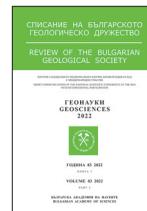




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## Biomass ash as a new potential resource of phosphorous for industry

### Пепелта от биомаса като нова потенциална суровина на фосфор за индустрията

*Stanislav Vassilev, Christina Vassileva*  
*Станислав Василев, Христина Василева*

Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, Block 107, 1113 Sofia, Bulgaria; E-mails: vassilev\_stan@yahoo.com, ch\_vassileva@yahoo.com

**Abstract.** The content and modes of occurrence of phosphorous (P) in eight biomass ashes (BAs) were studied. It was found that BAs are enriched in P as its concentration varies in the range 0.3–4.4% (mean 1.7%). The highest contents of P (>2 %) are characteristic of ashes produced from agricultural residues, namely plum pits, sunflower shells and corn cobs. It was identified that the modes of P occurrence in BAs are related mostly to apatite and whitlockite. Hence, BAs having renewable and C-neutral origin could be alternative and very perspective resource for the potential recovery of P and its utilization in industry in contrast to finite and non-renewable phosphate rocks.

**Keywords:** biomass ash, phosphorous, phosphates, content, utilization.

### Introduction

Phosphorous and phosphates are among the strategic for EU elements and minerals for the manufacture of critical materials in industry because they have high economic importance, and their supply security is at risk. This element has a widespread utilization in industry such as production of chemicals, fertilizers, food, feed, drinks, pyrotechnics, electronics, plastics, as well as various applications in metallurgy, pharmacy, construction materials and others (Cieslik, Konieczka, 2017). The total P consumption has increased fivefold during the last 50 years (Chen, Graedel, 2016) in order to satisfy the rapidly growing demand. Approximately 20 Mt of P are annually extracted from the earth mostly from sedimentary phosphate (apatite) rocks (Jupp et al., 2021) as the P concentrates produced from these rocks commonly contain about 14–15% of P or 32–33% of  $P_2O_5$  (Smol et al., 2016). It is well known that the world reserves of industrial P and quality of phosphate ores decrease and the production costs increase at present. On the other hand, the asymmetric distribution of P resources around the

globe (Morocco, Western Sahara, China, the USA, and Russia) accompanied by price volatility could lead to sensitive security situations. Therefore, the technologists are particularly interested in alternative P resources such as waste products from renewable sources due to the global warming and climate change.

Phosphorus as a biophile and nutritious element is vital to the growth of plants and animals because is unreplaceable by other elements. This non-metal is much more concentrated in different types of terrestrial and aquatic phytomass and zoomass in comparison with magmatic and sedimentary rocks, coals, soils, and other natural objects. Even more, as a result of biomass combustion, P shows a very high enrichment factor in biomass ash (BA) because the ash content of biomass is low (normally 1–10%). Thus, P in BA is one of the most abundant elements and usually follows the concentration order:  $K > Ca > S > P$  according to their contents in the world reference plant ash where P is about 4% (Cohen, Dunn, 2014). Extremely high P concentrations (>10%) were detected for ashes produced from meat-bone meal, chicken litter and sewage sludge as these con-

tents are comparable to those for phosphate rocks (Vassilev et al., 2017). Additionally, the phosphate rocks are finite and non-renewable resources, while BA has renewable and C-neutral origin. The direct combustion of biomass is the dominant conversion process currently used for bioenergy production and as a result between 170 Mt (Zhai et al., 2021) and 480 Mt (Vassilev et al., 2013a) of BA may be generated worldwide annually. Hence, about 7–19 Mt of unutilized P (or 16–44 Mt of  $P_2O_5$ ) are discharged with BA per year. For a comparison, the annual demand for P fertilizers is between 17 and 35 Mt at present (Chen, Graedel, 2016). It should be stated that the production of BA worldwide is expected to be about 1000 Mt per year in future due to the rapidly increasing bioenergy production (Zhai et al., 2021). The above presented data clearly show that BA has the potential to be a huge P resource for industry. The major purposes of the present study are: (1) to identify the content, modes of occurrence, and significance of P in different BAs; and (2) to understand how the fundamental knowledge may be implemented for the potential sustainable utilization of P.

## Material and methods

Eight BAs, namely beech wood chips ash (BCA), corn cobs ash (CCA), marine macroalgae ash (MMA), plum pits ash (PPA), rice husks ash (RHA), switchgrass ash (SGA), sunflower shells ash (SSA), and walnut shells ash (WSA), were laboratory produced in an oven at 500 °C for 2h under static air. These ashes were additionally thermally treated at 700, 900, 1100, 1300 and 1500 °C for 1h under static air. Light microscopy and powder X-ray diffraction (XRD) were used for the identification of phase and mineral composition of BAs, while the contents of P in BAs (500 °C) were determined by laser ablation inductively coupled plasma (ICP) – mass spectrometry (MS) as explained earlier (Vassilev et al., 2014b).

