofuels – Part I. Toxicological effects of heavy metals

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**Abstract:** *Analysis of selected heavy metals in biomass for preparation of biofuels – Part I. Toxicological effects of heavy metals.* In the first part of the article attention was paid to toxicological effects of heavy metals (As, Cd, Pb, Ni, Cr) in various forms of biomass (sawdust, beech wood shavings, wood chippings, wood pellets and briquettes) for human health and the environment to obtain current and comprehensive knowledge of the biomass used in the preparation of biofuels. The paper presents the results of elemental analysis of accessory elements, which are sources of emission in the combustion process biofuels prepared from biomass (dendromass).

**Keywords:** biomass, dendromass, biofuels, heavy metals, toxicological effects, elementary analysis, environmental characteristics

### INTRODUCTION

Preparation of alternative fuels from biomass, particularly of dendromass, in form of wood pellets belongs nowadays to one of the most frequent ways of ecological fuel preparation used in households and in bio-gas stations (besides phytomass, zoomass and hygienically treated biodegradable waste) [8, 9].

Apart from global improved ecological characteristics and significantly less negative environment effect from fuels prepared from biomass it is necessary to quote that biomass except essential chemical elements contains also both elements having relevant effect on noxious substances production during biomass combustion [15], for example sulphur, chlorine, nitrogen, heavy metals and also presence of certain accessory substances that create hazardous chemical substances [12, 13] during their thermal decomposition [7-9]. Generally is valid that increased amount of these elements in fuel is proved by increased content of harmful substances in exhaust gases [1, 6].

Biomass compared to fossil fuels with relatively low sulfur content in the wood 0.02 to 0.05 wt. % [6, 7, 16]. Sulphur in the burning process is converted to sulfur oxides which are pollutant to the environment and also be irritating to the human respiratory system. But determination the sulfur content (by method the elemental analysis), the following information about environmental and toxicological characteristics of the biofuel [8-12].

The nitrogen content in the biomass of a share of 0.01 - 0.2 wt. % [6, 16]. The nitrogen contained in the fuel is taking part in the burning of the formation of nitrogen oxides in the flue gas (NO<sub>x</sub>). Nitrogen oxides are irritating to the respiratory system too and in high concentrations can be toxic [1, 8-10].

The aim of the first part of the paper is to provide comprehensive information on the toxic action of heavy metals (As, Cd, Cr, Ni, Hg) present in the preparation of biomass for biofuels from woody biomass - dendromass (pellets, briquettes). Attention is also paid to evaluating the

content of selected elements (sulphur, nitrogen), which are in the process of thermal conversion (by burning biofuel) source of pollutant emissions.

## MATERIAL AND METHODS

To assess selected heavy metals (As, Cd, Cr, Ni, Hg) in dendromass. Five types of samples were used: wood pellets (Fig. 1), wood briquettes (Fig. 2), sawdust (Fig. 3), beech wood chippings (Fig. 4), wood shavings (Fig. 5).

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. Pellets are produced exclusively from waste material as sawdust, wood chippings or wooden dust, respectively.

Pellets for experimental measurement were prepared from beech wood. For assessment purposes of hygienic environmental characteristics – content of some heavy metals, also beech wood chippings and waste product – wooden dust were analyzed together with beech pellets and wood briquettes.

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%.



Fig. 1 Wood pellets



Fig. 2 Wood briquettes



Fig. 3 Sawdust



Fig. 4 Wood chippings



Fig.5 Wood shavings

## HEAVY METALS IN THE DENDROMASS

### Arsenic

Elementary form of arsenic is not considered to be a toxic substance because it is not soluble but under thermal degradation in the process of oxidation-reduction reactions it sublimates (at temperature 600 °C) [1].

Mechanism of arsenic toxic effect impacts whole enzymatic systems, it is bound on –SH protein groups, disconnects oxidative phosphorylation that takes place in mitochondria and in final result it damages tissue respiration. After inhalant penetration of arsenic compounds into an

organism, toxicity is expressed locally at respiratory tract – by pain on thorax, irritative cough, and bronchitis [1, 4].

### **Cadmium**

The source of cadmium in biomass is deposition in the dissipation of Cd by anthropogenic processes, most notably fossil energy use. Cadmium (Cd) is present in biomass in low concentrations where it penetrates from contaminated soils due to industrial pollution. Releasing of Cd occurs also during combustion of fossil fuels and Cd can migrate into soil where dendromass is present [1, 14].

