New insights into biomass combustion ash categorisation: a phylogenetic analysis

By Jihua Zhai[1]; Ian T Burke[2]; William M Mayes[3]; Douglas I. Stewart[1]*

[1] School of Civil Engineering, University of Leeds, Leeds, LS2 9JT, UK

[2] School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK

[3] Department of Geography, Geology and Environment, University of Hull, Hull,

YO11 3AZ, UK

* Corresponding Author: d.i.stewart@leeds.ac.uk

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Abstract: Combustion of biomass within power stations is a more sustainable way to generate electricity than the use of fossil fuels provided the feedstock is sustainably grown. The physical and chemical properties of biomass combustion ash from different feedstocks was statistically analysed using 168 published database records. Plant taxonomy of the feedstock has a strong influence on the major element composition of the ash, and biomass feedstocks that are burnt commercially can usefully be categorised as hardwood, softwood, grass crop residues, and non-grass crop residues. The most abundant elements in hardwood ashes are calcium > potassium > phosphorous, whereas in the softwood ashes they are calcium > silicon > potassium. The most abundant elements in eudicot straw ashes are potassium > calcium > chlorine > phosphorous, and in grass straw ashes they are calcium > potassium > calcium > chlorine. Differences in major element chemistry between the feedstock categories are visualised using a ternary plot of the normalised calcium oxide, dipotassium oxide, silicon dioxide contents. Other properties depend principally on whether the feedstock is herbaceous or woody. Herbaceous feedstocks produce significantly more ash (typically 5-9%) than woody feedstocks (typically 1-2%) and their ash has a significantly lower initial deformation (melting) temperature than ash from woody feedstocks, and thus has greater potential to form slag and foul the furnace. These findings allow for the impact on ash characteristics to be include in commercial and operational decisions about power station feedstock.

1. Introduction

Anthropogenic CO_2 emissions are a significant cause of climate change, which accounted for three-quarters of the global warming potential of anthropogenic emissions in 2010 [1]. Worldwide, electricity and heat generation are the largest source of anthropogenic CO_2 emissions due to their heavy reliance on fossil fuels, accounting for ~40% of the global total in 2016 [2]. Thus, there is a strong incentive to use alternative energy sources for heating, and particularly for electricity generation that release less CO_2. Despite the criticisms that it may promote deforestation and can displace food production, burning of biomass within power stations is seen as a more sustainable way to generate electricity than fossil fuels, provided the biomass is a waste from another industry or grown sustainably (further crop growth reduces the half-life of the CO_2 in the atmosphere [3]).

Ash is an inevitable by-product of biomass combustion. Industrial scale combustion forms ash with one of two characteristic size fractions: bottom ash (or sometimes slag) that is discharged from the grate (median size typically >1mm), and fly ash recovered from the flue gases (median size typically 10–100 μm) [4-8]. Effective reuse of these ashes or, as an absolute minimum, their safe disposal is essential to the environmental sustainability of using biomass fuels. Biomass ashes are mainly composed of the inorganic constituents of the feedstock, together with some unburned organic phases. They have been characterised as a heterogeneous poly-component inorganic-organic mixture with variable compositions, which contain non-crystalline (amorphous) semi-crystalline and crystalline phases [6]. In a review of ash from 120 different sources Vassilev et al. [6] have identified 229 phases or minerals found in biomass ash, with quartz, calcite, sylvite, arcanite, anhydrite, char, glass, lime, periclase and hematite as the common mineral phases. Further, there are usually compositional differences between the fly and bottom ash from the same feedstock, as volatile phases vaporised in the furnace (particularly salts and heavy metals) can condense onto the fly ash [4, 5, 9]. Similarly, different furnace technologies (e.g. grate furnace or fluidised bed) also affect ash composition due to differences in the furnace temperature [9]. Such a detailed view of biomass ash composition is not helpful when attempting to identify different potential reuse strategies for an industrial by-product. It implies that detailed knowledge of the biomass composition and the combustion technology are necessary to reliably predict the characteristics of the ash. Whereas practical and commercial considerations, such as seasonal availability and supply security, may necessitate rapid decisions about feedstock. Thus, there is a pressing need for more general guidance on how ash characteristics vary with type of feedstock.

The elemental constituents of an ash must be derived from the elemental constituents of the biomass, and while there is loss of organic matter and phase changes in the furnace, and fractionation of volatile constituents between the ash fractions, the bulk characteristics of the ash are likely to be correlated with the composition of the feedstock. Many different types of biomass are used worldwide to provide heat on a domestic scale, but commercial biomass combustion for electricity generation requires large volumes of consistent feedstock, so primary fuels are forestry or agricultural residues. Their sources can thus be classified as softwood, hardwood, grasses (which includes all cereal crops), and other crop residues. Crops grown and harvested specially for biomass combustion, such as willow (hardwood) and miscanthus (grass) also fall in one of these categories. Thus, primary biomass fuels are all derived from land plants (Embryophyta), but these plants fall into three distinctly different groups from an evolutionary standpoint (Fig. 1). All the extant softwoods are gymnosperms (they have unenclosed seeds) and taxonomically they are grouped in a single division Pinophyta in the order Pinales [10, 11]. The gymnosperm lineage separated from flowering plants (angiosperms) about 270-330 Myr ago [12-15]. Similarly, all grasses are from the family Poaceae within the monocotyledon (monocot) clade of the angiosperms, whereas the majority of hardwoods that are used as a commercial fuel are Rosids (e.g. oak, beech, walnut, willow) within the eudicotyledon (eudicot) clade of the angiosperms (the remainder are Asterids also within the eudicot clade of the angiosperms) [11, 16]. Other crop residues used as biomass fuels (e.g. rapeseed, sunflower, alfalfa) also belong to the eudicots (rapeseed and alfalfa are Rosids and sunflower is an Asterid). The eudicot lineage separated from the monocot (grasses) lineage around about 143-157 Myr ago [17, 18].

These evolutionary differences are reflected in the structural differences between softwood, hardwood, herbaceous eudicot and monocot stems (biomass fuels that are burnt commercially are overwhelmingly plant stems, such as straw, stalks, and wood). Between node points (e.g. buds, leaves, and branching points) the stems of gymnosperms and eudicots typically consist of a ring of vascular bundles (for the transport of water and food) between outer and inner regions of ground tissue, whereas the vascular bundles in monocots are arranged in more than one ring or are scattered throughout the cross-section [19]. Wood is formed during the secondary (lateral) growth by most gymnosperms (softwoods) and by woody eudicots (hardwoods). It is composed of secondary xylem tissue produced within the vascular bundles [20], which in hardwood contain vessels for the transport of sap but not in softwood where sap is transported by evolutionarily more primitive tracheid cells [21]. Thus, the distribution organic tissues within the stem of plants is determined by evolution. The inorganic constituents that remain after biomass combustion will reflect the composition of the organic tissues from which they originate, so there are likely to be systematic differences in the composition of the ashes produced by combustion of different feedstocks.

