

SEQUENTIAL LEACHING ANALYSIS TO INVESTIGATE THE SINTERING PROCESS OF COAL, CEREAL PELLETS AND WOOD PELLETS ASH

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The presence of inorganic elements in solid fuels is not only considered a direct source of problems in the furnace but is also connected with the release of pollutants into air during combustion. This article focuses on the sintering characteristics of biomass and coal ashes, in particular on the leaching processes, and their impact on the tendency to sinter ash. Biomass and coal ash with high alkali metal concentration can deposit in boiler sections and cause severe operating problems such as slagging, fouling and corrosion of boiler and heat exchanger surface, limiting heat transfer. Two biomass types and one coal ash with different origin and different chemical compositions were investigated. A sequential leaching analysis was employed in this study to elucidate the modes of occurrence of metals that can transform into fuel extract. Sequential leaching analysis was conducted as a two-step process: using distilled water in the first step and acetic acid in the second step. The chemical composition of ashes, before and after each step of the leaching process was studied using ICP-OES method. The standard Ash Fusion Temperature (AFTs) technique was also employed to assess the sintering tendency of the tested samples. It was observed that the presence of key elements such as sodium, potassium, magnesium and sulphur (elucidated in the leaching process) plays a significant role in sintering process. The sintering tendency enhances when the concentration of these elements increases.

Keywords: coal, biomass, leaching, ash fusion behaviour

1. INTRODUCTION

The presence of inorganic elements in fuels can cause serious operational problems such as slagging, fouling and corrosion in boiler parts. Moreover, ash residue generated by solid fuel-based power generation represents a severe environmental hazard. The technique to treat raw coal in order to obtain coal-derived extracts was first reported by Renganathan et al. (1988). Since then, this technology has developed significantly but the extent to which inorganic elements are leached depends upon various factors as studied by Kalembkiewicz and Sitarz-Palczak (2015), e.g. the concentration in ash, the mode of occurrence and the combustion conditions. Therefore, as indicated by Izquierdo and Querol (2012) it is currently considered that as a general rule there is no direct correlation. Different researchers have suggested diverse leaching methods, and this flexibility by Tiwari et al. (2015) is precisely what allows to develop tailoring approaches to specific site or material conditions. Understating fuel mineral matter transformation under thermal treatment is the key question for environmental efficient power plants and so the motives underlying the mobility of an element would be an asset for better control over environmental impacts. Nevertheless, the organometallic chemistry in coal matrix is much more complicated. The ion-exchangeable cations

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are those soluble in a weak acid like acetic acid and removing them prior to coal extraction influences their elution. As reported by Sakanishi et al. (2004) and Wang et al. (2005) some elements were slightly reduced while some were not affected. No attempt has been made to elucidate the chemical forms of the acetic acid-insoluble metals in coal extracts. Some metals (especially transition metals) can exist as organometallic complex such as metalloporphyrin or its derivatives in coal as reported by Bonnett and Czechowski (1987); Callot et al. (1990); Richaud et al. (2000). Metalloporphyrins are believed to originate from coal precursors including heme and chlorophylls of the biological deposits that have transition metals as the nutrients for their growth. In such a configuration, a metal is bound with nitrogen-containing functional groups to form a formula like $C_{32}H_{36}N_4Fe$ reported by Bonnett and Burke (1985) or presents as a complicated structure formed during coalification, which according to Zhang et al. (2008) can be intimately associated with oxygen and/or nitrogen-containing organic macromolecules. Da Silva et al. (2018) proposed a comprehensive characterization of metal concentrations in coal combustion residues to minimise potential adverse impacts on the environment. But for an individual metal in coal extract, its content is in the order of hundreds of parts per million (milligrams per kilogram) or much less, which is too low to be measured by the conventional instruments like X-ray diffraction, SEM or even Mossbauer spectrometer.

Bearing the above considerations in mind, an indirect method was employed in this study to elucidate the modes of occurrence of metals that can be transformed into a coal extract. During the combustion process of biofuels ash depositional problems also arise from a complex physical and chemical transformations among the fuel elements at elevated temperatures. The behaviour of ashes in the system is highly dependent on fuel and slagging and fouling phenomena may be intensified by the relative concentrations of certain key elements, especially alkali and alkali earth metals in combination with silica, chlorine and sulphur (Jenkins et al., 1997). Recent studies by Yaxin et al. (2017) have focused on alkali metal (Ca, Na) removal or their leaching dynamic behaviour as published by Chuan et al. (2017).

