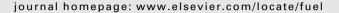


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#### Review article

# Ash contents and ash-forming elements of biomass and their significance for solid biofuel combustion



Stanislav V. Vassilev a,b,\*, Christina G. Vassileva b, Yun-Cai Song a, Wen-Ying Li a, Jie Feng a

<sup>a</sup> Key Laboratory of Coal Science and Technology, Taiyuan University of Technology, 79 Yingze West Street, Taiyuan 030024, Shanxi, PR China <sup>b</sup> Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, Block 107, Sofia 1113, Bulgaria

#### HIGHLIGHTS

- Ash yields of numerous biomass varieties were characterized.
- Contents of 12 ash-forming elements in numerous biomass varieties were studied.
- Challenges related to ash of biomass for biofuel application were described.

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#### ABSTRACT

Inorganic matter and some ash-forming elements of biomass may cause numerous technological and environmental problems during biomass processing. Therefore, an extended overview of the ash contents and ash-forming elements of biomass and their significance for solid biofuel combustion was conducted based on reference peer-reviewed data plus own investigations. Initially, some general considerations such as current bioenergy situation and different aspects related to biomass use as biofuels, as well as some common issues concerning the main advantages and disadvantages of ash contents and ashforming elements of biomass are discussed. Then, definition, specification, terminology clarification and composition related to inorganic and mineral matter of biomass and biomass ash (BA) are considered. Further, the contents and concentration/depletion trends of ash (for 532 biomass varieties) and 12 ash-forming elements based on traditional and complete ash analysis of Si, Ca, K, P, Al, Mg, Fe, S, Na and Ti oxides (141 BA varieties) plus elemental Cl (87 BA varieties) and Mn (156 BA varieties) were characterized. The correlations and associations among the ash yields and contents of ash-forming elements of natural biomass (127 biomass and BA varieties) were also identified using the present database. Finally, the origin and significance of ash-forming elements and their associations established in biomass, namely (1) Si - Al - Fe - Ti; (2) Ca - Mg - Mn; and (3) K - P - S - Cl - Na were described and the benefits and obstacles of these associations for biofuel combustion were evaluated. It was found that the high ash yields and contents of some ash-forming elements such as Cl, K, Na, P, S and some other elements with unfavorable modes of element occurrences (chlorides, sulphates, carbonates, oxalates, nitrates and some oxyhydroxides, phosphates and amorphous material) in biomass and BA may provoke the most critical technological and environmental challenges during biomass processing and especially during biomass thermochemical conversion.

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<sup>\*</sup> Corresponding author at: Institute of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Acad. G. Bonchev Street, Block 107, Sofia 1113, Bulgaria. E-mail address: vassilev\_stan@yahoo.com (S.V. Vassilev).

#### Nomenclature AB aquatic biomass HAB herbaceous and agricultural biomass AHB animal and human biomass wastes SEM scanning electron microscopy **TGA** thermo-gravimetric analysis BA biomass ash wood and woody biomass CB contaminated biomass and industrial biomass wastes **WWB** DAI detrital/authigenic index, which is the ratio between the XRD X-ray powder diffraction sum of Si + Al + Fe + Ti oxides and sum of Ca + Mg + weight% Mn + K + P + S + Cl + Na oxides DTA differential-thermal analysis

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#### 1. Introduction

It is widely accepted that biofuels combustion does not contribute to the greenhouse effect due to the  $\rm CO_2$  neutral conversion thanks to the renewability of biomass. The focus on bioenergy as an alternative to fossil energy has increased tremendously in recent times because of global warming problems originating mostly from fossil fuels combustion. It was highlighted that the utilization of biomass resources will be one of the most important factors for environmental protection in the 21st century [1]. Therefore, extensive investigations have been carried out worldwide currently to enhance biomass use for energy production.

Biomass recently contributes about 15% of the world energy supplies as heat, electricity and fuels for transportation and it was estimated that by 2050, up to 33-50% of the world's current primary energy consumption could be met by biomass ([2] and references therein). The annual world production of biomass with potential energy application at present is considered to be approximately 7 billion tonnes [2]. Numerous biomass varieties among biodiversity groups, namely (1) wood and woody biomass; (2) herbaceous and agricultural biomass; (3) aquatic biomass; (4) animal and human biomass wastes; (5) semi-biomass (contaminated biomass and industrial biomass wastes) such as municipal solid waste, refuse-derived fuel, sewage sludge, demolition wood and other organic wastes; and their (6) biomass mixtures can be used for that purpose [3]. In total about 95–97% of the world's bioenergy is currently produced by direct combustion of biomass. Hence, approximately 480 million tonnes of biomass ash (BA) may be generated worldwide annually [2]. This quantity is comparable to that of coal ash, namely 780 million tonnes produced per year at present [4]. The perspective of increasing large-scale combustion of natural biomass and its co-combustion with semi-biomass and solid fossil fuels (coal, peat, petroleum coke) seems to be one of the main drivers for biofuel promotion by many countries world-wide [2]. Therefore, some of the major open questions related to extensive biomass combustion include if there are any technological problems and environmental risks related to biomass and BA and what we are going to do with this huge amount of combustion residue.

Two fundamental aspects related to the use of biomass and BA are: (1) to extend and improve the basic knowledge on their composition and properties; and (2) to apply this knowledge for their innovative and sustainable utilization. It is well known that the systematic identification, quantification and characterization of chemical and phase composition of a given solid fuel and its conversion products are the initial and most important steps for their proper utilization. This composition defines properties, quality and application perspectives, as well as any technological and environmental problems or advantages related to biofuels and their products [2]. Therefore, extensive reference peer-reviewed data plus own investigations for both biomass and BA systems were used recently to perform several extended and consecutive overviews related to: chemical and phase-mineral composition and properties of biomass and BA; behavior of biomass during combustion; and potential utilization, technological and ecological advantages and challenges of biomass and BA [2,3,5-10]. Additional investigations on trace element concentrations and associations in biomass and BA have been conducted [11]. New chemical, phase and mineralogical classifications of biomass or BA have also been introduced and applied in the above listed studies.

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