The supposition that the taxonomy of the feedstock will influence the composition of biomass ash is supported by systemic differences in the silicon content between taxonomically distinct groups of plants, and variation in the amount of ash produced by different categories of feedstocks (grasses produce far more ash than woody biomass [22]). Deposition of Si in plants mostly occurs in epidermal cells, and is thought to be an evolved defensive response to pathogens and pests [23]. Hodson et al. [24] undertook meta-analysis of the data from 735 different species of land plants which showed variations in the shoot Si concentration with taxonomic grouping, with high Si accumulation in the taxonomic families that contain grasses and palms, and to a lesser extent in the families that include common hardwoods (including oak, beech, birch, alder, hazel, hornbeam, walnut, hawthorn, cherry, elm, willow, poplar).

This study reviews 168 database records reporting the major element chemical composition of biomass combustion ash from different feedstocks and proposes an evolutionary-based system for categorising biomass derived ash into four categories: hardwood ash, softwood ash, eudicot straw ash and grass straw ash. Systematic differences in the ash properties between these categories are qualitatively and quantitatively determined. Finally, guidance is offered to commercial generators of electricity from biomass to help them make rational decisions about feedstock variation.

2. Methodology

Biomass ash sample characterization data was recovered from the Energy Research Centre of the Netherlands (ECN) Phyllis2 classification database (https://phyllis.nl/Browse/Standard/ECN-Phyllis#). The Phyllis2 databases are designed and maintained by the Netherlands Organization for Applied Scientific Research for the Netherlands Government. Phyllis2 contains around 3000 compositional data records from biomass fuels organized based on a mixture of plant physiology and practical considerations. Of these data records, 168 contain the major element chemical composition of their corresponding combustion ashes and these were selected for the present study. These records also contain incomplete details of other relevant ash properties such as trace metal composition and ash melting temperatures, which were also complied and included in the present study. No data on organic contaminant composition of ashes (e.g. PCBs, dioxins) were available in the Phyllis2 database. The ash composition data consisted of data from both hardwood and softwood samples and a wide range of crop straws ashes (Table 1). All the extracted data, along with their corresponding Phyllis2 database ID numbers, is provided in the supplementary information (S.I. Tables S1 - S4).

Major element data was transformed to nominal oxide format prior to use (e.g. elemental Ca data was converted to CaO wt. %, etc.), and any data reported as below laboratory detection limits were given a value of zero. In addition, when the nominal oxide compositions are reported on ternary diagrams, the oxides being reported were normalized to 100% on a total oxide composition basis.

Ash composition data were analysed to test the null hypothesis that there was no significant difference in median elemental composition between the four ash types using a Kruskal-Wallis test. Dunn's post-hoc test was then used to test pairwise differences in the median values between the different ash types where significance was apparent ($p <0.05$). All analyses were undertaken in IBM SPSS v24.

3. Results

3.1. Ash content derived from biomass

The median ash content produced by each biomass type (Table 2) indicates that eudicot straw (median 8.8%) and grass straw (5.2%) tend to produce more ash upon burning than either hardwood (1.6%) or softwood (1.0%). Kruskal–Wallis analysis of the ash contents indicates that there are two or more separate populations within the overall dataset (Table 2; $p < 0.001$), and while the pairwise comparisons show that there is no significant between the hardwood and softwood ash contents or between the eudicot straw and grass straw ash contents, woody biomass (hardwood or softwood) has significantly lower ash content than straw biomass (eudicot straw and grass straw) ($p < 0.001$).

A subset of the biomass ash database records considered in this study also report biomass feedstock data (see S.I. Fig. S5). Hardwoods contain significantly more volatile matter (median 84%) than eudicot straw (78%) and grass straw (77%). Softwoods also have higher volatile content than grass straw, but are not significantly different from either hardwoods or eudicot straw. Hardwoods contain less fixed carbon (median 15%) than either softwoods or grass straw (17-18%). Ultimate analysis (the relative time proportions of the major components, carbon, hydrogen, nitrogen, oxygen and sulphur), again indicates only very modest, albeit significant differences between some of the biomass categories. Hardwood, softwood and eudicot straw have slightly higher C content (medians 50-52%) than grass straw (49%), while there is no significant difference in H content across biomass categories. Grass straw has a higher O content (median 44%) than softwood and eudicot straw (40-42%) but is similar to hardwood (43%). Eudicot straw has a significantly higher S content (median 0.22%) than grass straw, hardwood and softwood, with grass straw (0.11%) having a significantly higher S content than hardwood or softwood (0.01-0.05%). N content follows a similar pattern being significantly higher in eudicot straw (median 2%) than any other biomass categories.

3.2. Ash chemical compositions

Fig. 2(a)-(d) shows the chemical compositions (in the form of common oxide) of four ash categories. The abundant oxide phases in hardwood ashes (median concentration >5% w/w) are $CaO > K_2O > P_2O_5$ (Table 2), whereas in the softwood ashes they are $CaO > SiO_2 > K_2O$. The abundant oxide phases in eudicot straw ashes are $K_2O > CaO > Cl_2O > P_2O_5$, and in grass straw ashes they are $SiO_2 > K_2O > CaO > Cl_2O$.

Kruskal–Wallis analysis of the elemental oxide contents indicates that there are significant differences in sample medians between ash types for each of the oxides reported except Na_2O (Table 2; $p< 0.05$ for SO_3 and $p < 0.001$ for other oxides). Pairwise comparisons of the CaO content indicate there is no significant difference between the hardwood ash and softwood ash (the pairwise elemental oxide comparisons are reported using superscript letters in Table 2), but both have a significantly higher CaO content than grass straw ash. Eudicot ash also has significantly higher CaO than grass straw but is not significantly different from hardwood or softwood ash. Similar pairwise comparisons indicate that the eudicot straw ash has a significantly higher K_2O content than the hardwood ash and the grass straw ash, which in-turn have significantly higher K_2O contents than the softwood ash (but there is no significant difference between the hardwood and grass straw ash). Also, the grass straw ash has a significantly higher SiO_2 content than the other three ashes. The SO_3 and Cl_2O contents of the ash are important indicators of the amount of volatile sulphur and chlorine in the feedstock, which can result in acid gas emissions that cause high temperature corrosion and may require additional air-pollution control measures. There are no significant differences in SO_3 content between the ash categories in pairwise comparisons (the overall median value across all ash categories was 3.0%, range: 0.1-14.0%). In comparison, the median Cl_2O contents of the eudicot and grass straw ashes were similar and both were significantly higher than either hardwood or softwood ashes, which had similarly low Cl_2O values. However, the small sample size for softwood and hardwood Cl_2O data must be noted (N = 4 for both). Lastly, the hardwood and eudicot straw ashes have significantly higher P_2O_5 contents than the softwood and grass straw ashes. Statistical analysis of the other main elemental oxides can be found in Table 2.