## Results and discussion

The chemical composition of the BAs studied is highly variable as the contents of oxides fluctuate in large ranges, particularly for  $SiO_2$  (1–90%), CaO (1–63%),  $K_2O$  (4–50%),  $SO_3$  (1–28%),  $Na_2O$  (0.1–14%), MgO (0.5–12%), and  $P_2O_5$  (1–10%) (Vassilev et al., 2014b).

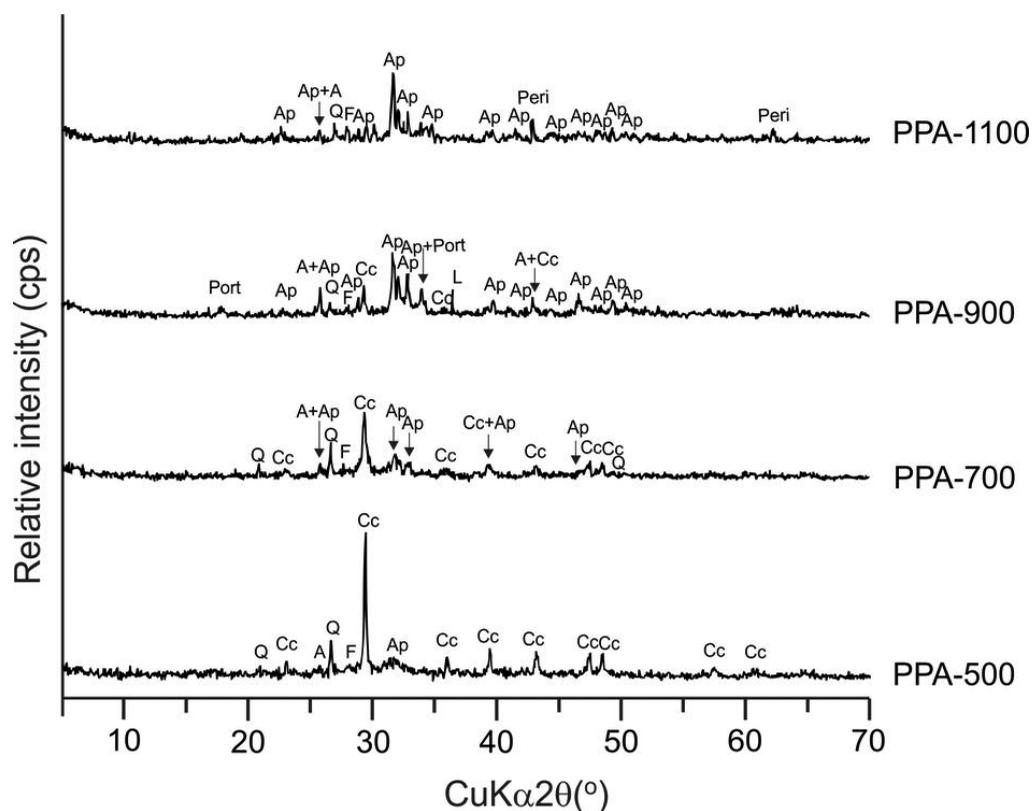
The contents of P in these BAs are given in Table 1.

It can be seen that these concentrations vary in the range 0.3–4.4% (mean 1.7%) and they are lesser or comparable to the world reference plant ash. The greatest contents of P (>2%) are characteristic of ashes produced from agricultural residues such as plum pits, sunflower shells and corn cobs. The phase-mineral composition of the eight BAs studied (Vassilev et al., 2013c, 2014a) consists mainly of inorganic amorphous matter, carbonates (calcite, kalicinite, fairchildite, and butschliite) and silicates (quartz, cristobalite, tridymite, plagioclase, leucite, and kalsilite), and to a lesser extent, oxyhydroxides (lime, portlandite, and periclase), sulphates (anhydrite and arcanite), phosphates (apatite and whitlockite) and chlorides (sylvite and halite), plus some char.

The reference data show that P in BA may occur in more than 26 phases and minerals, mainly alkaline, alkaline-earth, Al and Fe phosphates and, to a lesser extent, other P-containing phases (Vassilev et al., 2013c). The modes of P occurrence in the BAs studied are represented by two Ca phosphates, namely apatite and whitlockite. Apatite was identified in BCA, PPA and SSA, while whitlockite was found only in BCA. Their genesis could be original (as unchanged relics of Ca phosphates) if P fertilizers containing hydroxylapatite and other Ca phosphates were used for plant growing. It is well known that the melting point of many Ca phosphates are higher than 1200 °C. However, the origin of apatite and whitlockite is mostly newly formed during biomass combustion due to the transformation of organically bound Ca and Ca-bearing minerals in biomass and their subsequent phosphation by flue gases or solid-state reactions. The phase transformation of original phases, containing Ca and P (organic matter, oxalates, carbonates, phosphates, and sulphates) in biomass includes their decomposition, oxidation and phosphation and result in crystallisation/recrystallization of newly formed: (1) whitlockite (500–900 °C); and (2) apatite (500–1100 °C) in BAs. Hence, the phosphation of newly formed Ca oxyhydroxides to whitlockite and apatite occurs at 500–1100 °C (Vassilev et al., 2013c). The XRD data of PPA produced at 500–1100 °C are illustrated in Fig. 1 for a confirmation. It can be seen that apatite occurs at 500–1100 °C as the most intensive formation is observed at 900–1100 °C. The PPA sample

