

MINERAL PHASE TRANSFORMATION OF WOOD AND CEREAL PELLETS – ELECTRICAL TEST AND FACTSAGE™ CALCULATIONS

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Abstract: The fusion behaviour of biomass ash-forming materials is an important factor in assessing the propensity to form undesirable slag and fouling deposits in the boiler. The characteristics of the fuel used affect the extent and severity of the problem, thus growing efforts are put on finding reliable methods for its characterization. Combustion and co-combustion of biomass have gained popularity in combating climate change and reducing carbon dioxide emissions into the atmosphere. Nevertheless, biomass encompasses a wide range of different types and its use increases operational risks due to the diversity of the chemical composition. This study is based on characterising the mineral phase transformations of two kinds of biomass (wood pellets and cereal pellets) using various laboratory-based methods on fuel ashes. Measurements of changes in the electrical properties of the ash during the sintering process (dielectric loss factor) were performed using a QuadTech Plus 7600 bridge in the frequency range 500Hz - 1MHz. Thermodynamic analyses were performed by means of FactSage™ modelling. The results were compared with those of standard tests, AFT and oxide index calculations, which were employed to predict slagging and fouling propensities. The observed changes in dielectric loss depend on the frequency and temperature of sintering. FactSage™ thermodynamic equilibrium calculations proved very useful in predicting the ash melting behaviour and the chemical changes occurring in the ash. The existence of a melt phase, occurring at even lower temperatures of those given by the AFT, is in accordance with the high slagging and fouling hazards predicted by empirical indices.

Keywords: biomass, ash, slagging, fouling.

Introduction

In the past decades, numerous investigations have been carried out worldwide to enhance biomass use for energy conversion processes as a replacement for conventional fossil fuels. Biomass has the status of renewable energy and it is widely accepted that its combustion does not contribute to the greenhouse effect and other harmful effects on the environment. Biomass combustion and co-combustion systems not only have been proved CO₂ neutral, but also have achieved low CO-, NO_x- and TOC-emission levels, which are comparable with those of fossil fuel fired systems. However, while increasing the energy production share from biomass it has also increased the need to devise acceptable methods to assess the properties of biomass ash.

Biomass contains various forms of alkali and alkali earth metals (sodium, potassium, magnesium, calcium, etc.), significant amounts of silica and it is also enriched in chlorine and phosphorus [1]. This heterogeneous composition determines mineral transformations and chemical reactions occurring during thermo-chemical conversion and arise major problems for biomass

utilization [2]. Biomass ash easily melts and volatilizes leading to slagging, fouling, erosion and corrosion hazards within the boiler.

The prediction of biomass ash fusion behaviour is a subject of study in numerous research and different laboratory based methods have been used to analyze the propensity of fuels to slag and foul heat transfer surfaces of boilers [3]. Commonly used analytical techniques for fossil fuels have been also extended to biomass fuels, including ash fusion characteristics tests and empirical calculations of elemental oxides ratios. Biomass ash, alike to coal ash, is a multicomponent system of powder material which do not have a specific melting point. But the ash fusion behaviour of different biofuels is a major concern to power plants and so the Ash Fusion Test (AFT) stands as the most commonly used method for evaluating the melting behaviour of any solid fuel [4]. Empirical indices based on ash chemical composition are also widely used to predict the deposit formation and ash slagging/fouling propensity. They were originated for coal fuels although, with the proper modifications, they can also be applied to biomass. Despite these calculations they do not provide any information on the

real behaviour of a fuel during combustion, they are used as preliminary indicators.

Transformation properties of the inorganic ash components and ash fusion characteristics may be also investigated by means of thermodynamic calculations [5]. FactsageTM thermochemical software allows for the calculation and manipulation of phase diagrams and complex phase equilibria. Processes involving mineral matter transformation can be analyzed over a wide range of temperatures, giving insight into specific mineral reactions during combustion processes [6]. Therefore, the limitations of the above mentioned methods to predict ash fusion behaviour in real boilers may be overcome by thermodynamic analysis.