3.3. Trace metal concentration in biomass ash

Contaminant trace metal concentrations are reported in a subset of the data records considered in this study (Fig. 3). The median Cu concentrations in the biomass ashes are 90, 329, 72, and 42 mg/kg for the hardwood, softwood, eudicot straw and grass straw ashes, respectively. The median Pb concentrations in the biomass ashes are 135, 29, 3, and 4 mg/kg for the hardwood, softwood, eudicot straw and grass straw ashes, respectively. The median Cd concentrations in the biomass ashes are 10, 1, 0, and 0.1 mg/kg for the hardwood, softwood, eudicot straw and grass straw ashes, respectively. For comparison, the Finnish limits for ash use as a forest fertiliser are 700, 150 and 17.5 mg/kg for Cu, Pb and Cd respectively [5]. The equivalent Swedish limits are 400, 300 and 30 mg/kg, respectively [25]. The Cu concentration in softwood ash is significantly higher than in either straw ash (S.I. Table S6), but the difference between the two straw ashes is not significant (contaminant trace metal concentrations were reported for insufficient hardwood ash samples for statistical inference). Similarly, the Pb and Cd concentrations in softwood ash are significantly higher than in eudicot straw ash, although grass straw ash is not significantly different from either softwood ash or eudicot straw ash. Hg concentrations are only reported for three softwood samples, but all three values are non-zero (median value 1.7 mg/kg), so these values are significantly higher than the zero (i.e. below detection limit) values reported for the two straw ashes. Cr concentrations are only reported in three data records so no inference can be drawn from the data.

3.4. Ash fusion temperatures

Fig. 4 reports initial deformation temperature (IDT), softening temperature (SOT), hemispherical temperature (HT) and fluid temperature (FT) of the four ash types (these temperatures are important in evaluating ash slagging, fouling and corrosion effects on the boiler and thus its conversion efficiency [26-28].

Hardwood and softwood ashes have significantly higher IDTs (medians 1363°C and 1196°C, respectively; see S.I. Table S7) than the eudicot straw and grass straw ashes (860°C and 910°C, respectively), but the difference between the wood ashes and the difference between the straw ashes are not significant. Softwood ash has a significantly higher SOT (median 1244°C) than the eudicot straw and grass straw ashes (920°C and 1025°C, respectively), but the difference between the straw ashes is not significant (no data is reported for hardwoods). It is harder to discern the trends in HT and FT data, but both the mean and median HT and FT of grass straw are lower than those of the other ashes (S.I. Table S7).

4. Discussion

4.1. Biomass categorisation

A wide range of factors can affect the chemical composition of potential biomass plants [e.g. plant species, soil characteristics, nutrition and stresses during growth, plant maturity, timing of the harvest, plant component being harvested, etc.; 22, 29-34], but it is impossible to recognise all these factors in any functional system for classifying the ash produced by biomass combustion. This complexity has meant that most published work has tended to use only very broadly defined categories to characterise biomass ash properties, such as “herbaceous and agricultural biomass (HAB)” and “wood and woody biomass (WWB)” [35], which provide the user with very little information except the likely ash content.

The hypothesis underlying the statistical analyses presented in this paper is that the biomass feedstock will be a major factor in determining the inorganic elements within a biomass ash, and that feedstocks will exhibit systematic differences due evolutionary divergence. The statistical analyses of database records clearly support this hypothesis. The four biomass categories proposed consistently divided into two or more statistically significant groups based on their content of each abundant elemental oxide, and their ash content. Specifically, the biomass ash categories considered in this paper divide into those that have a comparatively high or low CaO context, those which have a comparatively high or low SiO_2 content, those that have a comparatively high or low P_2O_5 content, those that have a comparatively high, intermediate or low K_2O content, and those that have a comparatively high or low ash content. The four biomass ash categories can be clearly differentiated by considering even a subset of these measures in combination. Hardwood ashes have relatively high CaO and P_2O_5, intermediate K_2O and relatively low SiO_2 and ash contents. Softwood ashes have relatively high CaO, but relatively low SiO_2, K_2O, P_2O_5 and ash contents. Eudicot straw ashes have relatively high K_2O, CaO, P_2O_5 and ash, but relatively low SiO_2 contents. Grass straw ashes have relatively high SiO_2 and ash, intermediate K_2O, but relatively low CaO and P_2O_5 contents.

4.2. Chemical composition classification

Vassilev et al. proposed a chemical classification system for biomass based on its inorganic composition [36]. They identified that the ash-forming elements are either authigenic or detrital in origin (either elements required for plant growth, or fine mineral grains that become associated with plant matter), and grouped the inorganic elements into three major elemental associations;

- Ca-Mg-Mn - Elements probably derived from plant matter that form oxalates and carbonates
- K-S-P-Cl - Elements probably derived from plant matter that form phosphates, sulphates, chlorides and nitrates
- Si-Al-Fe-Na-Ti - Elements that are potentially derived from detrital material associated

with the biomass

While the rationale behind these elemental groups needs further confirmation (e.g. Si deposition by plants can be a defensive response to pathogens, pests and grazers; [23], and Al uptake and localised sequestration can be a plant adaptation to Al-toxicity [37]), representing their relative proportions on a ternary diagram has been shown to differentiate between ashes from markedly different fuels (e.g. HAB and WWB) [6, 7, 22, 36]. Presenting the data collated in this study on a "Vassilev" style ternary diagram (Fig. 5(a)) confirms its utility and, despite some scatter, supports the biomass ash categorisation proposed in this study (each ash category plots in a distinct region of the diagram). Most of the 90 grass straw ashes plot in the low CaO+MgO+MnO areas of the diagram, the 28 softwood samples plot in the low $K_2O+P_2O_5+SO_3+Cl_2O$ areas of the diagram, whereas the 24 hardwood and 26 Eudicot straw ashes plot in the low $SiO_2+Al_2O_3+ Na_2O+TiO_2$ areas of the diagram.