Cd together with Pb and Hg compete with Zn in bounding positions at metallothionein. Mechanism of Cd toxic effect is expressed in inhibition of sulphurhydryl (sulfhydryl) enzymes where Cd competes with Cu, Zn, and Fe [4].

Acute toxicity usually develops after inhalation of Cd vapours (in form CdO) and is expressed by nausea, vomiting, pneumonia with later occurring of pulmonary oedema [5].

### **Lead**

Lead can be in inbreathed air present in vapour form (alkyl-lead form from vehicle exhausting gases). High lead concentration is recorded also in plants and wooden plants alongside roads [14]. Presence of Pb in polluted environment is a reason that it is indicated also in biomass (dendromass, phytomass).

Respiratory tract is the main way for penetration of lead into organism. Lung inhalation depends on certain parameters, for example on volume of inbreathed air, as well as on particle size because only particle sized  $< 0.5 \mu\text{m}$  is captured in lungs. Inorganic lead is distributed into soft tissues (liver, kidneys) at first. Lead intoxication can be seen by neurotoxicity (paresthesia, muscle fatigue) in a clinical record file, also encephalopathy can occur [2].

Organic lead compounds (tetraethyl-lead and tetramethyl-lead) are lipophilic compounds that are easily absorbed by skin and lungs and are distributed into fat tissues. Tetraethyl-lead damages central nervous system but does not cause anaemia [2, 4].

### **Chromium**

During fossil fuel combustion Cr is released and deposited in lungs. It belongs among trace amount elements in low concentrations; and participates in metabolic processes of saccharides (carbohydrates) and lipids in organism [1, 4].

Inorganic  $\text{Cr}^{6+}$  compounds quickly penetrate cell membranes; this fact is connected with toxicity thereof. Compounds with  $\text{Cr}^{6+}$  are absorbed by lungs and skin. Chromium from lungs is released only slowly so its presence in blood and in urine seems to be only in low concentrations and thus it is not possible to determine accurate Cr concentration in organism. Chromium  $\text{Cr}^{6+}$  is bounded in erythrocytes that fulfils transport function. Chromium is excreted by kidneys.

Elementary Cr metal is practically undamaging but if it participate in thermal decomposition in oxidation-reduction reactions and changes into  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  compounds, its toxic impacts are connected with huge oxidation reaction [2, 3].

### **Nickel**

Nickel (Ni) is considered to be an essential element [1], but it is also significantly toxic. However, there exists significant difference between the dose required for correct metabolism functioning and the toxic one. Higher Ni concentrations originate during combustion [14], where the most toxic Ni compound – tetracarbonylnickel  $\text{Ni}(\text{CO})_4$  is created that is lipophilic and it penetrates through barriers (hematoencephalic, placental, and lungs) easily and its inhalation by lungs occurs. Carcinogenity of respiratory tract and allergic contact dermatitidis prevail by Ni compounds intoxication from toxicological standpoint.

Determination of hazardous elements was measured by AAS method (Atomic absorption spectroscopy) after mineralization by microwave decomposition. Results obtained from

analysis of selected hazardous elements – heavy metals is described in the second part of the paper.

#### ELEMENTARY ANALYSIS OF BIOMASS TESTED SAMPLES (N, S) FOR PREDICTION OF ENVIRONMENTAL CHARACTERISTICS

Elementary analysis has significant impact on complex assessment of chemical composition of identified materials (biomass – dendromass) and on consequent evaluation of selected fire technical and (determination of gross heat of combustion and calorific value, flash point temperature, ignition temperature) and environmental characteristics (determination of emission of solid and gaseous polluting substances) [7-11, 14].

The principle of method for elementary composition determination of biomass tested samples (total nitrogen according to STN ISO 13878, total carbon according to STN ISO 10694, total sulphur according to ISO 15178) is based on sample combustion in a jet of oxygen gas in super refined grade at 900 °C temperature and thermal conductive detection of gaseous products from subsequent oxidation-reduction reactions by the FLASH EA 1112 apparatus (Comp. Thermo Finningen). Biomass samples are grinded before analysis itself. After blank sample measurement and calibration, correctness of measurement is checked by reference materials.