A possible different route to evaluate the biomass ash fusion characteristics may be taken from the ceramic industry as biomass ash is the combination of silica and metal oxides, which in turn, is very similar to the raw materials of conventional silicate ceramics industry [1]. The electrical conductivity method may be used to interpret phase changes during powder sintering [8] as the electrical conductivity is related to the concentration

of metal ions and it depends on the temperature increase [7]. The dielectric properties of selected biomass ash samples as a function of temperature and frequency were measured.

Materials and methods

Materials

Two kinds of biomass feedstock – wood pellets (WP) and cereal pellets (CP) – have been used in this study. The wood pellet sample represents a woody biomass source from forestry and/or forestry residues which have had no chemical treatments or finishes applied. The cereal pellet sample is a typical example of agricultural residue. Both biomass samples have been ashed at 350°C in a muffle furnace for 26 h. The ash elemental composition in terms of the main oxides is given in Tab. 1. WP displays high contents of SiO₂, CaO, Fe₂O₃, and Al₂O₃, whereas CP is characterized by high P₂O₅, SiO₂, K₂O, Fe₂O₃ and MgO contents.

Tab. 1. Chemical composition of selected ash samples (wt %).

	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Mn ₃ O ₄	TiO ₂	CaO	MgO	SO ₃	P ₂ O ₅	Na ₂ O	K ₂ O	BaO	SrO	Cl	CO ₂
WP	21.5	14.9	2.34	0.12	0.65	17.3	4.06	4.29	6.39	0.28	7.8	0.04	0.04	0.41	7.59
CP	22.6	8.2	0.88	0.04	0.11	3.04	7.87	3.42	30.2	0.51	21	0.01	0.01	0.08	0.03

Experimental methods

Ash Fusion Test (AFT)

The ash fusion temperature profile of a coal is one of the parameters widely used to assess ash fusibility and melting characteristics with respect to temperature [3]. It determines the behaviour of biomass ash in the process of biomass combustion by monitoring the changes on a molded ash sample as the temperature increases. The AFT test supplies four temperatures describing the softening and melting behaviour of ash under thermal treatment: initial deformation temperature (IDT), spherical temperature (ST), hemispherical temperature (HT), and fluid temperature (FT).

FactsageTM calculations

The equilibrium calculations, performed by minimization of the total Gibb's free energy for the system, were used to determine thermodynamically stable chemical and physical forms at a set of temperatures ranging from 700°C to 1000°C. By input of the main oxides obtained from the chemical analysis of the ash samples, thermochemical calculations were performed and the liquidus temperatures were established (temperatures at which the solids begin to precipitate and first liquid-slag oxide melt appears in the system).

Dielectrical properties

The electrical experiment was realized by placing the ash sample on an isolated base in Faraday cage to reduce outer interference and connecting it via two electrode system to the electronic precision LCR Meter QuadTech 7600. The tested samples were prepared with the ashes that were obtained in combustion process, pressed to form a cylinder with a diameter equal to 20mm and thickness about a few millimeters. Samples were isothermally heated by 2 hours in a muffle furnace, at temperatures ranging from 500°C up to 1000°C with 100°C step. After the heating process, the samples were cooled to room temperature in a dry atmosphere so the dielectric loss tangent ($\tan \delta$) could be measured in the frequency range 500Hz – 1MHz.

Results and discussion

Based on the ash chemical composition expressed as major oxides found in Tab.1, the following indices were determined. The calculated indices, together with the slagging and fouling tendencies are shown in Tab. 2. The corresponding propensities have been marked as severe (S), high (H), medium (M) and low (L) according to data available in literature [9].