Review of the data in Table 2 suggests that "Vassilev" style ternary diagram shown in Fig. 5(a) could be simplified by plotting only the most abundant constituent in each of the three groups: CaO, SiO_2 and K_2O (see Figure 5(b)). On the revised ternary diagram, data from three categories of ash exhibit closer grouping than in Fig. 5(a), with very little difference in the grouping of the fourth.

Although P_2O_5 and Cl_2O were each either the third or fourth most abundant nominal oxide in two ash categories, the decision was made to omit them from the simplified ternary diagram (Fig. 5b). This is because the Kruskal–Wallis analysis clearly indicates that the biomass categories group differently on the basis of their K_2O, P_2O_5 and Cl_2O contents (hardwood ash groups with grass straw ash for K_2O content, with eudicot straw ash for P_2O_5 content, and with softwood ash for Cl_2O content) so it is not appropriate to sum them on a classification diagram. Therefore, K_2O alone was selected from this group of elemental oxides as it is more abundant than the other two in all four categories of ash.

All the hardwoods included in the data analysis are Rosids (part of the eudicot clade of angiosperms; see Fig. 1), as are alfalfa and rapeseed (the remaining eudicot grass is an Asterid). However, the herbaceous eudicots ashes form a single group that is distinct from the woody eudicot ashes (see Fig. 5). The principal difference between woody and herbaceous eudicots is that there is far more secondary growth in the stems of the former (i.e. wood) and this is composed of secondary xylem tissue [20]. The xylem is a critical part of the Ca^{2+} delivery system in plants [38], and this probably accounts for the higher CaO in woody eudicot ash than in herbaceous eudicot ash.

4.3. Contaminant trace metal associations

All the eudicot straw ashes were below the Finnish and Swedish limits on Cu, Pb and Cd content for use as a forest fertiliser (data was available for 48 samples). Similarly, almost all of the monocot grass straw ashes were below these same limits (1 of 66 samples failed to meet the more stringent Finnish limit for Pb content). Whereas a noteworthy proportion of the softwood ashes exceeded both the Finnish and Swedish limits on for either Cu content, Pb content, or both (contaminant trace metal concentrations are reported for insufficient hardwood samples for further comment). Part of the reason why softwood ashes tend to contain more contaminant trace metals than either eudicot straw or grass straw ash may be associated with the lower ash content of woody biomass, as the estimated mean Cu content of the original biomass is similar for three biomass types (Table 3), and as are the estimated mean Pb and Cd contents of the original softwood and grass straw [interestingly, the estimated trace metal contents of unburnt biomass are similar to those reported elsewhere in the literature; 39, 40, 41]. However other explanations, such as differences in metal uptake mechanism by different plant types or more stringent limits on the soil metal contents for agriculture than forestry cannot be discounted.

Uptake of metals not required by, and potentially harmful to plants is likely to be an artefact of nutrient uptake [i.e. uptake of a divalent contaminant metal might be via the Ca^{2+} uptake pathway; 42, 43, 44]. The correlation of Cu, Pb and Cd with CaO content was analysed by treating all the ash samples as a single dataset (S.I. Fig. S1 and Table S8). There is considerable scatter in the data, which is to be expected as contaminant metal uptake must be affected by soil concentrations, but there are modest but significant positive correlations between Cu and Ca (Spearman's Rank $r_s = 0.59$, $p < 0.001$), Cd and Ca ($r_s = 0.30$, $p = 0.046$) and Pb and Ca ($r_s = 0.35$, $p = 0.016$).

4.4. Organic contaminants in biomass ash

When organic matter is incinerated polychlorinated dibenzodioxins/dibenzofurans (PCDD/Fs) may form in the furnace from Cl present in the feedstock. Formation occurs as the combustion gases cool and is thus sensitive to the rate of flue gas cooling [45-48]. The rate of production of PCDD/F precursors increases slowly with Cl concentration at the Cl levels of typical feedstocks [49], but transition-metal species associated with the ash particles, especially copper compounds, can promote PCDD/Fs formation [45, 46, 50, 51]. However, production of PCDD/Fs is usually more dependent of the combustion technology used than on the feedstock [47]. This makes systematic collection of PCDD/F data difficult as current databases are organised by feedstock. With a standard domestic furnace typical PCDD/Fs concentrations are about 5 ng/kg I-TEQs in softwood ash and 8-24 ng/kg I-TEQs in grass straw ash [47] (PCDD/F concentrations are report in international toxic equivalents, I-TEQs, per unit dry mass). These concentrations are more than two orders of magnitude lower than the provisional requirements for low persistent organic pollutant content limit in wastes stated in the Basel Convention general technical guidelines [52], and more than an order of magnitude lower than the maximum stated in Japan's environmental quality standard for soil [53], but close to the UK limit for poultry litter ash to be used as fertiliser of 20 ng/kg I-TEQs [54]. Thus, disposal of ash from biomass combustion is unlikely to present a problem, but close management of the furnace and feedstock may be required for feedstock with higher Cl contents (such as eudicot straw and grass straw) if the ash is to be applied to agricultural soils.

4.5. Associations of ash fusion behaviour and ash chemical composition

While this paper is focussed on the chemical composition of biomass ash (which determines whether the ash can be put to beneficial use and/or the issues associated with disposal), commercial operators of biomass power stations need to balance multiple constraints when making decisions about feedstock composition [55]. In addition to concerns with availability, cost and calorific value, operators need to consider the ash fusion characteristics of different feedstocks, as fusing of ash particles can result in slagging, fouling and corrosion within the furnace, and thus thermal conversion efficiency and maintenance requirements for a biomass power station [26, 56, 57].

The temperature at four defined points (IDT, SOT, HT and FT) are used to characterise the ash melting process and thus the likelihood that ash particles will fuse together [26, 58], but there still debate about which best correlates with the ash fusion characteristics of biomass [59-61]. The softening temperature (SOT) is generally used as the index of coal ash fusion behavior, but initial work on biomass ash suggests that the initial deformation temperature (IDT) may be the better index for biomass [27]. IDT is also the most widely reported of these indices in the Phyllis2 data records considered in this study (it is reported in 80/168 records), and as IDT is the temperature at which melting is first recorded, it is the lowest of the four defined temperature points.

