



Trace element concentrations and associations in some biomass ashes



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HIGHLIGHTS

- Trace element contents in some biomass ashes and their types were studied.
- Correlations and associations among major, minor and trace elements were described.
- The leading importance of modes of trace elements occurrence was emphasized.
- Some challenges related to trace elements in biomass ash were discussed.

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ABSTRACT

The phase-mineral and chemical composition of biomass ashes (BAs) produced from 8 biomass varieties, namely beech wood chips, corn cobs, marine macroalgae, plum pits, rice husks, switchgrass, sunflower shells and walnut shells, was studied for the elucidation of trace element (TE) concentrations and their associations. For that purpose the contents of 60 major, minor and TEs in high-temperature BAs produced at 500 °C were determined by inductively coupled plasma and laser ablation mass spectrometry, as well as scanning electron microscopy equipped with an energy dispersive X-ray analyser. The phase-mineral composition of BAs was studied by light microscopy, powder X-ray diffraction, differential-thermal and thermo-gravimetric analyses plus some leaching, precipitation, ashing (500–1500 °C) and other procedures. The composition and properties of the biomass fuels studied and their ashes were characterized, and some general considerations about TEs in them are described. An elucidation of the TE contents in BAs and their ash types was conducted and a comparison with coal ashes was also performed. An explanation of the correlations and clarification of the associations of TEs with major and minor elements, as well as with different constituents (organic matter, inorganic matter, cellulose, hemicellulose, lignin, inorganic amorphous matter, silicates, phosphates, carbonates, oxides, hydroxides, sulphates and chlorides) in biomass and BAs are given. It was revealed that the greatest ecological challenges related to some TEs in biomass and BA include their: (1) high concentrations; (2) unfavourable modes of occurrence; (3) enhanced volatilization and limited retention and capture performance during biomass combustion; and (4) increased leaching behaviour during biomass and BA processing or storage.

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1. Introduction

Extensive reference peer-reviewed data plus own investigations for both biomass and biomass ash systems were used recently to perform several extended and consecutive overviews related to: (1) chemical composition of biomass [1]; (2) organic and inorganic phase composition of biomass [2]; (3) phase-mineral and chemical composition of biomass ash (BA) [3]; (4) potential utilization, technological and ecological advantages and challenges of BA [4]; and (5) behaviour of biomass during combustion, namely

phase-mineral transformations of organic and inorganic matter [5] and ash fusion and ash formation mechanisms of biomass types [6]. New classifications based on data from proximate, ultimate, ash, structural and mineralogical analyses, and ash-fusion tests of biomass or BA have also been introduced therein [1–6]. It was highlighted in the above overviews that despite the low contents of trace elements (TEs) in biomass and BA they have very important ecological and technological impacts during sustainable utilization of solid biofuels and their products.

Numerous studies related to TE concentrations in biomass and BA and their behaviour during thermo-chemical conversion including combustion, pyrolysis, gasification and liquefaction, as well as co-combustion, co-pyrolysis and co-gasification of coal

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Nomenclature

BA	biomass ash	MS	mass spectrometry
BC	beech wood chips	OM	organic matter
CC	corn cobs	PP	plum pits
daf	dry, ash-free basis	R^2	correlation coefficient
db	dry basis	RH	rice husks
DTA	differential-thermal analysis	SEM	scanning electron microscopy
DWR	dry water-soluble residue	SG	switchgrass
EDX	energy dispersive X-ray analyser	SS	sunflower shells
FC	fixed carbon	TE	trace element
IAM	inorganic amorphous matter	TGA	thermo-gravimetric analysis
ICP	inductively coupled plasma	VM	volatile matter
IM	inorganic matter	WS	walnut shells
LA	laser ablation	XRD	X-ray powder diffraction
MM	marine macroalgae	%	weight%

with biomass have been performed worldwide ([7–52] among others). Consequently, significant data for contents of TEs in biomass, biochar and BAs such as low-temperature and high-temperature laboratory ashes and industrial bottom ashes, slags and fly ashes, along with behaviour of TEs during thermal treatment of different biomass varieties have been generated. However, serious shortcomings related to TE studies have been identified and most of the short-comings are similar to those determined for chemical and phase investigations of biomass and BA [1–6]. Therefore, an attempt to summarize these problems was undertaken and is described below.