Base to acid ratio:

$$R_{b/a} = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + TiO_2 + Al_2O_3} \quad (1)$$

Base to acid ratio + P:

$$SR = \frac{Fe_2O_3 + CaO + MgO + K_2O + Na_2O}{SiO_2 + TiO_2 + Al_2O_3} \quad (2)$$

Slag viscosity index:

$$SI = \frac{SiO_2}{SiO_2 + Fe_2O_3 + CaO + MgO} \times 100 \quad (3)$$

Iron to calcium ratio:

$$IC = \frac{Fe_2O_3}{CaO} \quad (4)$$

Silica to aluminium ratio:

$$SA = \frac{SiO_2}{Al_2O_3} \quad (5)$$

Fouling index:

$$Fu = R_{b/a} \times (Na_2O + K_2O) \quad (6)$$

Tab. 2. Calculated Oxide Indices of selected samples.

		WP	CP
Oxide Index	$R_{b/a}$	1.81 (S)	1.72 (S)
	SI	2.07 (H)	3.00 (H)
	SR	37.22 (H)	54.18 (H)
	IC	0.86 (H)	2.70 (H)
	SA	9.19 (S)	25.68 (S)
	Fu	14.63 (H)	37.04 (H)

In general, all calculated indices consistently predict high slagging and fouling tendencies. The lower content of alkali (K and Na) of the wood sample explain the main differences between them. Although, traditionally such empirical indices have been used to predict coal deposition tendencies, their applicability on biomass samples show good agreement to one another. Nevertheless, they do not provide a reliable indication on

deposit growth rate on real boilers as they solely depend on chemical composition.

The physical aspects related to deposition mechanisms are better explained by the Ash Fusion Test. Biomass ashes have highly variable chemical and phase-mineral composition and so they display variable AFTs, especially when compared with coal. The four characteristic AFTs of selected samples are shown in Tab. 3.

Tab. 3. AFT characteristic temperatures

		WP	CP
Ash Fusion Test (AFT)	IDT	1070	820
	ST	1150	1060
	HT	1165	1130
	FT	1170	1160

Ash fusibility predictions have been generally achieved using correlations between fusion temperatures and standardized chemical composition of ashes in a base-to-acid ratio ($R_{b/a}$). The alkali earth metals Mg and Ca, the alkali metals K and Na, and Fe are considered the base constituents, lowering the melting temperatures. The acid constituents are Si, Al and Ti and their presence normally contribute to increase the ash melting point [10]. The correlation of ash fusibility temperature with ash composition is depicted in Fig. 1.

The flow temperature (FT) is generally considered as an important parameter in power industry. In order to avoid ash deposition hazards, operating temperature should be above it. However, it is important to note that normal AFT analysis provide an average flow property and do

not indicate exactly at what temperature the first melt/sinter occurs. Therefore, thermochemical modeling can assist in identifying and quantifying slag formation at temperatures not reflected by normal AFT analyses. The formation of the liquid and solid phases is directly related to the composition and the temperature stability ranges of the phases involved. FactSage™ equilibrium calculations were performed to simulate slag-liquid formation during a typical combustion process based on biomass ash chemical composition. The models presented below (Figs. 2-3) assist to correlate slag flow temperature simulation with actual measured ash flow temperatures (FT).

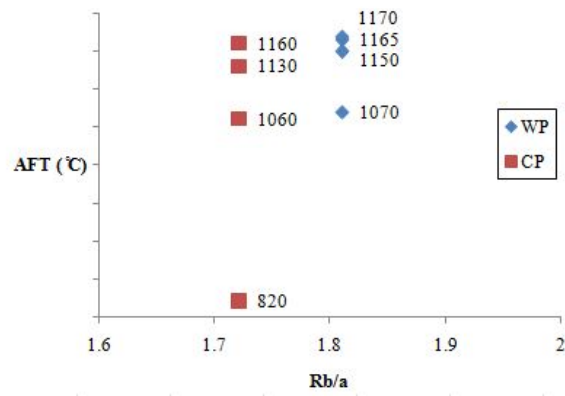


Fig. 1. Correlation of AFTs with $R_{b/a}$.