Measuring conditions for elementary analysis of biomass samples [14]:

- Temperature of furnace: 900 °C
- He gas pressure: 250 kPa
- He gas flow rate: 130 ml/min
- O<sub>2</sub> pressure: 300 kPa
- O<sub>2</sub> flow rate: 250 ml/min
- Sample delay time: 12 s
- Calibration method: linear fit.

Results of elementary analysis are evaluated directly in percentages while calibration is carried out as regards organic materials with known content of determined constituents.

#### RESULTS AND DISCUSSION

Results of quantitative evaluation from elementary analysis were used for calculation of calorific value [7-9] from gross heat of combustion as one of important fire technical characteristics of products prepared from biomass for prediction total characteristics materials for production of biofuels [14].

Table 1 Result values of elementary analysis of tested samples of biomass

Sample	Nitrogen total (% wt.) **	Sulphur total (% wt.) **
Wood pellets	3.21*	0.075*
Wood briquettes	3.04	0.058
Sawdust	2.99*	0.069*
Wood chippings	0.163*	0.033*
Wood shavings	0.171	0.046

Notes: \*Results published in Ružinská, E. et al., 2014 [14]

\*\*Extended uncertainty of measurement U (k=2) for determination of nitrogen total is 8.1 %; sulphur total – 10.4 %, respectively.

From elementary analysis results (Table 1) that total nitrogen content evaluated in beech pellets, beech sawdust as well as in beech wood chippings and shavings significantly varies. In the Table 1 we can see that the lowest content of nitrogenous are shown wood shavings.

Reference sources refer total nitrogen content in biomass (fuel wood with bark) in range < 0.5 % mass percentage; beech wood with bark – 0.22 % [16]. Only sample of beech wooden chippings meets this value (0.163 %) and wooden shaving (0.171 %).

Extremely high value was recorded for beech sawdust (2.99 %) [14] and for unbroken pellets (3.21 %) and wooden briquettes (3.04 %). Indication of these increased values can be caused probably also by presence of nitric fertilizers that were present in growth site of wood-plant used for pellets preparation.

Since nitrogen contained in fuel (pellets) participates in nitrogen oxides (NO<sub>x</sub>) origin in exhaust gases during combustion process, such high value has significant adverse environmental impact on environment and it is even comparable with nitrogen content in peat (1.5 -2.5 %) or coal (up to 3.5 %), respectively [6, 15, 16].

From elementary analysis of quantitative evaluation of total sulphur results that its content is very low (pellets – 0.075 %; sawdust – 0.069 %; wood chippings - 0,033 %, wood shavings – 0.046 %; briquettes – 0.058 %), when compared with the value referred to in reference 0.015 % [6, 14] at extended uncertainty of measurement U = 10.4 %. This low sulphur content indicates that beech pellets from environmental assessment show favourable aspect comparing with classic fossil fuel (coal – 0.39 - 0.94 %) [6,7].

## RESULTS

The evaluation of the selected components constituting the various forms of biomass (pellets, briquettes, wood shavings, wood chips, sawdust) showed that it is important to know the elemental composition of the assessment of the calorific value of biomass preparation of biofuels [14], compared with traditional fossil fuels.

Monitoring environmental impacts of new fuels from biomass (dendromass) indicated the need to assess the content of heavy metals in the burning process (as source of heat). Pollutants that are generated during the combustion process depends on their variable representation in the biomass, which will participate in the different amounts of emissions, however in a smaller volume than traditional fossil fuels.

In the first part of the article attention was paid to toxicological effects of heavy metals in various forms of biomass (dendromass) for human health and the environment to obtain current and comprehensive knowledge of the biomass used in the preparation of biofuels.

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**Streszczenie:** *Analiza zawartości wybranych metali ciężkich w biomase do produkcji biopaliw - Część I. Efekt toksykologicznych zawartości metali ciężkich.* W ramach pierwszej części pracy przedstawiono badania nad efektem toksykologicznym wpływu metali ciężkich (As, Cd, Pb, Ni, Cr) zawartych w różnych formach biomasy (trociny, wióry z drewna bukowego, strużyny, pelety i brykiety) na zdrowie człowieka i środowisko. Badania prowadzono w celu aktualizacji i uzupełnienia wiedzy na temat biomasy stosowanej w produkcji biopaliw. W pracy przedstawiono wyniki analizy elementarnej surowców, będących źródłem emisji metali ciężkich w procesie spalania biopaliw wytwarzanych z biomasy (dendromasy).

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