The obvious pattern is that wood ashes have a significantly higher IDT than straw ashes, however four of the elemental oxide contents also show a statistically significant correlation with two or more of the defined temperature points (IDT correlates with all four of these nominal oxides). IDT, SOT, HT and FT are all positively correlated with the CaO content (confidence 99%; see S.I. Table S9), and 36% of the variance in IDT can be explained by the CaO content. IDT and SOT are both negatively correlated with both the K_2O and Cl_2O contents (conf. 99%); 18% of the variance in IDT can be explained separately by the K_2O and Cl_2O contents. IDT, HT and FT also exhibit a weak negative correlation with the SiO_2 content (conf. 95%, 95% and 99%, respectively), but SiO_2 can only explain 4% of the variance in IDT. Thus, IDT increases as CaO content increases, but decreases as K_2O, Cl_2O, and to a lesser extent SiO_2 increase.

5. Conclusions

Statistical analysis of the chemical composition of 168 biomass combustion ashes from different feedstocks shows that the plant taxonomy of the feedstock has a strong influence on the major element chemical composition of the ash produced. The biomass feedstocks that are burnt commercially for electricity generation can usefully be categorised as hardwood, softwood, grass crop residues (e.g. straw from cereal production), and non-grass crop residues. The abundant nominal oxide phases in hardwood ashes are CaO > K_2O > P_2O_5, whereas in the softwood ashes they are CaO > SiO_2 > K_2O. The abundant nominal oxide phases in eudicot straw ashes are K_2O > CaO > Cl_2O > P_2O_5, and in grass straw ashes they are SiO_2 > K_2O > CaO > Cl_2O. SO_3 and Cl_2O composition are important for high temperature corrosion effects in furnaces and environmental emission control. Cl_2O content was significantly higher in eudicot and grass straw ash than softwood and hardwood ash, while SO_3 content was variable but not significantly different between ash classes.

Other properties depend principally on whether the feedstock is herbaceous (eudicot straw and grass straw) or woody (hardwoods and softwoods). Herbaceous feedstocks produce significantly more ash (typically 5-9%) than woody feedstocks (typically 1-2%) but, possibly as a result, the ashes generally contain lower concentrations of contaminant trace metals. Also the initial deformation temperature (IDT) of ash from herbaceous feedstocks (typically 860-910°C) is significantly lower than that of woody feedstocks (typically 1196-1363°C), which is an indicator that such ash has a higher potential to form slag and foul the biomass furnace).

Operational decisions about the specific choice feedstock for use in a commercial biomass combustion power station depend on a range of practical and business-related considerations. For example, seasonal availability and supply security may necessitate occasional, and sometimes rapid, feedstock changes. However, the ash reuse or disposal strategy will always be an important consideration when managing such change. The data in this paper indicate how the ash characteristics are likely vary with the type of feedstock, and thus can facilitate dynamic decision-making. An alternative fuel within the same feedstock category is likely to cause only a modest change in the ash's physical and chemical characteristics, whereas a change between categories (e.g. from cereal crop residues to wood-pellets from coniferous forestry) is likely to have a more substantial impact of ash's physical and chemical characteristics.

Finally, it is noted that incomplete data on contaminant trace metals and organics hinder the beneficial reuse of biomass ash as in the absence of data regulators often make conservative decisions regarding approval of new ash reuse proposals.

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Table 1. Number and type of ash data records used in this study.

Hardwood ash (24)	**Softwood ash (28)**	**Eudicot straw ash (26)**	**Grasses straw ash (90)**
Beech (1)	Fir (3)	Rapeseed (11)	Barley (12)
Birch (1)	Pine (12)	Sunflower (6)	Maize/corn (8)
Oak (4)	Spruce (4)	Alfalfa (9)	Rice (15)
Willow (14)	Mixed fir/pine/spruce (4)		Rye (2)
Poplar (4)	Unspecified (5)		Sorghum (8)
			Wheat (45)

Table 2. Median and full range of ash composition data (wt. %). K-W *H* shows the Kruskal-Wallis *H* statistic with level of significance (** denotes $p < 0.001$; * denotes $p < 0.05$: degrees of freedom = 3 for all tested items in the left-hand column). Different superscript letters in a row indicate a significant difference in median value between sample populations based on post-hoc pairwise comparisons (Dunn's Test with Bonferroni correction, $p < 0.05$). For example, a population labelled ^{a} is significantly different ^{b}, ^{c} or ^{d}, while ^{ac} would not be significantly different from a population annotated as ^{a} or ^{c}, but would be significantly different from those labelled ^{b} or ^{d}.

Item	Hardwood	Softwood	Eudicot Straw	Grass Straw	K-W *H*
CaO	37.4 (10.9-65.0)^{a}	32.0 (8.8-51.2)^{a}	20.1 (6.6-66)^{ab}	8.7 (0.5-26.5)^{c}	108.0**
MgO	4.1 (0.1-18.4)^{a}	4.9 (0.6-13.5)^{a}	2.5 (0.6-16)^{ab}	2.4 (0.6-6.1)^{b}	37.2**
K_2O	14.7 (4.6-26.5)^{a}	8.5 (1.0-23.9)^{b}	28.0 (8.0-44.2)^{c}	14.3 (2.0-41.0)^{ad}	42.6**
P_2O_5	9.3 (0.2-17.0)^{a}	2.9 (0.1-11.6)^{b}	5.9 (0.7-40.9)^{a}	2.9 (0.4-11.6)^{b}	36.6**
SO_3	2.3 (1.1-4.0)^{a}	1.8 (0.1-13.5)^{a}	3.8 (0.8-14.0)^{a}	2.5 (0.3-11.1)^{a}	9.5*
Cl_2O	1.4 (0.3-1.8)^{a}	0.2 (0.02-0.42)^{a}	10.8 (3.1-22.5)^{b}	7.3 (0.3-36.0)^{b}	19.8**
SiO_2	2.7 (0.4-27.4)^{a}	20.1 (2.8-57.2)^{a}	4.2 (0.3-30.5)^{a}	50.7 (16.2-93.3)^{b}	114.7**
Al_2O_3	1.1 (0.1-11.1)^{a}	4.1 (0.4-14.7)^{b}	0.3 (0.1-3.8)^{c}	0.8 (0.1-4.4)^{ac}	50.3**
Fe_2O_3	0.5 (0.2-2.9)^{a}	2.1 (0.4-9.3)^{b}	0.3 (0.1-51)^{ac}	0.7 (0.1-7.1)^{ac}	42.9**
Na_2O	0.9 (0.1-3.1)^{a}	0.8 (0.2-23.5)^{a}	0.4 (0.1-6.8)^{a}	0.5 (0.1-10.5)^{a}	7.6
TiO_2	0.1 (0.1-0.3)^{a}	0.3 (0.1-1.2)^{b}	0.1 (0.1-0.7)^{ab}	0.1 (0.1-0.2)^{a}	29.1**
Ash content	1.6 (0.3-4.6)^{a}	1.0 (0.1-5.2)^{a}	8.8 (2.9-12.9)^{b}	5.2 (2.7-22.1)^{b}	78.7**

Table 3. Calculated trace metal concentration in the different biomass feedstocks estimated from the concentrations in the ash samples and the ash content (µg trace metal per g dry weight biomass).