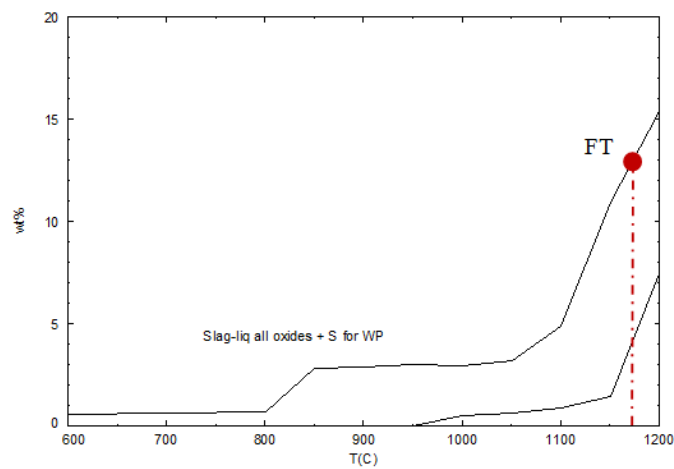


Fig. 2. WP Ash sample slag-liquid phase.

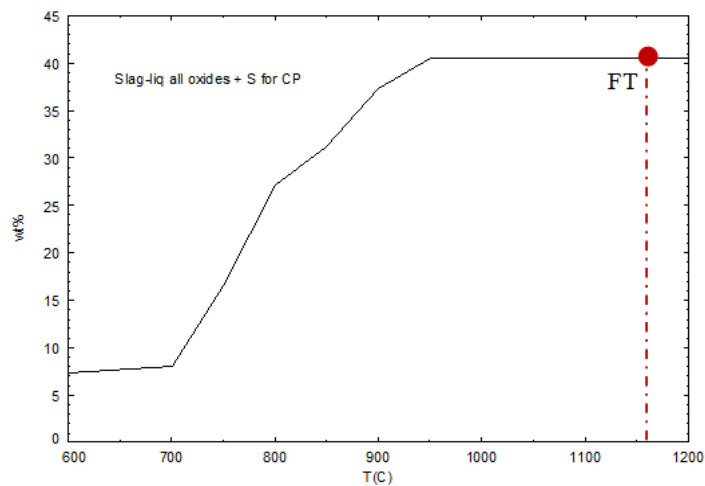


Fig. 3. CP Ash sample slag-liquid phase.

The thermodynamic equilibrium predictions illustrate the presence of a liquid phase even at temperatures lower than 600°C for both kinds of samples. However, the

amount of liquid slag differs and shows different trends while increasing temperature. For WP ash sample, it remains constant until 800°C, slightly increases until

850°C and then becomes stable again with a sharp increase at around 1100°C. Up to this temperature, it could be considered as a window for operation at significant lower temperatures than those proposed by the AFT analysis. For CP ash sample, the amount of liquid slag sharply increases from about 700°C and it remains fairly constant from about 950°C. The operation temperature requirement of calculated AFTs expressed as flow temperature (FT) is in agreement with

the thermodynamic model for the cereal pellet ash sample. Although, it can be observed than in the case of the wood pellet ash sample, the amount of slag liquid formation continues to increase above the FT temperature. The mass fraction of slag formed at each characteristic temperature of the AFT test is summarized in tab. 4. The slag formation trend with increasing temperature is graphically shown in Fig. 4.

Tab. 4. Mass fraction of slag formed at AFT characteristic temperatures.

		WP		CP	
		T [°C]	Slag wt [%]	T [°C]	Slag wt [%]
AFTs	IDT	1070	4.6	820	28.5
	ST	1150	12.5	1060	40.5
	HT	1165	15.6	1130	40.5
	FT	1170	16.6	1160	40.5

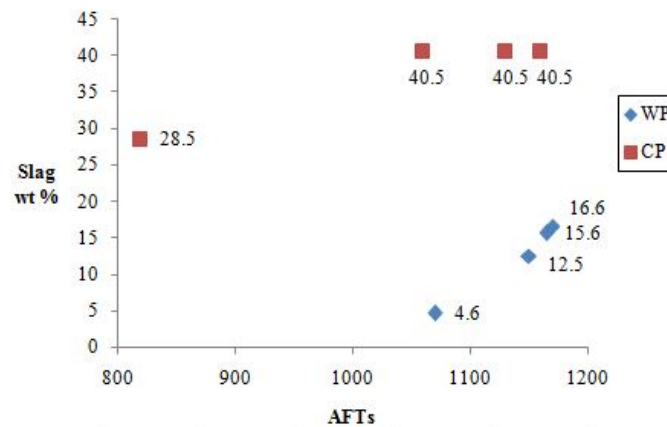


Fig. 4. Correlation of AFTs with Slag wt %.

