INVESTIGATION OF WASTE BIOMASS ASH FROM PAPER INDUSTRY

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ABSTRACT

The main part of companies in Bulgaria are built, however in the 70s, and upgraded last decade. The country supplies around 80 % of its supplies of paper, paperboard and pulp with own production. Integrated treatment of wastes is a priority for realizing closed life cycle of materials. The aim of the present work is to investigate the composition and other important characteristics of biomass wood ash wasted from paper industry. The correlations and associations among the chemical characteristics are also studied to find some basic trends and important relationships between two similar wastes from different enterprises. It was proved that all samples taken contained Ba, Cr, Mn, Ni, Co, Al, Fe, Cu and Zn far below the legal limits for such type of products. A product has a certain anti-acidic effect. The other positive result was that the content of iron is between 34 to 60 mg per 1 kg dry waste. The microscopic photos confirmed that the particles are close to the nano-size materials. The content of the elements C, N, H is in good quantities and ratios, which is a prerequisite for their use as a soil improver.

By the results of this study, it was confirmed that all samples produced as a result of the thermal treatment and final low water content achieved are free from pathogen microorganisms and different weed seeds, affecting the yield and soil sustainability. That allows determining the optimal ratio between the used components with a view to obtain products with desired thermal stability and physico-chemical properties as soil improvers.

Keywords: pulp production waste, biomass ash, thermal treatment.

INTRODUCTION

The main part of companies in Bulgaria are built, however in the 70s, and upgraded last decade. The country supplies around 80 % of its supplies of paper, paperboard and pulp with own production. Integrated treatment of wastes is a priority for realizing closed life cycle of materials [1].

There is a trend to utilize the waste in another industry. For example, the bark and wood residues can be used as a raw material for particle board and chemical pulp production. Furthermore, energy can be produced by burning wood waste from the debarking plant, black liquor from the pulp making process, and bio sludge from wastewater treatment plants, as a forest fertilizer, or a raw material for the synthesis of a porous, ceramic composite [2 - 7], material for CO_2 capture [3]. The utilization of such materials in concrete not only makes it economical, but also helps in reducing disposal concerns [4, 5]. Wood ash can be used in concretes and mortars, geopolymers and alkali-activated materials, road construction and soil stabilization, bricks, panels, and other green construction materials. This paper explores the possibility and potential of using wood ash in civil engineering [6 - 8]. However, the application of wood ash on agricultural or forest land showed greater environmental benefits than the use in concrete in cases where both its liming and fertilizing potentials are assumed to be achieved at the same time [9].

Wood ash generated as a tree bark combustion product from paper industry, is a prerequisite for establishment of "green cover" on local soils by using native plants that are the best adapted to the local environment that is essential in Eco restoration management. Various studies indicated that fly ash can be used to reclaim soil and enhance agriculture production. Vegetation surveys showed that the sown native species, grow rapidly, and provide erosion control and stabilization of soils [10].

Wood ash depot rehabilitation through ecological engineering that revitalizes ash disposal sites while simultaneously contributing to resources generation and carbon sequestration is a strategy to combat the adverse effects of climate change [11]. To achieve a sustainable circular economy for wood ash, the reuse of wood ash in agriculture and forestry is important [12]. Ash, which is obtained from wood, consists of two main parts - soluble and insoluble in water. The amount of the soluble part is 10 - 25 % of the total amount of ash. Its composition includes sodium and potassium carbonate, salts of hydrochloric acid, and also some salts of phosphoric acid. About 60 - 70 % of the all soluble ash are sodium and potassium carbonates. If the wood has been in water for a long time, the amount of soda and potash content in it is reduced. Some types of wood contain bound phosphorus in the heartwood and sapwood. It was established that its quantity is greater in the upper parts of the tree stems.

Wood ash contains all the mineral nutrients that are not volatile in the thermal combustion process. They are in the same elements proportions as they were in the structure of the wood mass used for burning, thus been suitable for improving the structure and stock of soils. Only the nitrogen from the wood mass is mainly destroyed and passes into the waste gases generated during the burning of the wood. Both the source wood waste and the resulting wood ash have an alkaline reaction and this makes them extremely suitable for use as improvers for acidic soils.

The aim of the present work is to investigate the composition and some important characteristics of biomass from wood ash wasted from paper industry. The correlations and associations among the chemical characteristics are also studied to find some basic trends and important relationships between two similar wastes from different enterprises.