Item	Mean trace metal concentration in biomass (µg/g)				Literature values
	Hardwood [a]	Softwood	Eudicot straw	Grass straw	(µg/g)
Cu	1.7	11	7.4	4.9	5-20 [b]
Pb	2.6	1.5	0.40	2.1	0.01-3.85 [b, c]
Cd	0.19	0.05	0.005	0.02	<1 [b, d]

[a] Note: Trace metal concentrations are only reported for 2 hardwood ash samples within the dataset.
[b] Jung [41]
[c] Fergusson [40]
[d] Adriano [39]

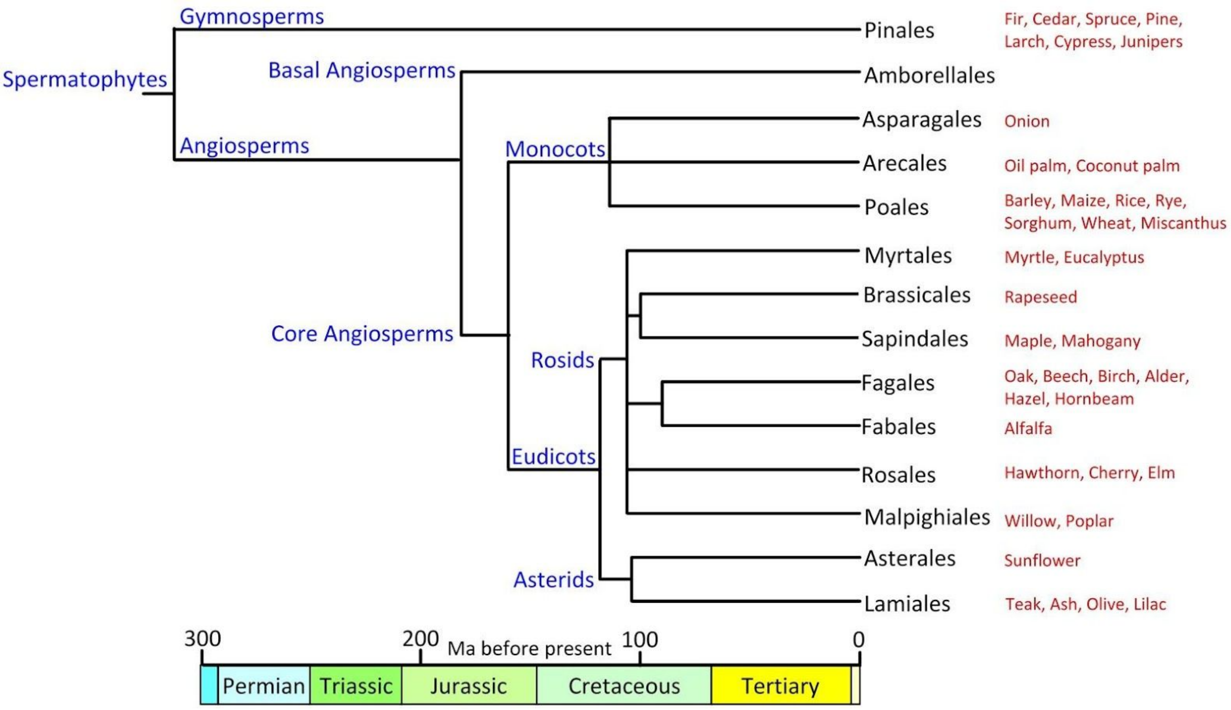

Fig. 1. Approximate phylogeny of spermatophytes (seed plants) determined using TimeTree[14, 62]. TimeTree estimates phylogenetic relationships and species divergence times from the synthesis of all available molecular clock analyses [63]. Potential biomass fuels are shown next to the order to which they belong.