Figs. 5-6 represents the proportion of major oxides in the slag phase with respect to temperature. The presence of alkali and alkali earth metals is notorious in both systems. Together with K_2O and Si_2O , containing species form the major portion of the slag for both kind of biomasses.

When ash-forming constituents are subjected to high temperatures, a number of mineral transformation reactions occur. These reactions are particularly important as they are responsible for the nature of the ash deposits on boiler surfaces and the nature of ash residue.

For WP ash sample, all major oxides present in the slag phase increase in weight percent up to 800°C and remain fairly constant until 1000°C. At higher temperatures the chemical compounds become more thermally active phases and therefore exhibit quite different behaviours.

The main transformations observed correspond with solid-solid phase transitions (as is the case of $CaMgSi_2O_6$ and $Ca_3(PO_4)_2$) or solid-liquid phase transitions undertaken by the mineral form of potassium sulphate (K_2SO_4). Complex silicate minerals as andradite ($Ca_3Fe_2Si_3O_{12}$) are also present in the system but decrease in mass fraction while increasing temperature. The contrary occurs with iron oxide (Fe_2O_3), which increases in the system in detriment of other compounds. The presence of gas phases (CO_2) can be also observed although, they seem not to be affected by the temperature rise and the mass fraction remains stable at about 6%. Both calcium and iron are considered fluxing elements affecting ash viscosity, therefore the high presence in the system in combination with other elements will ultimately determine the slagging characteristic of the biomass fuel.

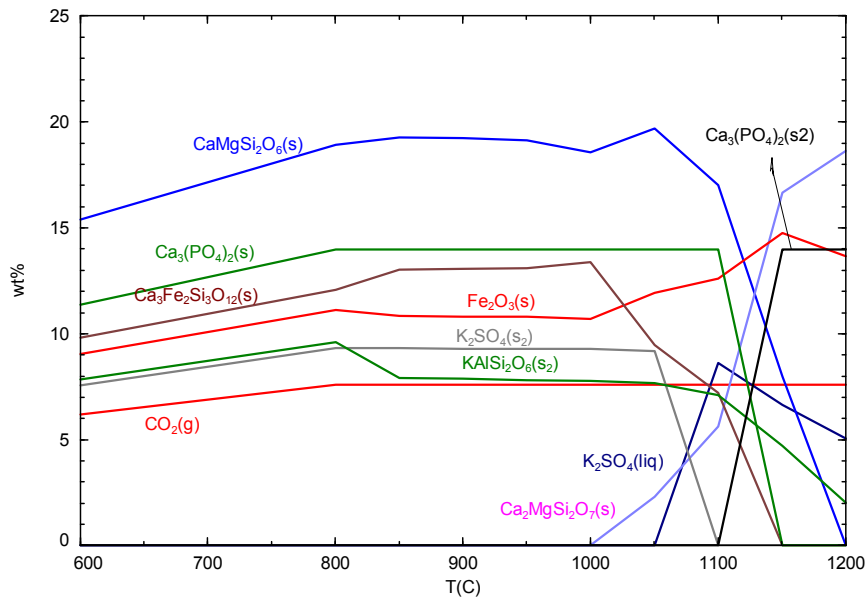


Fig. 5. Proportion of major oxides in the slag phase for WP ash sample.