EXPERIMENTAL

Materials

The industrial waste is taken from the cellulose production plant closed depot in the same town. The depot area is about 135600 m^2 with the deep average about 7 m. The estimated quantity of that waste in it is above 106 tons. The biomass studied includes two similar wastes ash from biomass from different enterprises. The aim is to trace the variability of the wood used and how this affects the chemical composition. The other characteristics of this ash are published in a previous article [14].

Methods

Analysis was performed on an ICP-Atomic emission spectrometer (High Dispersion ICP-OES Prodigy of the Teledyne Leeman Labs USA company with dual plasma monitoring (axial and/or radial)). The construction of the optical system is "Eshelle" and the detector "L-PAD", with high resolution (0.007 nm), continuous spectral range (from 165 to 1100 nm). The spectrometer is equipped with a so-called "free running" RF generator, which provides power up to 2 kW at 40.68 MHz.

Quantitative elemental analysis of dry soil samples for the content of carbon, nitrogen and hydrogen was carried out with an automatic analyser EA 3000 of the Italian company EuroVector. The analytical method includes burning of the sample at a high temperature (980 - 1100°C) and determining the component by gas chromatography.

The shape and size of particles in the samples were studied using a scanning electron microscope (SEM) Philips PH Model 515, operating in the regime of secondary electron emission (SEE).

The spectral distribution of infra-red absorption was measured using Fourier Transformed Infrared (FT-IR) spectrophotometer Varian 660-IR (Austria, 2009) covering the range of 400 - 4000 cm^{-1}, KBr tableting.

Apparatus STA PT1600 TG-DTA/DSC (STA Simultaneous Thermal Analysis), produced by LINSEIS Messgeräte GmbH, Germany was used. Thermal analysis was carried out in dynamic mode of heating in the temperature range 293 - 1250 K at a heating rate of 10 K min^{-1}. The type of the sample is a powder with a particle size of 0.5 mm. Static air is the atmosphere. The stabilized corundum crucibles are used.

RESULTS AND DISCUSSION

The chemical composition of wastes is the first step and initial approach for characterization. It was found repeatedly that biomass shows a wide diversity and its composition is significantly or highly variable [2, 3, 11, 13]. The composition of natural biomass depends on various factors, name type of biomass, plant species or part of plants, growth processes, growing conditions, location, seasons, blending of different biomass types some similarities or differences in common chemical characteristics for biomass varieties, reported in almost all investigations [13].

Inevitably this also affects biomass wood ash. Table 1 presents the results of ICP analysis of the sample (EKO 1) plant closed depot and sampling at 2 years (2012 - 2020) of wood ash from an operating depot (PB1- PB6).

Using ICP techniques the elements were tested in the citric extract. It was proved that all samples taken contain Ba, Cr, Mn, Ni, Co, Al, Fe, Cu and Zn far below the legal limits for such type of products. The highest content of

Table 1. ICP analysis of the sample (EKO 1) plant closed depot and sampling at 2 years (2012 - 2020) of wood ash from an operating depot (PB1- PB6).

	EKO1	PB1	PB2	PB3	PB4	PB5	PB6
P	2.34	3.505	3.158	3.239	3.001	2.828	2.991
K	-	24.23	22.26	23.36	18.00	18.38	23.61
Na	16.68	17.02	14.90	15.50	14.02	13.49	15.16
Ca	336.90	121.9	110.4	121.4	139.0	133.2	142.8
Mg	15.16	14.85	14.64	15.15	13.72	13.29	14.68
Ba	0.67	1.153	1.072	1.117	1.009	0.983	1.127
Cu	0.12	0.532	0.480	0.491	0.524	0.504	0.534
Fe	57.50	57.1	53.7	60.1	34.2	37.9	56.4
Al	69.01	135.3	129.4	138.3	108.2	107.5	131.8
Zn	0.59	2.825	1.584	1.523	1.411	1.262	1.269
Mn	1.27	1.072	1.074	1.087	0.981	0.948	1.031
Cr	0.04	0.218	0.191	0.234	0.244	0.203	0.215
Ni	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Co	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mo	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
V	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
B	< 0.01	0.610	0.568	0.578	0.525	0.513	0.565
S	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Hg	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
As	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Pb	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cd	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001	< 0.001

375 mg per 1 kg dry waste was found for calcium, when the content of Mg is about 25 mg per 1 kg dry waste. This is the reason that all samples taken have an alkaline reaction. So, such a product will have a certain anti-acidic effect. The other positive result was that the content of iron is between 34 to 60 mg per 1 kg dry waste. During the periodic sampling of the active landfill, no strong variability in the chemical characteristics was observed over the years, which suggests stability in the use and recovery of the waste. They have similar concentrations to the closed depot.