Table 1. Contents of P in eight biomass ashes produced at 500 °C

Biomass ash	RHA	MMA	WSA	SGA	BCA	CCA	SSA	PPA	Mean
P (%)	0.26	0.42	1.03	1.07	1.09	2.10	2.86	4.44	1.66



**Fig. 1.** XRD patterns of plum pits ashes (PPAs) produced at 500, 700, 900 and 1100 °C (based on Vassilev et al., 2013c). Abbreviations: A, anhydrite ( $\text{CaSO}_4$ ); Ap, apatite ( $\text{Ca}(\text{PO}_4)_3(\text{Cl},\text{F},\text{OH})$ ); Cc, calcite ( $\text{CaCO}_3$ ); Cps, counts per second; F, fairchildite ( $\text{K}_2\text{Ca}(\text{CO}_3)_2$ ); L, lime ( $\text{CaO}$ ); Peri, periclase ( $\text{MgO}$ ); Port, portlandite ( $\text{Ca}(\text{OH})_2$ ); Q, quartz ( $\text{SiO}_2$ ).

thermally treated at 1300 °C shows only amorphous matter due to the melting of apatite or its dissolution by the initial melt in the system.

The reference data reveal that the water-soluble and bioavailable P leached from BAs is relatively low, namely 0–15% (mean 2.3%) (Vassilev et al., 2013a), which is lesser than the traditional P fertilizers. Hence, P in BAs is insoluble or occurs in limited mobile proportions depending on the abundance of water-soluble P components. It seems that this phenomenon is mainly related to the combustion temperatures of biomass. For instance, it was noted that the sequential phase-mineral transformations in biomass with increasing combustion temperature include: (1) initial formation of intermediate, less stable, and more water-soluble phosphates and other P-bearing phases in BA originated from both organic and inorganic matter of biomass (normally at 500–900 °C); and (2) subsequent transformation of the above phases to more stable and less water-soluble phosphates and P-containing phases in BA (commonly at 900–1500 °C) (Vassilev et al., 2013c, 2014a). Hence, the P bioavailability in BA decreases with increasing combustion temperature. It was found that the alkaline and Ca-alkaline

phosphates are commonly water-soluble mineral species in BAs (Jupp et al., 2021). Furthermore, monocalcium phosphate monohydrate and monocalcium phosphate anhydrous are highly soluble in water, while dicalcium phosphate anhydrous and dicalcium phosphate dihydrate are soluble (Leng et al., 2021). On the other hand,  $\alpha$ -tricalcium phosphate,  $\beta$ -tricalcium phosphate, tetracalcium phosphate and hydroxyapatite are much less soluble to almost insoluble in water (Leng et al., 2021). For instance, apatite requires more acidic conditions (with  $\text{pH} < 5.5$ ) to be dissolved (Kanbar et al., 2021). Hence, the increased values of Ca/P molar ratio of phosphates decrease the solubility of these salts.

The above own and reference chemical, geochemical and mineralogical data indicate that P in BA may have some potential technological and/or environmental impacts. The greatest challenges related to P in BA include its: (1) concentration, (2) modes of occurrence, (3) volatilization, and (4) water leaching behaviour; and such topics have been discussed earlier (Vassilev et al., 2013b, 2017). Shortly, the recovery of P from BA enriched in this element is possible using dry or wet separation processes (sieving, flotation, leaching by water

and acidic or alkaline solutions) and such P could be used in industry. Portions of nutrient P in BA (produced at lower temperature) are water-soluble and bioavailable and such ashes can be used as soil amendments (liming, neutralization, stabilization) and fertilizers for supplying plant-growing. Synthesis and production of minerals, ceramics, geopolymers, adsorbents, and other materials from BA enriched in P may also be favourable for industry. In contrast, some low-melting P phases such as K, Na and K-Mg phosphates (in contrast to Ca phosphates) together with other alkaline, Cl and S minerals in BA can be responsible for problems related to ash deposition, sintering, agglomeration, fouling, slagging, and corrosion during biomass combustion in power plants. On the other hand, toxic and potentially toxic trace elements (As, Cd, Cr, Hg, REE, V, and radioactive Rn, Th, and U) can associate with phosphates in BA and they are prone to pose environmental and health concerns during BA processing and storage. Finally, P has low volatility and belongs to the medium volatile elements during the thermochemical conversion of biomass; however, some limited volatilization of P from phosphates (plus hazardous trace elements associated with them) is possible. Such a volatilization may cause some environmental and health problems related to soils, water and plants surrounding the biomass-fired power stations. Hence, the utilization of biomass and BA enriched in P may have both beneficial and detrimental possessions for industry and environment and detailed studies are required for that purpose.

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