Nunes et al. (2016) described plants that are harvested several times a year, such as cereals, which in general exhibit severe slagging and fouling behaviour compared to wood fuels in most thermal systems. Several authors in different years (Arvelakis et al., 2005; Fernandez Llorente et al., 2008; Skrifvars et al., 1998; Steenari and Lindqvist, 1998; Van Dyk and Keyser, 2014) established that due to the dynamic flow of nutrients within the earth, they usually contain large quantities of oxides with low melting points, K and P. In addition, they also contain substantially lower levels of heavy metals.

Considering that the fusion temperature is correlated with the chemical composition of the fuel and the fuel ashes, the purpose of this paper is to investigate and compare the sintering tendency of coal, cereal pellets and wood pellets and to determine which inorganic elements significantly affect Ash Fusion Temperatures (AFT).

2. MATERIALS AND METHODS

Three different fuels were used in this study to investigate the sintering tendency using sequential leaching: (1) hard coal, (2) cereal pellet and (3) wood pellet. The proximate and ultimate analyses of each sample are shown in Table 1.

The experimental approach is based on a combination of standard analysis and chemical fractionation (leaching) in order to predict behaviour of inorganic compounds of fuels. The ash chemical analysis was made using inductively coupled plasma optical emission spectroscopy ICP-OES method by iCAP 6500 Duo ICP. Chemical fractionation was an indirect method chosen to elucidate the modes of occurrence of metals that can transform into coal extract. The leaching methodology employed in this study involved

Table 1. Proximate and ultimate analysis

	(1) Coal	(2) Cereal Pellet	(3) Wood Pellet
Proximate analysis, wt% dried			
Volatile matter	32.8	81.23	81.98
Fixed carbon	54.13	16.41	16.68
Ash	13.07	2.36	1.34
Ultimate analysis, wt% daf			
C	86.8	49.76	55.29
H	5.67	7.27	6.90
N	1.66	2.23	0.43
S	0.71	0.16	0.05
O*	5.15	40.58	37.33

a sequential water and acid leaching prior to sample extraction. Raw samples were initially leached by distilled water using solid to liquid ratio of 1:5 (water-soluble metal salts were removed) and subsequently by acetic acid (ion-exchangeable cations were removed). Each leaching was carried out by stirring mixtures of samples with water and acid for 24h under ambient conditions. Then, approximately half of the residual solid was removed, vacuum-dried, and saved for further experiments (Zhang et al., 2008). ICP-OES was used to determine concentrations of the elements in raw ash samples and also in residues after each leaching stage.

Traditionally, the characterisation of coal ash for its tendency to slag has been directly related to its bulk chemistry and ash fusion temperatures (Gupta, 1998; Van Dyk and Keyser, 2014). In this study, the standard Ash Fusion Test AFT was performed on both raw and leached samples according to PN-ISO-540 standard. The AFT test supplies four temperatures which describes the softening and melting behaviour of ash when it is heated: deformation temperature (DT), spherical temperature (ST), hemispherical temperature (HT), and fluid temperature (FT) (Vassilev et al., 2010). The characteristic temperatures of the samples were compared to investigate the correlation between ash composition and their AFTs before and after leaching.

3. RESULTS AND DISCUSSIONS

The ultimate analysis (ICP-OES) results of the coal sample after each leaching stage are shown in Table 2. Taking into account that the concentration of TiO₂ is very low (about 0.06–0.08%) and therefore, to avoid the introduction of a large calculation error, SiO₂ was assumed to be not leachable by water and acetic acid, and results obtained during sequential leaching were normalized with respect to SiO₂, according to Eq. (1). SiO₂ was chosen as the leading element after recalculating the results for the three main elements; Si, Al, and Fe and obtaining convergent results of around 2–3%. Consequently, Tables 3 and 4 show the ultimate properties of cereal pellet and wood pellet, respectively.

$$\text{normalized} \left(\text{MeO}_{L1 \text{ or } L2}^{\text{wt}\%} \right) = \text{MeO}_{L1 \text{ or } L2}^{\text{wt}\%} \cdot \frac{\text{SiO}_2 (\text{row_fuel})}{\text{SiO}_2 (L1 \text{ or } L2)} \quad (1)$$

Regarding the ultimate properties of each sample, different quantities of the species containing a certain metal are present, which were recalculated and presented as metal content in the ash in Fig. 1.