The slag phase in the CP ash sample is primarily formed by sulphur and phosphorus compounds, which are of particular importance when considering the combustion of biomass materials. Sulphur species react with alkali and alkali earth metal oxides forming hazardous

sulphates and/or sulphites. Phosphate compounds in the biomass are generally involved in volatilisation-condensation reactions and subsequent deposition on boiler surfaces [11].

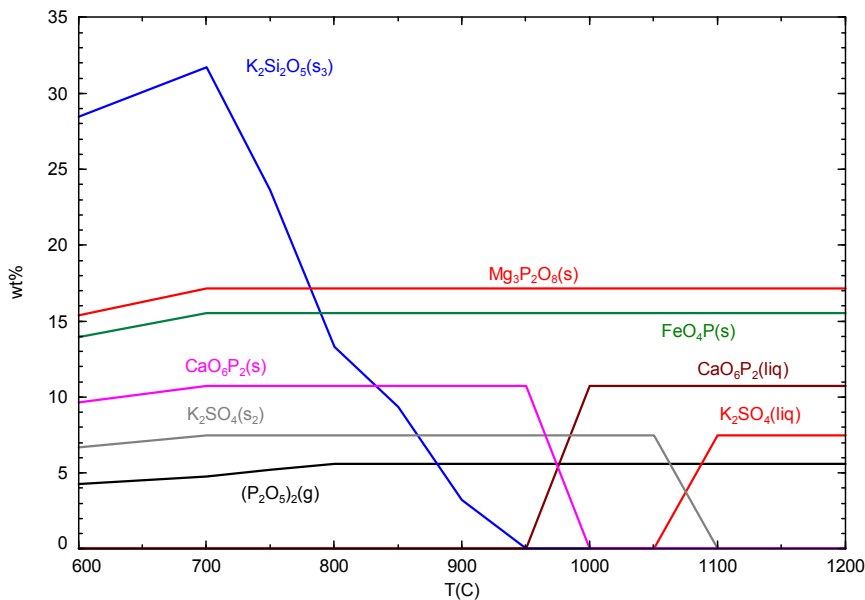


Fig. 6. Proportion of major oxides in the slag phase for CP ash sample.

For CP ash sample, all major oxides present in the slag phase increase in weight percent up to 700°C and remain fairly constant until 950°C. Potassium silicate ($K_2Si_2O_5$) is the only compound in the system which presents a sharp decreasing trend in this range of temperatures. By having the major mass fraction at lower temperatures

(33% at 700°C) the compound disappears at 950°C. The main transformations observed at higher temperatures (950-1100 °C) correspond with solid-liquid phase transitions undertaken by alkali and alkali earth metals in combination with phosphate (CaO_6P_2) and sulphate compounds (K_2SO_4). Magnesium and iron phosphates

($Mg_3P_2O_8$ and FeO_4P , respectively) are the major compounds in the system at high temperatures. Contrarily to other oxides, their mass fraction remain stable with rising temperature. It is neither affected by the temperature increase in the gaseous phase of the system: phosphorus pentoxide ($(P_2O_5)_2$).

The dielectric properties of biomass ash can provide valuable information about phase changes and the transformation of the microstructure of the sample. Fig. 7 illustrates the variation in $\tan\delta$ as a function of frequency for different temperatures. High values of $\tan\delta$

are found at lower frequencies, decreasing steeply as frequency increases for all the range of temperatures. The dielectric loss values are related to the dielectric constants (ϵ), thus high $\tan\delta$ values indicates high ϵ . At lower frequencies, the high carrier accumulations result in high dielectric constants and high dielectric losses are attributed to ions migration within the material [8]. When frequency increases, dielectric materials generally exhibit a low dielectric behaviour due to lower ion mobility and small deformation within the structure of the material [12].

