

Article

Study of Dendromass Ashes Fusibility with the Addition of Magnesite, Limestone and Alumina

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Abstract: The fusibility of ash from woodchip combustion is characterised in the present work. The impact of the increase in MgO, CaO, and Al₂O₃ content in the bio-ash on the classification of ash into categories according to slagging and fouling indices was evaluated. The ash was characterized based on the chemical composition using slagging and fouling indices. However, these ash composition changes did not assign the ash into categories of the indices F_U, S_R, R_S, and B/A (fouling, slagging, slag viscosity, basicity), with less ash inclination to slagging and fouling. The indices were primarily derived for ashes from coal combustion. The indices values characterizing the ash were compared with measured results of ash melting according to STN ISO 540. The measured ash fusibility values showed that the addition of magnesite, limestone, and alumina to dendro-ashes increases the DT (temperature of deformation), HT (temperature of hemisphere), and the AFI (ash fusibility index). There is no conformity between the values of the indices and the measurement of ash fusibility temperatures. In terms of temperatures in the combustion chamber, the measured sintering (T_{sin}) and DT are suitable for evaluating the tendency of ash to slagging and fouling as well as an accretion of ash particles sticking to the lining.

Keywords: dendromass; ash; chemical composition; ash indices; ash fusibility



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1. Introduction

The use of biomass appears to be a suitable substitute for fossil fuels and is also partly a solution to the increasingly stringent environmental regulations in the EU. Increasing requirements for reductions of CO₂ emissions and pollutants (solid, liquid, and gaseous) are inevitably leading to a transition from coal to biomass. One of the significant limiting factors for industrial combustion of biofuels is the increased aggressiveness of bio-ash. Ash deposition and fouling of power equipment is a complex chemical-physical process. The bio-ash is formed by burning biomass; CO₂ and water vapour are produced, and mineral substances are released which interact with the flying particles of ash. Sticky particles of ash are captured on the furnace linings of refractory materials and slowly foul and clog the boiler chamber, grates, etc. In addition to these components, the flue gases contain several aggressive gases; SO₂, chlorides, sublimates of potassium, sodium, and other salts [1–6].

The chemical and mineralogical composition of ash depends on the fuel's composition and the type of biomass, and determines its physical properties [1–4]. Bio-ashes contain a high proportion of CaO (4–60 wt.%), SiO₂ (1–65 wt.%), K₂O (2–35 wt.%), and smaller amounts of MgO, Fe₂O₃, Na₂O, S, Cl, and P. These heavy metals are present in trace amounts [5,6]. As mentioned in previous studies [3–9], silica in the presence of alkalis (Na,

K) forms low-temperature glassy melts which, as well as alkaline vapours, are aggressive towards refractory linings in boilers and metal parts in heat exchangers.

The combustion of alternative fuels (biomass, municipal and commercial wastes, etc.) increases the refractory material quality requirements of the boiler and industrial oven linings. The sticking of slag ash particles on the lining, the clogging of grates, and fouling of heat-exchange areas in the energy aggregates poses a major problem during the combustion of biofuels and some industrial and municipal wastes. An ash inclination to agglomeration in the combustion bed, slagging, fouling, etc., is evaluated in industrial practice by indices derived from the chemical composition of ash/slag from coal combustion, which are substantiated by long-term experience. Although the research focused on the verification of these indices to bio-ash is not satisfactory [3,5,6,10–23], an effort to use some of them for the assessment of bio-ashes remains.

The indices predicting the thermal behaviour of ash are mostly expressed from the chemical composition of the ash, eventually on correlation of fusibility temperature. Some indices from the literature [3] are briefly described in Table 1. The glassy slag forms when silica is a predominating element in the ash. Accordingly, the silica content in biomass can be a suitable slagging and agglomerate indicator. The oxides of acidic group ($\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2 = \text{A}$) with a higher melting temperature form a low melting slag in combination with basic oxides ($\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O} = \text{B}$). The alkali vapor atmosphere contributes to the formation of sticky silica ash particles and to its slagging. Therefore, the B/A ratio is considered as an index for ash deposit prediction according to the intervals given in Table 1. An agglomeration index (BAI) was developed to indicate ash agglomeration in the bed and category ranges were based on observed bed temperatures. The slagging index (R_s) considers an influence of Fe_2O_3 , which can influence the creation of low temperature slag located in the bed. The content of Fe_2O_3 in coal-ash is higher than in bio-ash. The fouling index (F_U) takes into account the effect of alkalis ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) which evaporate and attack the flying ash particles. The alkali (10–25 wt.%) in biomass fuels forms a low temperature eutectic slag with silica [2]. In consequence, the bio-ash has a higher slagging and fouling tendency. It is interesting that the slag viscosity index (S_R) does not include the alkali (K_2O , Na_2O). This may be due to the low alkali content of the coal for which the index was derived. The alkali content in bio-ash is several times higher. Definition of the classification ranges (low, medium, high) is based on the knowledge of the variation of coal ash/slag quality with increasing SiO_2 content.