Table 2. Ultimate Properties of coal ash

wt%	From ICP-OES			Normalized to SiO ₂			Normalized to 100%		
	Raw	L1	L2	Raw	L1	L2	Raw	L1	L2
SiO ₂	48.9	51.6	54.6	48.9	48.90	48.90	50.53	50.53	50.53
Al ₂ O ₃	25.4	27.2	28.1	25.4	25.78	25.17	26.25	26.63	26.00
TiO ₂	0.08	0.08	0.06	0.08	0.08	0.05	0.08	0.08	0.06
Fe ₂ O ₃	5.67	5.94	6.05	5.67	5.63	5.42	5.86	5.82	5.60
CaO	3.65	2.54	0.53	3.65	2.41	0.47	3.77	2.49	0.49
MgO	2.57	2.17	1.26	2.57	2.06	1.13	2.66	2.12	1.17
SO ₃	3.57	0.95	0.19	3.57	0.90	0.17	3.69	0.93	0.18
Na ₂ O	0.98	1.01	0.89	0.98	0.96	0.80	1.01	0.99	0.82
K ₂ O	2.79	2.9	2.93	2.79	2.75	2.62	2.88	2.84	2.71
P ₂ O ₅	0.6	0.66	0.61	0.6	0.63	0.55	0.62	0.65	0.56
Mn ₃ O ₄	1.06	1.12	1.18	1.06	1.06	1.06	1.10	1.10	1.09
BaO	0.14	0.16	0.17	0.14	0.15	0.15	0.14	0.16	0.16
SrO	0.07	0.06	0.03	0.07	0.06	0.03	0.07	0.06	0.03
Cl	0.04	0.05	0.08	0.04	0.05	0.07	0.04	0.05	0.07
CO ₂	1.26	1.22	0.03	1.26	1.16	0.03	1.30	1.19	0.03

Table 3. Ultimate Properties of cereal pellet ash

wt%	From ICP-OES			Normalized to SiO ₂			Normalized to 100%		
	Raw	L1	L2	Raw	L1	L2	Raw	L1	L2
SiO ₂	22.6	29.9	36	22.6	22.60	22.60	23.06	23.06	23.06
Al ₂ O ₃	0.88	1.18	1.46	0.88	0.89	0.92	0.90	0.91	0.94
TiO ₂	0.11	0.14	0.21	0.11	0.11	0.13	0.11	0.11	0.13
Fe ₂ O ₃	8.2	11.2	13.4	8.2	8.47	8.41	8.37	8.64	8.58
CaO	3.04	3.76	3.25	3.04	2.84	2.04	3.10	2.90	2.08
MgO	7.87	8.85	7.56	7.87	6.69	4.75	8.03	6.83	4.84
SO ₃	3.42	0.29	0.26	3.42	0.22	0.16	3.49	0.22	0.17
Na ₂ O	0.51	0.29	0.13	0.51	0.22	0.08	0.52	0.22	0.08
K ₂ O	21	13.3	4.37	21	10.05	2.74	21.43	10.26	2.80
P ₂ O ₅	30.2	28.6	25.1	30.2	21.62	15.76	30.82	22.06	16.08
Mn ₃ O ₄	0.04	0.06	0.07	0.04	0.05	0.04	0.04	0.05	0.04
BaO	0.01	0.02	0.02	0.01	0.02	0.01	0.01	0.02	0.01
SrO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Cl	0.08	0.11	0.07	0.08	0.08	0.04	0.08	0.08	0.04
CO ₂	0.03	0.03	0.17	0.03	0.02	0.11	0.03	0.02	0.11

Table 4. Ultimate Properties of wood pellet ash

wt%	From ICP-OES			Normalized to SiO ₂			Normalized to 100%		
	Raw	L1	L2	Raw	L1	L2	Raw	L1	L2
SiO ₂	21.5	23.8	36.1	21.5	21.50	21.50	24.51	24.51	24.51
Al ₂ O ₃	2.34	2.5	3.93	2.34	2.26	2.34	2.67	2.57	2.67
TiO ₂	0.65	0.74	0.52	0.65	0.67	0.31	0.74	0.76	0.35
Fe ₂ O ₃	14.9	16.3	24.4	14.9	14.72	14.53	16.99	16.79	16.57
CaO	17.3	19	5.88	17.3	17.16	3.50	19.72	19.57	3.99
MgO	4.06	4.52	1.22	4.06	4.08	0.73	4.63	4.66	0.83
SO ₃	4.29	0.83	0.68	4.29	0.75	0.40	4.89	0.85	0.46
Na ₂ O	0.28	0.22	0.32	0.28	0.20	0.19	0.32	0.23	0.22
K ₂ O	7.8	3.4	1.34	7.8	3.07	0.80	8.89	3.50	0.91
P ₂ O ₅	6.39	7.33	7.81	6.39	6.62	4.65	7.29	7.55	5.30
Mn ₃ O ₄	0.12	0.14	0.22	0.12	0.13	0.13	0.14	0.14	0.15
BaO	0.04	0.04	0.06	0.04	0.04	0.04	0.05	0.04	0.04
SrO	0.04	0.04	0.02	0.04	0.04	0.01	0.05	0.04	0.01
Cl	0.41	0.09	0.17	0.41	0.08	0.10	0.47	0.09	0.12
CO ₂	7.59	11	0.06	7.59	9.94	0.04	8.65	11.33	0.04