The microscopic photos (Figs. 1 and 2) confirmed the round shape of particles and dominant size is under 40 x 10^{-6} m, so quite close to the nano-size materials. The size is an important indicator for subsequent processing and the possibility of obtaining mixtures with good adhesion and strength indicators. Macropores are related to the vital activity of the soil, i.e. by enriching it with water and air. They are also associated with the movement of roots through the soil and are a habitat for a wide variety of microorganisms.

To evaluate the usability of ash for application as improver were investigated the main structural elements. The results of the conducted research show (Table 1) that the quantities and ratios of the elements C, N, H are suitable, which is a prerequisite for their use as a soil improver.

The results of the thermal investigations by TG-DTG-DTA of the wood ash sample EKO 1 in an air is shown in Fig. 3. The thermal analysis of the specimen presents the thermal behaviour when heated up to 1250K. The main thermal processes are in 2 temperature intervals – 600 - 900K and 950 - 1100K. The first takes place with an exothermic reaction, and the second one - with an endothermic one. Considering that the composition of the ash waste contains calcite - $CaCO_3$, quartz - SiO_2 and fairchildite - $K_2Ca(CO_3)_2$, the recorded effects should be attributed to the decarbonization of potassium-calcium carbonate at lower temperatures and of calcium carbonate at higher temperatures. However, it should be noted that in the first temperature range, dehydration of amorphous calcium hydroxide is also possible, which was not proven by microscopic observations, but due to the proven high content of calcium in wood ash, this possibility should not be excluded. So, during heating in a static air gas environment of biomass ashes, two stages of decomposition can be distinguished in total - the first stage of partial decarbonization of $K_2Ca(CO_3)_2$ and dehydration

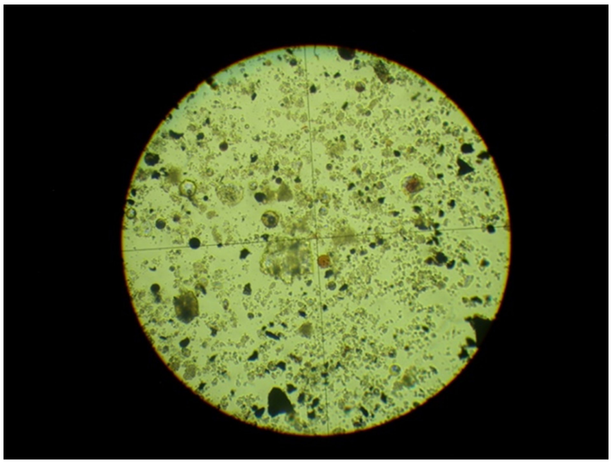

Fig. 1. Morphology of EKO1 in plain polarized transmitted light.

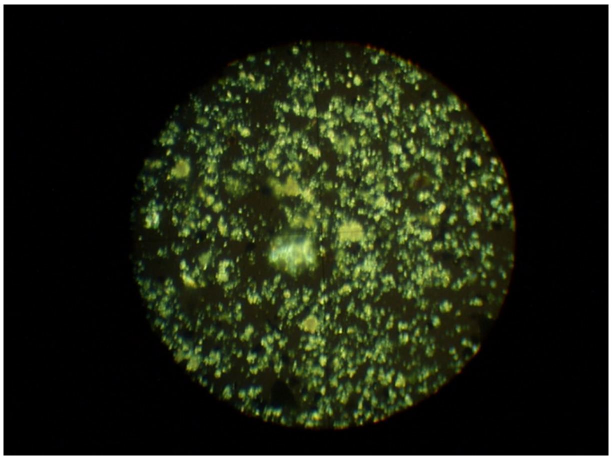

Fig. 2. Picture of sample EKO1 in cross-polarized transmitted light.

Table 2. Result of elemental analysis of sample EKO1.

Element	Percentage content (%)	Ratio	
C	22.45	C/N	46,77
N	0.48	C/H	27.71
H	0.81		

of amorphous calcium hydroxide and the second stage of decarbonization of the remaining calcium carbonate.