The long term experience and knowledge gained for TEs in the most studied solid fuels and their ashes, namely for coal, peat, petroleum coke and municipal solid waste or refuse-derived fuel have not been applied successfully enough in the field of biomass and BA. For example, the methods for TE investigations of biomass and BA have not been refined and implemented thoroughly. The detailed and complete data sets from simultaneous investigations on TEs and bulk chemical and phase-mineral composition for numerous biomass varieties and their solid combustion products are also scarce. Additionally, many findings about the behaviour of various TEs during thermo-chemical conversion of biomass are based only on theoretical thermodynamic, equilibrium and stoichiometric calculating tools (modelling) of chemical databases. These indirect investigations may be unrealistic for actual predictions in a multicomponent system like that for biomass products and this subsidiary procedure cannot replace the most important and real approach, namely direct (input, output) studies of the systems themselves. Furthermore, sequential chemical fractionation is mostly used to distinguish the modes of occurrence of elements (speciation or chemical forms of combination for individual element) in biomass fuels and their products. However, this indirect procedure cannot be applied to identify the actual modes of occurrence of elements in a multicomponent system. Thus, limited systematic interpretations can be made from such investigations as pointed out in previous papers [1–6].

It is accepted that BA does not contain toxic metals like in the case of coal ash ([53–56] among others). However, certain results for BAs show enhanced concentrations of many elements including also potentially detrimental levels of toxic metals. For example, the reference investigations show that very high maximum contents of elements such as Ag (18 ppm), Al (28.3%), As (0.16%), Au (25 ppm), Ba (2.07%), Ca (59.6%), Cd (657 ppm), Cl (14.2%), Cr (0.20%), Cu (1.0%), Fe (25.4%), Hg (8.9 ppm), K (52.8%), Mg (9.8%), Mn (12.0%), Mo (121 ppm), Na (22.1%), Ni (0.11%), P (17.9%), Pb (5.0%), S (10.3%), Sb (362 ppm), Se (86 ppm), Si (44.1%), Sn (552 ppm), Th

(112 ppm), Ti (16.5%), Tl (49 ppm), U (42 ppm), V (0.10%) and Zn (16.4%) were detected in some BAs, particularly filter fly ashes ([1,4] and references therein). Most of these concentrations are much greater than in coal ash [57,58] and many of them even have a unique resource recovery potential. Additionally, numerous TEs in biomass and BA tend to occur in much more mobile and hazardous compounds than in coal and coal ash ([1,3,4] and references therein). Finally, the common scientific approach used is to study the concentration and behaviour of individual elements in order to explain and evaluate different technological and environmental problems related to BAs. However, the actual reasons for such problems in a multicomponent system are most likely connected with modes of element occurrences, namely specific phases or minerals that contain such elements, similar to coal ash ([3–6] and references therein).

Therefore, some of the major and still open questions are related to the limited knowledge concerning: (1) the identification, content and origin of modes of TE occurrence; (2) the correlation of TEs with major and minor elements and other important characteristics; and (3) the association of TEs with different organic and inorganic constituents (structural components, inorganic matter types, mineral classes, groups and specific species) of biomass and BA. Elucidation of the above topics is essential and can assist directly or indirectly in different technological and environmental challenges associated with biomass utilization. Unfortunately, systematic studies on TEs in biomass fuels and their BAs are only at an early stage and a lot of future work is needed, especially in: (1) the development and standardization of reliable approaches and methods for TEs determination; (2) combined chemical, phase and mineral characterization for identification, speciation and elucidation of modes of TE occurrence; (3) behaviour of TEs during biomass processing; and (4) fate of TEs after formation and collection, and during utilization and storage of the waste products generated from solid biofuels. There are thus ample opportunities for new research in this area.

The above listed problems show that additional, systematic and detailed studies of TEs in biomass and BA based on proven, improved or new approaches and methods are required to reduce uncertainties. The major aims of the present study are: to supply additional results and to systematize the data; to describe some basic findings; and to clarify certain problems related to TEs. The present work includes own investigations of 8 biomass varieties and an attempt is undertaken to address the following objectives:

- (1) Characterization of the composition and properties of biomass fuels and their ashes.

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