It should be underline that ash is a heterogeneous material and the elements are not evenly distributed throughout. That is why the extent to which a particular ash component is leached depends upon the concentration in ash, the mode of occurrence and the possible reactions in the ash system involving the component. A common feature for all fuels is the sharp decrease of sulphur content on water washed ash samples, which is consistent with previous studies appointing sulphur as the major soluble element in ash due to its dominant surface association and the marked solubility of most sulphate-bearing compounds (Izquierdo and Querol, 2012).

Potassium and sodium are also quantitatively removed by water leaching from biomass, considering that these ash forming species are predominantly present in organic molecules and as ions dissolved in the cell fluid (Steenaria et al., 1999). In the case of coal, major cations (Ca, Mg, K, Na, Si, Al and Fe) present in the ash content belong to well-defined minerals such as kaolinite, quartz, calcite and pyrite. Elements remaining in washed coal include aluminosilicates and organometals encased completely in the coal matrix. The small content difference after leaching could be related to a small part of the inorganic matter present in the form of ions associated with the organic matrix.

The alkali metals eluted in each sample, calculated as percentage changes with respect to raw fuel and first step of leaching respectively, are shown in Fig. 2.

In coal, a large amount of S (75 wt%), Ca (34 wt%) and Mg (20 wt%) can be attributed to their water soluble fractions associated with the salts; calcium and magnesium sulphates. In contrast, only very small fractions of Na (2 wt%), Fe (1 wt%) and K (1 wt%) exist in the water soluble forms. In the coal water insoluble fraction there is also a large amount of S (81 wt%) and Ca (80 wt%), which can be attributed to their acetic acid soluble fractions in which metal can be assigned as their ion-exchangeable fractions. Mg, Na and K also exist in the acetic acid soluble forms at smaller fractions. In both biomass samples, leaching with water removes large fractions of alkali metals (> 50% of potassium and > 30% of sodium)

