A review of biomass ash properties towards treatment and recycling

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ABSTRACT

The generation of biomass ash (BA) is expected to increase in the future because biomass is generally recognized as carbon neutral fuel. Since BA is known, in many cases, to contain hazardous concentrations of trace elements, this will simultaneously produce more potentially hazardous ash. Soon this will need to be handled amidst stricter waste policies and a societal evolution towards a circular economy. In many cases, to allow recycling of BA, trace elements need to be removed for the protection of health and the environment. A better understanding of trace element origins in BA, and knowledge of which trace elements are most critical to advantageous recycling schemes are also needed. In this work available BA data were reviewed and processed for study by multivariate statistical analyses. This allowed for reorganization of the complex nature of BA data into simpler forms for interpretation. An established connection between peat fuels and As was thoroughly reinforced. Wood co-fired with peat would produce BA most advantageous for any recycling, while other biomass for forest recycling and wood, bark and wood waste split between forest recycling and needing treatment or disposal. Some trace elements were still an obstacle to the recycling schemes presented, therefore current state of the art ash treatments for targeting individual trace elements or for total treatment of ash were discussed. Additionally, treatment methods for ash were reviewed because their options are varied, and the goal of utilization will be achieved through matching treatment methods and recycling targets. In the future, the method of using legislative limit values and multivariate analyses to determine BA recycling routes could be replicated for other national limit values and other wastes.

1. Introduction

The annual global generation of ash from biomass combustion was estimated to be approximately 480 million tonnes in 2013 [1,2]. The amount of biomass ash (BA) generated worldwide will likely continue to increase in the near future. Policies such as the European Union's low-carbon economy roadmap suggest that by 2050, the EU should cut greenhouse gas emissions by 80% compared with the 1990 level [3]. Utilization of biomass for energy is based on the idea that it is a carbon neutral fuel and will help cut greenhouse gas emissions. The combustion of biomass for heat and energy produces ash composed primarily of the inorganic elements naturally present in biomass. These ashes are often disposed of in landfills, which is currently becoming unattractive due to costs and could be impossible in the future due to EU policy instruments for a circular economy [4].

Several thermochemical conversion methods are regularly utilized to harness biomass energy. The most common energy recovery methods are grate furnaces, generally for smaller scale energy production of less than 20 MW, fluidized bed boilers for energy output of 20 to several

hundred MW and less common are pulverized fuel furnaces or other processes such as pyrolysis and gasification [5]. The recovery of ash generally occurs in two different forms, bottom ash and fly ash. Several physical mechanisms affect ash formation such as gravity, air entrainment and aerosol formation. Many chemical reactions are implicit in the formation of BA [1,6,7]. In the furnace, gravity will only affect creation of bottom ash on particles too heavy to be entrained in the flue gas. This is most pronounced in grate-fired furnaces and less so in fluidized bed or pulverized fuel furnaces where gravity is countered by the movement of bed material and flue gas entrainment, respectively. Entrained ash in the flue gas make up coarse fly ash particles, typically composed the major and minor biomass forming elements Ca, Mg, Si, K, Al and some unburned organic material [1]. Within the flue gas, condensation of vaporous species of K, Na, S, Cl and trace elements (TEs) occurs on these entrained ash particles. At the same time, aerosols are released from the fuel and nucleation combined with condensation of alkali and TEs takes place with the aerosols to produce fine particulates [5].

Several ash recovery control devices can be employed to capture

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bottom and fly ash. Bottom ash is collected through gravity in all cases except for fluidized bed furnaces where bottom ash is physically separated from the bed material. Some large entrained fly ash particles can be collected by gravity after the combustion chamber in settling chambers. However, fine fly ash and aerosols require cyclones, filters or scrubbers to be removed from flue gas [5]. It is important to note that these finer fractions of fly ash are known to have greater concentrations of TEs [8,9], which affect their potential for utilization [2].

In the recovered BA a multitude of elements exist that can be classified as TEs by a concentration of less than 0.1% [1,10]. An inventory of the documented elements present in biomass and BA, including TEs, and a catalogue of the respective phases and minerals has been presented by Vassilev et al. [1,10]. As many as 79 possible elements can be found in biomass and BA [10]. However, the typical number of elements or oxides of elements included in most of the studies are much fewer due to experimental, or practical constraints. Total elemental analyses of BA facilitate comparison of results to BA reuse limits and sequential leaching methods enable evaluating potential mobility under different conditions, as presented in Lanzerstorfer [11] and Pöykiö et al. [12], respectively. Concentrations of oxides are often included in studies of BA due to the quantity of previously published oxide data [1], and for ease of comparison to such data. These data are also useful for evaluating the quality of BA for reuse, for example, in cement and concrete products [13,14].