The sulphates remain undecomposed until the final temperature of the sample heating. IR spectroscopy confirms the composition of the sample - the bands at 713 cm^{-1}, 873 cm^{-1} and 1438 cm^{-1} are characteristic for the carbonate group, while 458 cm^{-1} and 1160 cm^{-1}

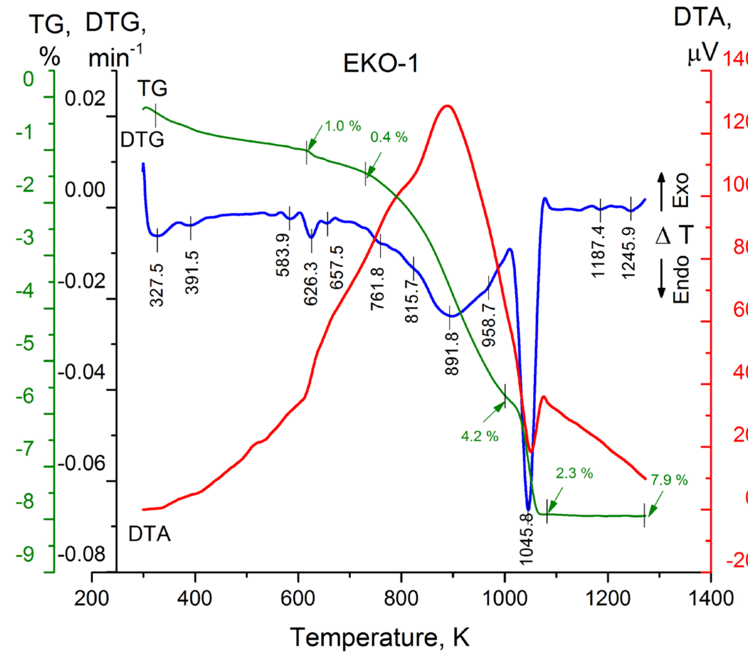

Fig. 3. TG-DTG-DTA of industrial waste EKO1.

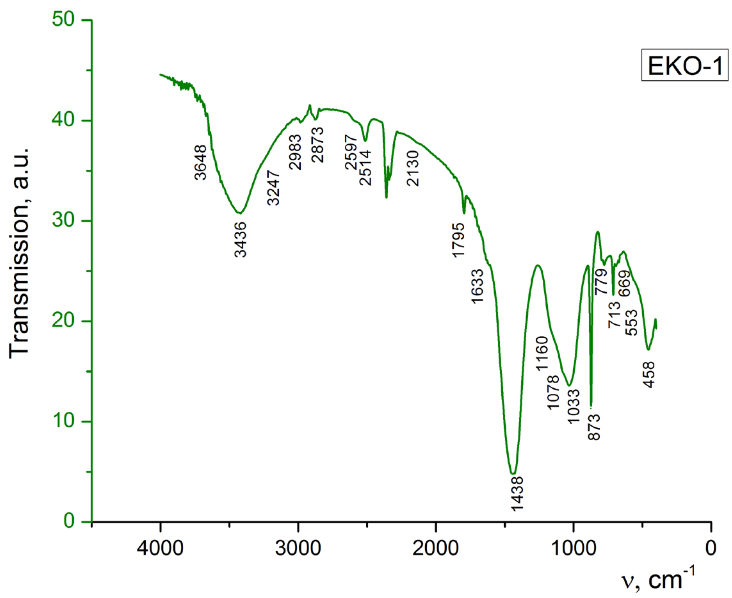

Fig. 4. IR of EKO1.

- for the sulphate group. The bands at 1033 cm^{-1} are characteristic for SiO_3. Experimental data show that the sample has different functional groups (Fig. 4). Hydrogen, oxygen, nitrogen, phosphorus and sulphur are included in the aromatic rings. With a high content of mineral ashes, it turns out that some of the functional groups contain metals. A number of nitrogen- and sulphur-based functional groups have been discovered. This shows that the relative concentration of each of the functional groups depends on the initial composition of the biomass, the final reaction temperature, the composition of the gas surrounding the char particle (at the final reaction temperature), the heating rate and any subsequent treatment.

CONCLUSIONS

The successful studies of industrial waste from cellulose production show the high remediation and adaptive potential of wood ash pointing their key role in the revegetation, stability, and resilience of an ecosystem. The analysed ashes exhibit good physical and chemical properties. They can be suitable for the use in agriculture as a liming agent to be applied on medium and heavy soils.

With the rapid entry of innovative technologies related to a more efficient circular economy in which resources are used more sustainable. The proposed actions aim, on the one hand, to "close the loop" within the life cycle of products by increasing recycling and reuse, and on the other hand, to generate benefits for both the environment and the economy. As a result, the carbon contained in the woody mass, which is estimated to be about 45 %, is expected to be returned to the soils. The possibilities of biological capture of CO_2 are really encouraging.

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