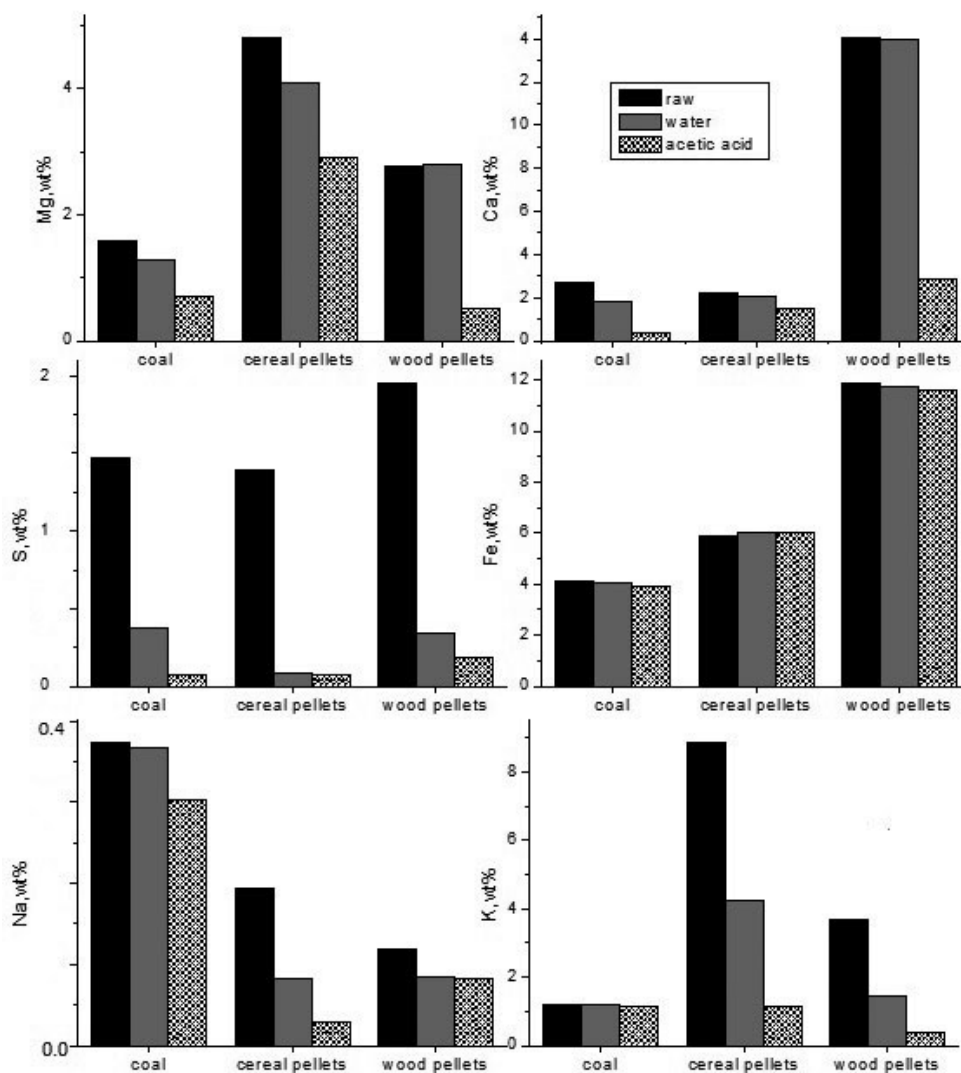


Fig. 1. Content variation of Na, K, Mg, Ca, S and Fe

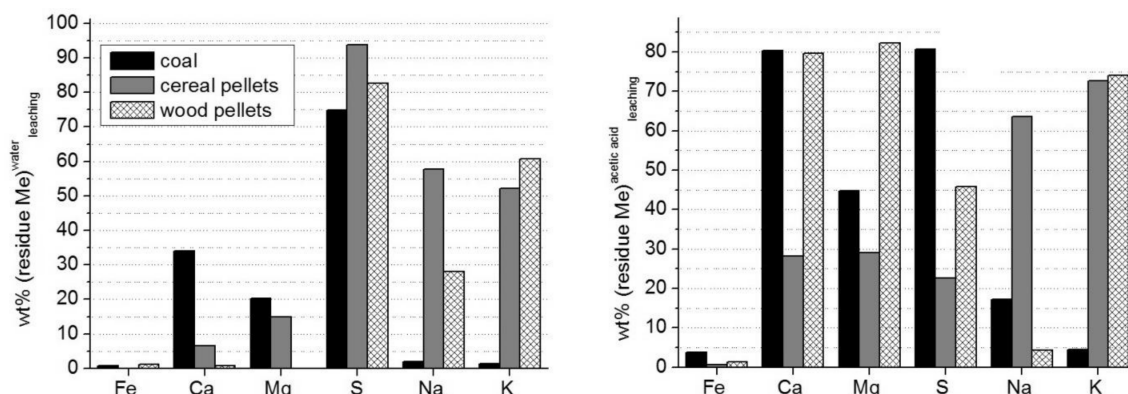


Fig. 2. Percentages of eluted elements

thus mitigating the undesirable ash fouling and slagging in combustion systems. In cereal pellets also S (94 wt%) and smaller proportions of Mg and Ca are water eluted. Contrarily, in wood pellet, Mg, Ca and Fe exist in the water insoluble form. Regarding their water insoluble fractions, large amounts of K, S, Mg and Ca exist in the acetic acid soluble forms. Na, Ca, Mg and S demonstrate an enormous discrepancy between samples. In both cases, the percentage of Fe eluted in acetic acid is smaller than 2%, indicating that Fe cannot be assigned as their ion-exchangeable fractions.

Most strikingly, Fe is the most prevalent species for coal, cereal pellets and wood pellets. In the case of the biomass samples, it can have an organic association with coal functional groups in the organic compounds which are insoluble in the acetic acid. In coal, Fe can be embedded in fine alumina-silicates particles. The latter case is probably for Fe considering the fact that the concentration of Fe in the washed coal is comparable with that of Al. In coal, a relatively large fraction of K and a slightly smaller fraction of Na can be embedded in fine alumino-silicates particles. The difference (about 1 wt%) indicates the amounts of ion-exchangeable cations in the coal. In cereal pellets, a relatively large fraction of Ca and Mg exists in an insoluble form. Probably Ca and Mg have an organic association with coal functional groups that are insoluble in the acetic acid.

The effect of sequential leaching on sintering temperature was studied by means of the standard ash fusibility temperature (AFT) test. Both physical properties such as the homogeneous/heterogeneous nature and ash chemistry affect measurement (Liu et al., 2007; 2013) although this study has been performed with specific focus on the effect of inorganic elements in coal and biomass ash. Three different key stages in the deformation and flow of samples were compared: DT – the temperature at which the first signs of rounding of the edges occur; HT – the temperature at which height becomes approximately half of the base diameter such that the test piece forms a hemisphere; and FT – the temperature at which the height of the melting ash layer becomes approximately half the height at the hemisphere temperature. Figure 3 illustrates the fusing temperatures obtained for all the raw samples and the samples after sequential leaching.