Table 1. Categorization of ash according to slagging and fouling indices and ash fusibility [3,10].

Characterization of Ash	Index Definition	Indices Value of Ash Inclination to Slagging, Fouling, and Ash Fusibility Temperature			
		Low	Medium	High	Extremely High
Silica content	$S = \text{SiO}_2$	<20	20–25	>25	-
Basicity	$B/A = \frac{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2}$	<0.5	0.5–1.0	1.0–1.75	>1.75
Slagging index	$R_s = \frac{B}{A} \cdot \text{Fe}_2\text{O}_3$	<0.6	0.6–2.0	2.0–2.6	-
Fouling index	$F_U = \frac{B}{A} \cdot (\text{Na}_2\text{O} + \text{K}_2\text{O})$	<0.6	0.6–40	>40	-
Slag viscosity index	$S_R = \frac{\text{SiO}_2 \times 100}{\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}}$	>72	65–72	<65	-
Alkalinity-Total alkali	$TA = \text{Na}_2\text{O} + \text{K}_2\text{O}$	>0.3	0.3–0.4	>0.4	-
Silica-Alumina ratio	$S/A = \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	<0.31 and >3	-	0.3–3.0	-
Bed agglomeration index	$BAI = \frac{\text{Fe}_2\text{O}_3}{\text{Na}_2\text{O} + \text{K}_2\text{O}}$	-	-	<0.15	-
Ash fusibility index [°C]	$AFI = \frac{4DT + HT}{5}$	>1342	1232–1342	1052–1232	<1052
Initial softening temperature [°C]	DT (IDT)-initial deformation temperature (softening)	>1100	900–1100	<900	-

Ash fusibility index (AFI) is calculated from measurement data from the observation of dimensional and shape changes of ash body during the heating. The measured initial deformation temperature (DT/IDT) and hemisphere temperature (HT) determine the AFI value; the index is defined in Table 1. The initial deformation temperature is defined by the first signs of edge rounding of the sample and defines the start of material softening.

Biomass contains potassium which, when burned with SiO_2 , forms compounds with very low melting temperatures. The aim of the studies [3,10,24,25] was to clarify the relationship between K_2O content and DT (start of sintering). In accordance with this correlation, different intervals for sintering tendencies were proposed depending on the DT values, as presented in Table 1. It should be mentioned that determining generally valid indices only on the basis of chemical composition is problematic, and an application of the indices derived for coal ash to bio-ash and waste-ash may then not provide satisfactory results.

The combustion of biomass, specifically wood chips, may be accompanied by a relatively high degree of unburned carbon (up to about 20%) [26]. One way to increase efficiency is to intensify the combustion process by enriching the air with oxygen [27]. This intensification will cause an increase in the temperature in the combustion chamber and in the entire heat-exchange system. The increase in temperature will affect the intensity of physico-chemical reactions, interactions of ash particles, the movement of flue gas, and the corrosion of refractory lining and metal parts of boilers. A possible way to prevent bio-ash slagging and agglomeration is to use additives that are added to the fuel to raise the melting point of the bio-ash [4,25–30].

In this paper, the effect of increasing content of MgO , CaO , and Al_2O_3 in various bio-ashes is evaluated. The bio-ashes were assessed on the basis of chemical composition using selected indices that predicted the inclination of the ashes to fusibility, slagging, fouling, and agglomeration, and the ash fusibility index was calculated from the measured data.

2. Experimental

2.1. Ashes and Modifying Additives

Several types of ash from a 16 MWt dendromass (wood chips) burning power plant were delivered for analysis in months 09 and 10 in 2022. The crumble slag from the boiler grate (S) and ash from the flue channel (T), cyclone (C), and fabric filter (F) were analysed. The composition of tested fractions of ash have been modified with the addition of powdery raw magnesite (M) (SMZ, a.s. Jelšava, Slovakia), powdery raw limestone (L) (Včeláre, Carmeuse Slovakia, s.r.o.), and powdery $\text{Al}_2\text{O}_3/99.9$ wt.% (A) (Lachema, n.p. Brno, Czechoslovakia). Additives were added to ash in the wt. ratio: ash:modification additives = 2:1. Labelling of sample is, for example: C09—ash from cyclone sampling in months 09th 2022; resp. C09M—ash from cyclone, 09th 2022 with magnesite additive (ash:additive = 2:1).