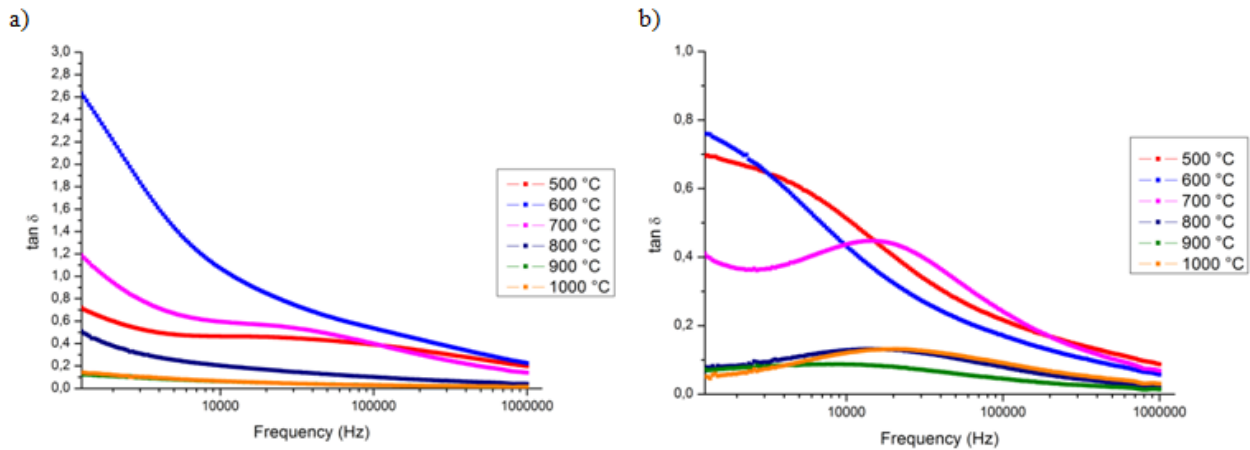


Fig. 7. Loss tangent ($\tan\delta$) versus frequency plots at different temperatures for: a) WP; b) CP ash sample.

From both graphs it can be seen that $\tan\delta$ increase from 500°C to 600°C, followed by a steady decrease up to 1000°C. In the case of the CP sample the plot shows a peaking behavior at about 700°C suggesting ionic relaxation, while the behaviour observed in the remaining temperatures is in agreement with ionic conductivity curves.

The variation of dielectric loss with temperature at three constant frequencies is shown in Fig. 8. For WP ash

sample the $\tan\delta$ values peak at around 600°C, followed by a steady decrease to 900°C where they remain constant. Therefore, three characteristic ranges can be noticed corresponding with high ion mobility, steady decrease and strong bonds at higher temperatures inhibiting ionic losses. It can also be observed that increase in frequency decreases the magnitude of dielectric loss.

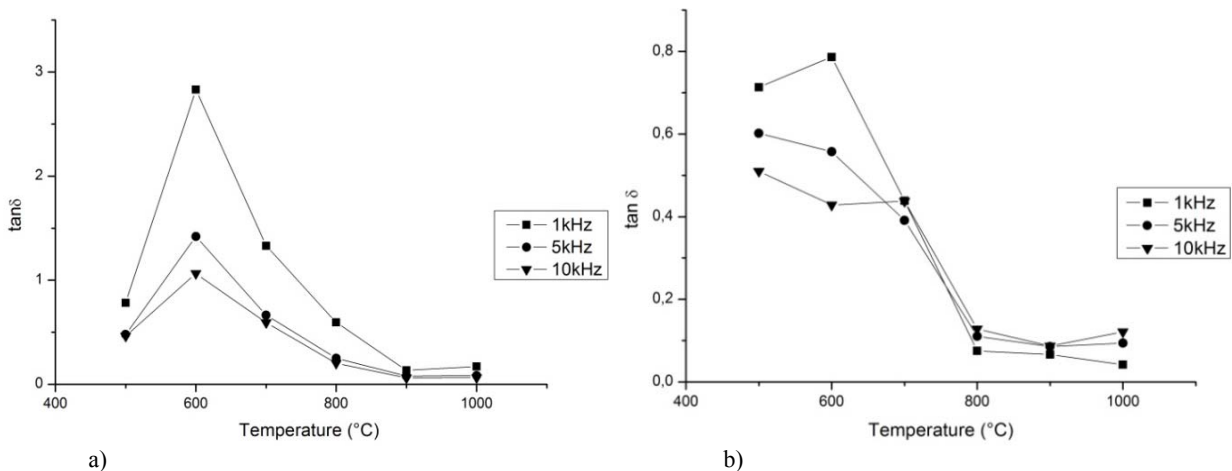


Fig. 8. Loss tangent ($\tan\delta$) versus temperature plots at different frequencies for: a) WP, b) CP ash sample.