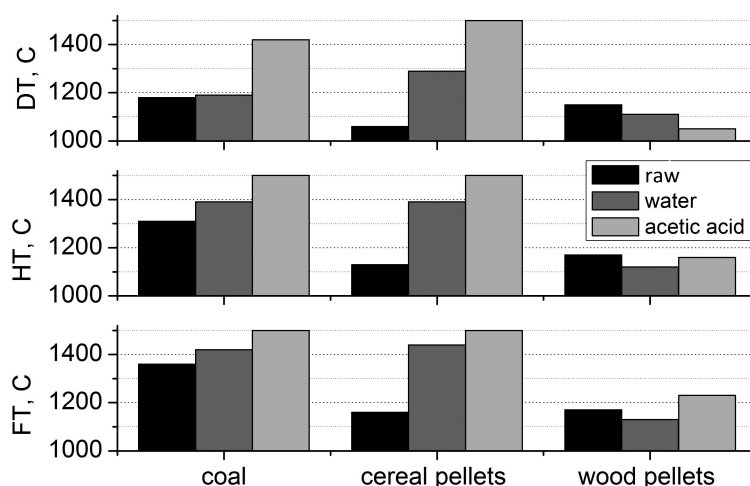


Fig. 3. DT, HT and FT temperatures for all samples in the sequential leaching procedure

AFT temperatures vary significantly between fuel types and fuel content. As reported by Vassilev et al. (2013) the AFTs of biomass ashes vary over larger intervals than the values of coal ashes. Considering the mean HT temperature, the value decreases in the order as follows: bituminous coal > wood and woody biomass > sub-bituminous coal > contaminated biomass > lignite > herbaceous and agricultural biomass. In this study HT normally has a lower value in biomass ashes than in coal ash.

For coal and cereal pellets, all characteristic temperatures behave qualitatively the same: raw samples have the lowest values while samples after acetic acid leaching present the highest values. On the other hand, this relation does not apply to the wood pellet sample given that the sample after water leaching displays lower values than the raw sample. Certainly, the AFTs of biomass are more variable than those of coal. Probably the reason for this fact is a very low ability of Ca and Mg to elute water, suggesting the existence of these metals in the form of salts dissolved from the soil water and solved from the acetic acid.

Correlations between characteristic temperatures and content of Na, K, Fe, Ca, Mg and S in raw samples and samples after water and acetic acid elution are shown in Figs. 4–6.