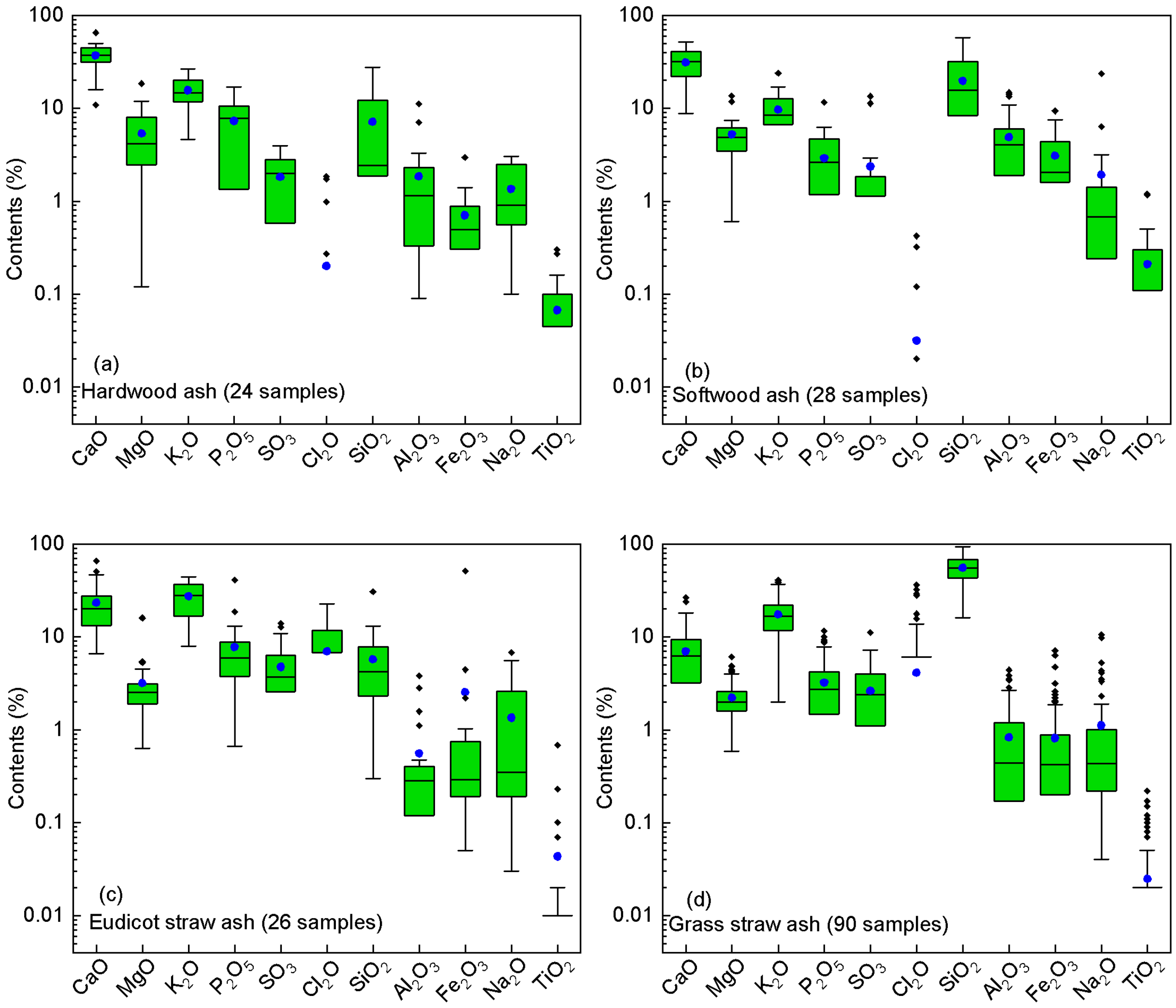

Fig. 2. Chemical composition of ashes derived from different types of biomass (shaded boxes show the median values and interquartile range; tails indicate 1.5 x IQR; · mean value; ♦ outliers).

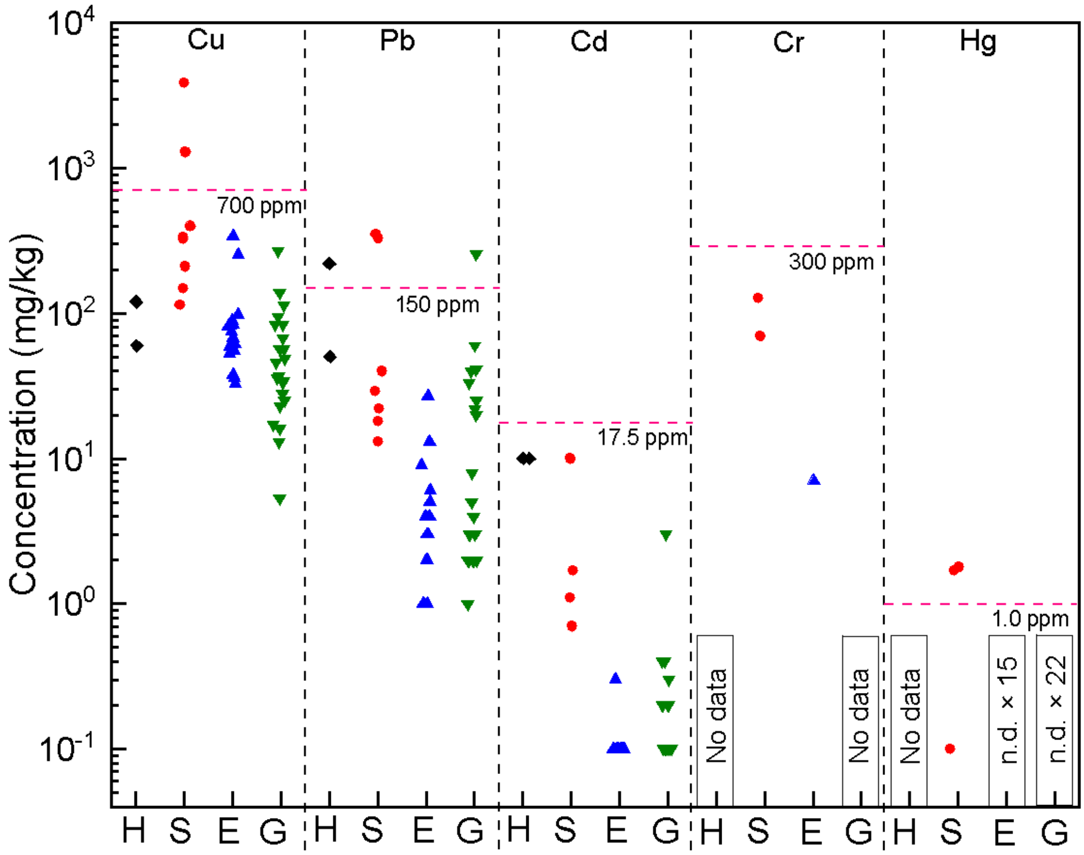

Fig. 3. Contaminant trace metal concentrations in four different biomass ashes (n.d. x n – not detected in n samples; pink dotted line – Finnish limits for ash to be used as a forest fertiliser [5]; H – hardwood ash; S – softwood ash; E – eudicot straw ash; G – grasses straw ash).