The same observation can be applied to the CP ash sample up to 700 °C although the nature of the curves differs significantly and only the one depicting the lowest frequency peaks at 600 °C. Some anomalies in the dielectric loss versus temperature plot can be observed at higher temperatures as the higher values of $\tan\delta$ correspond with higher frequencies. Nevertheless, the general trend of $\tan\delta$ values decreases with rising temperature, accordingly with the results presented above.

It is important to notice that biomass ash is a semi-dielectric material and despite it contains a reasonable amount of alkali metal ions, the role they play in the dielectric behavior is not fully understood. In order to interpret the dielectric properties of the ash properly, a thorough chemical analysis of the different constituents present in the ash is required.

Conclusions

The ash fusion behavior of two different kinds of biomass was analyzed by means of thermodynamic equilibrium models and measurements of changes in the dielectric properties. Standard methods like ash fusion tests (AFT) and oxide indices calculations were also employed and the results were compared.

A number of oxide indices were used to evaluate the slagging and fouling propensities of the samples. All of them indicate severe and/or high propensity for both kinds of biomass, although ash elemental composition was different from one another. Wood pellet ash sample is enriched in $\text{SiO}_2 > \text{CaO} > \text{Fe}_2\text{O}_3 > \text{K}_2\text{O} > \text{CO}_2 > \text{P}_2\text{O}_5 > \text{SO}_3 > \text{MgO} > \text{Al}_2\text{O}_3$, whereas cereal pellet ash sample is characterized by high contents of $\text{P}_2\text{O}_5 > \text{SiO}_2 > \text{K}_2\text{O} > \text{Fe}_2\text{O}_3 > \text{MgO} > \text{SO}_3 > \text{CaO}$.

Despite the indices show good agreement between the samples, the results from the ash fusion test remarked the differences regarding both chemical and physical characteristics. The four characteristic AFTs are lower for the cereal pellet ash sample, specifically the initial deformation temperature (IDT) which indicates that the physical changes in the CP sample appear much faster.

The contribution of different ash compositions to fusion behavior can be assessed by thermodynamic calculations, obtaining also specific information regarding the amounts of slag liquid formed at a given set of temperatures. The liquid slag of cereal pellet ash samples rises significantly from 700 °C while the amount of slag liquid formation in the wood pellet ash sample increases extensively from 1100 °C. The presence of alkali and alkali earth metals, potassium and sulphur is notorious in both systems. The main mineral transformation reactions occur at higher temperatures (950–1200 °C) as the chemical compounds become more thermally active phases and exhibit different behaviours. The thermodynamic equilibrium predictions show that the temperature at which transformation of ash begins to form threatening slag phases is lower than that defined by standard AFT measurements. That is why different attempts have been tried in last years to create measurement techniques able to define the potential of fuels sintering and slagging other than standard ones.

Measurement of dielectric properties of ash has been suggested and the changes in dielectric loss ($\tan\delta$) as a function of both temperature and frequency have been observed. High carrier accumulations at lower frequencies result in high dielectric losses due to ions migration and deformation within the structure of the material. The magnitude of the dielectric loss factor decreases with the rise of frequency. The electric method may provide valuable information about the phase changes and transformation of the microstructure of the samples during the heating process.

Biomass ash is a complex multicomponent system and further studies are needed to determine basic compositional, physical and chemical properties which may, in turn, improve the interpretation of the dielectric measurement.

Better characterization of biomass ashes will also benefit its use as raw material for different applications, improving the revenue of biomass fired power plants and tackling the current environmental health hazard of ash disposal.

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