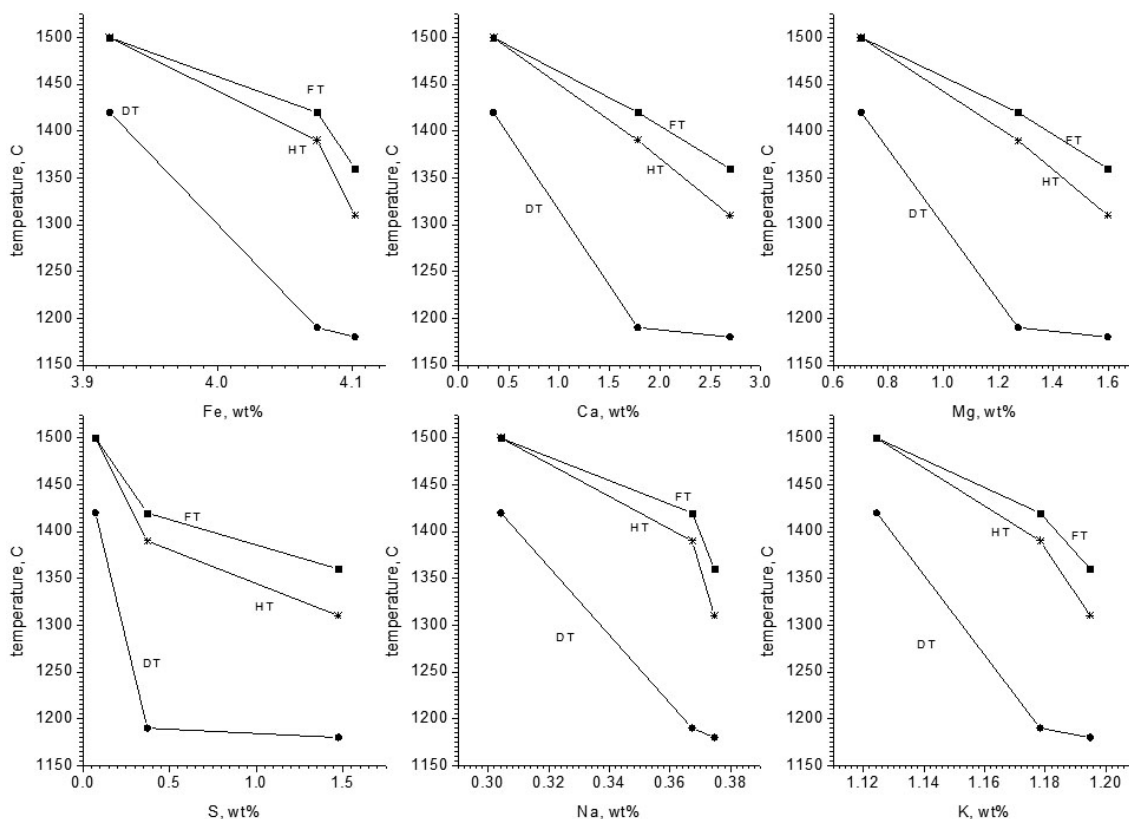


Fig. 4. AFT temperatures of raw, water eluted and acetic acid eluted coal ash

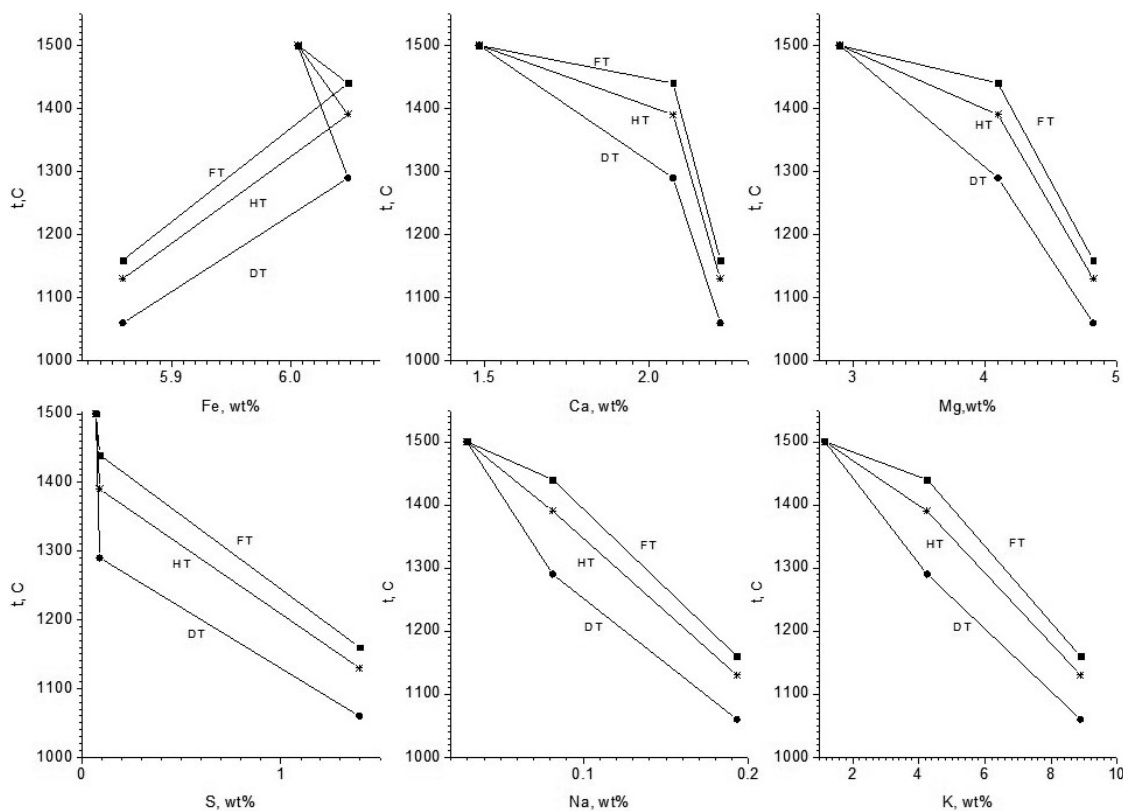


Fig. 5. AFT temperatures of raw, water eluted and acetic acid eluted cereal pellets ash

Iron is commonly found both in coal and biomass ash but its effect on the melting behaviour lies to a great extent in its valence. The decrease of the AFTs is caused by the increase in FeO, rather than Fe₂O₃