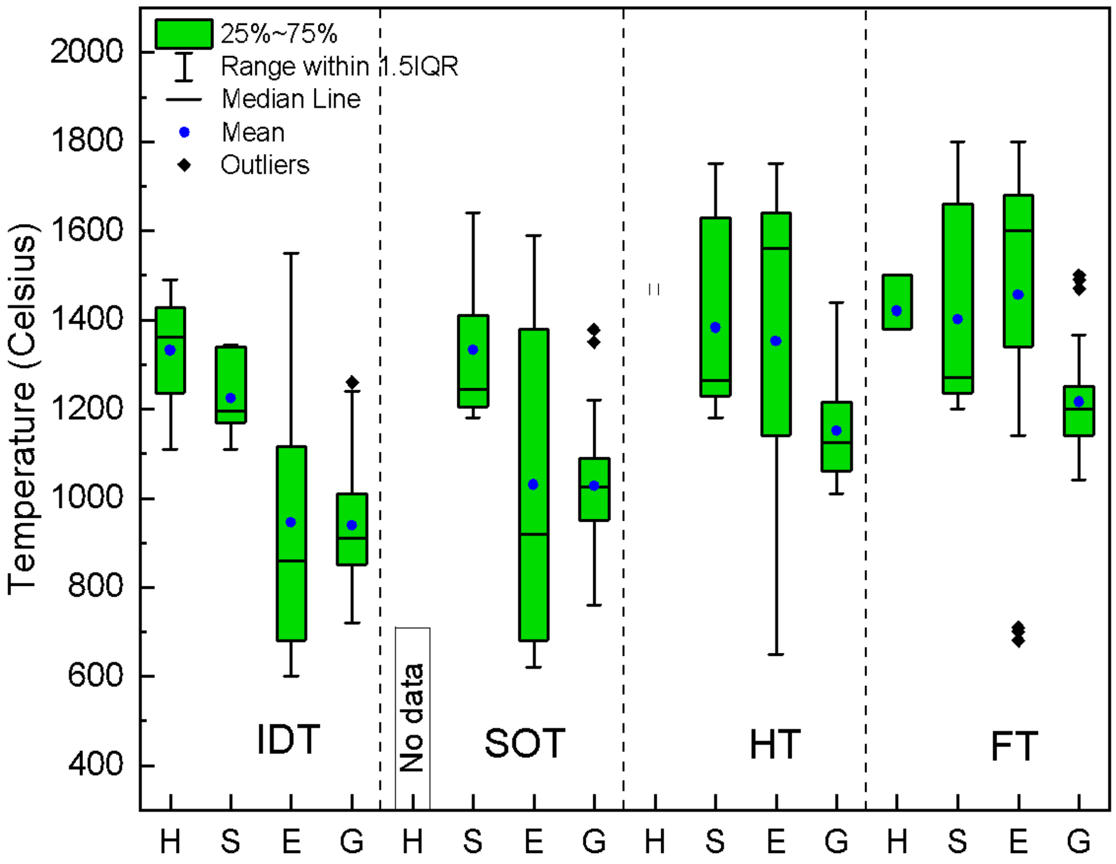

Fig. 4. Variation in the initial deformation temperature (IDT), softening temperature (SOT), hemispherical temperature (HT) and fluid temperature (FT) of ashes derived from different types of biomass (H – hardwood ash; S – softwood ash; E – eudicot straw ash; G – grasses straw ash).

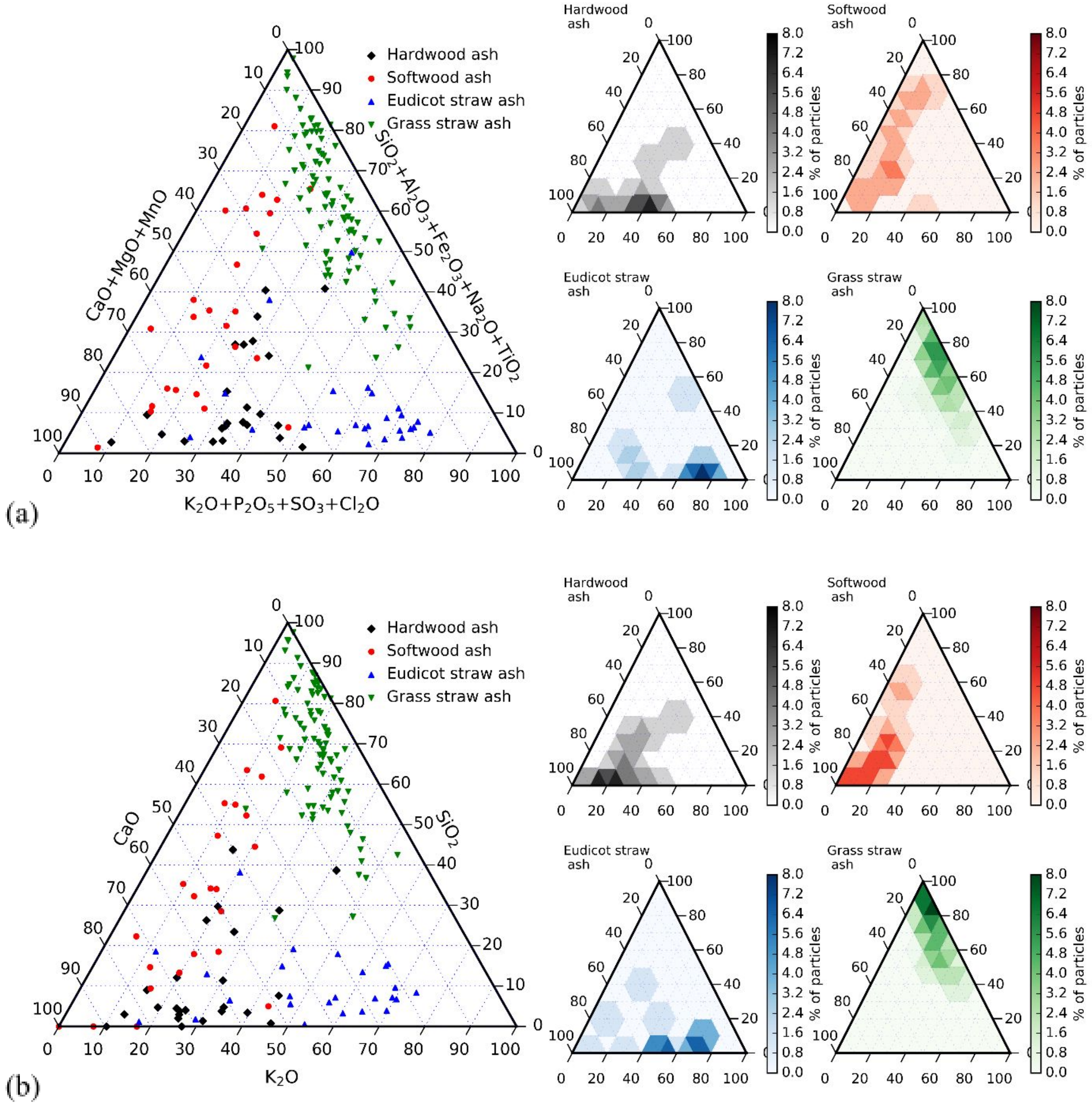

Fig. 5. Ternary diagrams for the classification of biomass ash based on inorganic constituents: (a) Using (CaO+MgO+MnO), ($K_2O+P_2O_5+SO_3+Cl_2O$) and ($SiO_2+Al_2O_3+Fe_2O_3+Na_2O+TiO_2$) as the end members [36] and (b) using CaO, K_2O and SiO_2 as the end members. Note: The Mn concentration is rarely reported in the Phyllis2 database, so is assumed to be negligible when plotting (a). The main ternary diagrams plot the chemical composition of all the ash samples, while the smaller graphs contain interpolated heat maps showing the percentage of samples for each ash category within each compositional bin.