Some TEs found in BA are regulated or potentially toxic. In Europe, the determination of landfill (inert, non-hazardous or hazardous) disposal of BA is conditional to the leaching concentrations of As, Ba, Cd, Cr, Cu, Hg, Mo, Ni, Pb, Sb, Se and Zn [2,15]. In the case of fertilizers or earth construction in Finland, total concentrations or leaching concentrations are needed for environmental protection [15,16]. Similar legislation exists throughout the EU and world, and recovered ash must often be handled as a controlled waste in commercial-industrial settings [5]. Furthermore contemporary management schemes prefer recycling of industrial solid wastes to disposal [4,5]. The utilization of BA can be hindered by the characteristic presence of several TEs, which are considered dangerous to health and the environment, but are naturally occurring in BA [10].

The complexity of TE presence in biomass is a result of influencing factors such as plant species, location and environmental conditions of growth [10]. The chemistry of BA is made more complex by the systems of harvesting, processing, energy recovery and ash recovery as variability in reported data is further introduced by the handling and analysis of BA [1]. Due to the heterogeneous nature of BA and the many variables complicit in the formation of BA, multivariate statistical analyses can be useful in separating genuine associations within ash data from variation generated by experimental uncertainties. For example, Camerani et al. [17], examined x-ray elemental maps of BA particles. Zhu et al. [18], examined fly ash particles through combination of extractions, non-destructive characterization methods and multivariate statistics to characterize the chemical speciation of the mineral components. Mäkelä et al. [19], analyzed various measured variables related to hydrothermal treatment of biomass and respective ash behavior for fuel applications, and Saquib et al. [20] used multivariate analysis in combination with sequential extraction to identify connections between fuel type and resulting chemical speciation within BA. However, no previous studies utilizing multivariate statistics to compare legislative limit values applied to analytical data and potential recycling schemes for BA were identified during the literature review.

In this study, principal component analysis (PCA) was utilized for transformation of complex BA analytical data into interpretable univariate forms. It was expected that PCA would identify linkages

between biomass fuel types and their resulting TEs and major forming elements in ash. In addition, multiple correspondence analysis (MCA) was selected to categorize elemental data using limit values for various treatment and recycling schemes. Connections between the most promising applications of BA and biomass fuel types were anticipated to be identified by MCA. Since the goal of recycling much of the BA generated is impeded by the presence of TEs, a short review of the current state of BA treatment based on the findings of this data synthesis is included.

2. Materials and methods

2.1. Data compilation

Experimental data was compiled on the elemental composition and of various BAs from literature sources [4,6–8,15–48] and Värmeforsk (Swedish Ash Program) [51]. Samples of BA were included only if they were collected from sources generating ash, such as power plants or pulp mills. BA samples produced in laboratory-scale experiments were not included. The fuel types from which the BA resulted were also recorded. Samples from the co-firing of biomass with coal or municipal solid waste were excluded from this study. The final dataset included 518 samples, with incomplete data for 28 elements, loss-on-ignition and total carbon. In managing BA analytical data from the above referenced sources, data flagged as below reporting limits (or equivalent designation) for specific analytes were regularly encountered. Those data were recorded as concentrations of zero for consistency. The inclusion of these samples was deemed more important from a sample-size perspective. In many samples, the literature reported concentrations of oxides instead of elemental concentrations. From those samples, the elemental concentrations were calculated using the molar ratio of element to oxide. All samples were standardized to the same concentration units of milligrams per kilogram. Since this study discusses BA which encompasses all the ash generated from woody biomass and other biomass types, biomass as a fuel type needed clarification. In the fuel type variable nomenclature, biomass was defined as energy crops, agricultural residues and undefined biomass types from the literature. Additionally, wood wastes included undefined wood waste, recovered wood, sawdust and sawmill residues. The data were sorted for use in the multivariate analyses by the following logic. It was decided that the focus of the statistical analyses should be on fly ashes, because it is accepted that fly ash typically contains higher concentrations of problematic TEs [10,52]. Therefore, samples of bottom ash, bed sand or mixtures thereof were removed, and 158 viable samples of fly ash data remained.

2.2. Statistical methods

PCA was chosen to distinguish correlations and groupings of final ash data related to associated elements and fuel types. PCA is a method for reducing the dimensions of multivariate data, by orthogonal transformation of variables into new components, which maximize variance in the foremost component with less variance accounted for in subsequent components. The components with the most variance describe the majority of the relationships between samples and variables through principal component scores and loadings, respectively. A detailed description of the method can be found in Jackson [53].

MCA is a subsequent step beyond performing correspondence analysis (CA) and allows investigation of the relationship patterns of categorical data. MCA adds a multivariate analysis similar to PCA for dimension reduction of the multivariate data produced by CA.