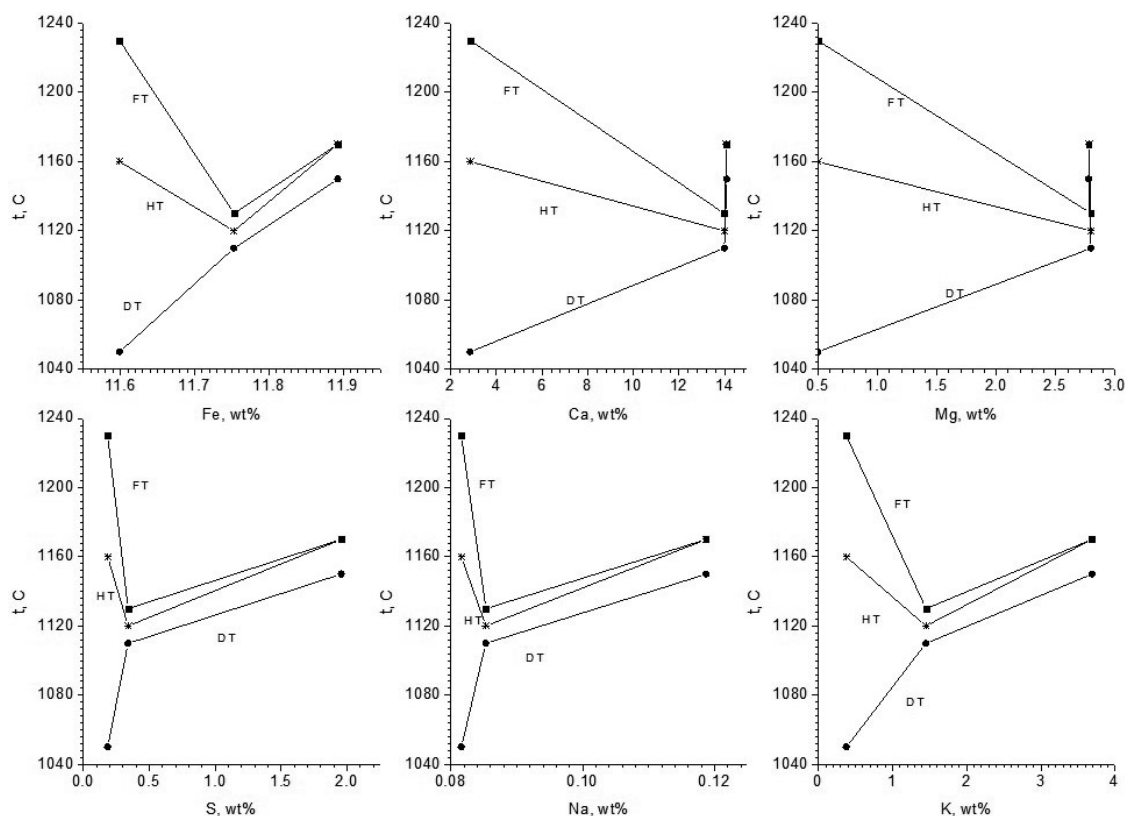


Fig. 6. AFT temperatures of raw, water eluted and acetic acid eluted wood pellets ash

(Liu B et al., 2013) as FeO most likely forms eutectic compounds with other oxides at high temperatures. Another example is found in the effect of calcium. CaO is a fluxing agent which is commonly used to reduce the AFTs of coal ashes. As shown in Fig. 4, the AFTs of all ash samples dropped as the content of Ca increased. The effect of potassium and magnesium on fusibility behaviour of the tested ashes reported similar results. The probable reasons might be the fact that those compounds could form eutectic with other minerals at high temperature, thus decreasing the AFTs. Overall, the major processes responsible for the characteristic ash fusion temperatures seem to be similar for both biomass and coal ashes (Vassilev et al., 2010) as the melting temperatures are mainly dependent on chemical composition, especially the mineral matters containing much more alkali metals compared to coal ash.

4. CONCLUSIONS

On the basis of the results obtained it can be concluded that:

- Biomass ash contains many elements (Na, K, Mg, P, S, Ca, Cl) that increase exploitation hazards, especially in co-combustion process.
- The high content of alkali metals is responsible for the reduction of ash sintering temperatures – leaching of such elements makes AFT temperatures rise.
- The presented leaching method seems to be a useful method of studying the behaviour of coal and biomass mineral matter transformation and predicting exploitation hazards.
- The deionised water leaching experiment did not remove a significant amount of elements.
- The acetic acid leaching experiment removed a significant amount of elements. However, for leaching unwanted elements it is necessary to use other strong mineral acids.

- AFT test of wood pellets seems to be less unreliable than those of coal because of a very low ability of Ca and Mg to elute water, suggesting the presence of these metals in the form of salts dissolved from soil water and solved from acetic acid.

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