The chemical composition of the basic fractions of ash and modified ash with the magnesite, limestone, and/or alumina oxide is given in Table 2. Chemical analyses were carried out by the classical method; melting decomposition of the samples, dissolution of melt in HCl /deionised water, and determination of the elements in solution by inductively coupled plasma atomic emission spectroscopy (ICP-AES/iCAP 6000 Series, Thermo Fisher Scientific Inc., Waltham, MA, USA). The presence of major phases in the samples was determined by X-ray powder diffraction analysis on a Rigaku MiniFlex600 (Rigaku Corporation, Tokyo, Japan), $\text{CuK}\alpha$, with PDXL2.4 software and ICDD database.

2.2. Indexes Used to Predict Behaviour of Ash at Higher Temperature

The slagging, fouling, and agglomeration indices were chosen to assess the behaviour of ashes in the combustion process and their tendency to melt formation. The indices' definitions and ash categorization by value are given in Table 1 [3,10]. The base of these indices is the chemical composition of the ash. The ash fusibility was determined by measurement of sintering temperature (T_{sin}), deformation temperature (DT), hemisphere temperature (HT), and flow temperature (FT) according to STN ISO 540. The sintering process leads to shrinkage of the sample while preserving its initial shape. The sintering temperature is defined as the drop in the height of the sample below 98% of the initial value [31,32]. The ash fusibility index is indicator of the temperature of ash agglomeration and sintering [14].

Table 2. Chemical composition of bio-ashes (basic and modified with magnesite (M), limestone (L) and alumina (A)).

Sample	Chemical Composition [wt.%]						Na ₂ O	K ₂ O	L.O.I.
	Al ₂ O ₃	SiO ₂	CaO	MgO	Fe ₂ O ₃	MnO			
S09	5.5	25	48.8	3.6	3.1	1.3	0.4	3.3	9
S10	5.9	35.6	28.0	4.0	2.9	0.8	1.0	8.2	10.8
T10	6.6	48.9	21.1	2.9	2.8	0.6	1.4	6.5	4.7
C09	3.2	17.2	47.6	3.5	2.5	0.8	0.3	3.7	21.1
C10	4.5	21.7	38.0	3.4	2.1	0.8	0.7	7.0	12.6
F09	1.2	3.2	50.3	4.1	1.5	1.2	0.3	15.1	23.1
F10	1.3	4.6	32.6	3.2	0.8	0.8	1.0	18.4	20.9
S09M	4.7	18.5	35.8	17.2	3.6	1	1	2.3	15.9
C09M	3.2	12.8	34.3	17.8	3.2	0.6	1	2.6	24.4
F09M	1.8	3.3	36	18.4	2.2	0.8	1	10.2	26
S09L	3.8	16.9	49.8	2.5	2.2	0.9	0.4	2.2	20.3
C09L	2.3	11.7	49.0	2.4	1.8	0.5	0.3	2.5	28.4
F09L	1.0	2.3	50.8	2.8	1.1	0.8	0.3	10.1	29.7
S09A	37.0	16.7	32.5	2.4	2.1	0.9	0.3	2.2	6.0
S10A	37.3	23.7	18.7	2.6	1.9	0.5	0.7	5.5	7.2
T10A	37.7	32.6	14.1	2.0	1.9	0.4	0.9	4.4	3.1
C09A	35.5	11.5	31.7	2.3	1.7	0.5	0.2	2.5	14.1
C10A	36.4	14.5	25.3	2.3	1.4	0.6	0.5	4.7	8.4
F09A	34.1	2.1	33.5	2.7	1.0	0.8	0.2	10.7	15.4
F10A	34.2	3.1	21.8	2.1	0.5	0.5	0.7	12.3	14.0

L.O.I—Loss on ignition.

2.3. Determination of Ash Fusibility according to STN ISO 540

The measurements of the ash fusibility were carried out according to STN ISO 540 [31] in a high-temperature microscope (Leitz-Wetzlar 1500, Carl Zeiss Jena GmbH, Jena, Germany) with a furnace up to 1500 °C. Powder ash samples were homogenised in a porcelain dish to a grain size below 0.063 mm and then pressed without a binding addition in a hand press (2.7 MPa) into a cylindrical tablet (ϕ 3 mm $\times$ 3 mm) with weight of 0.2 ± 0.02 g. The cylindrical sample was placed in a furnace on a corundum plate and heated in a static air atmosphere at the heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. The shape profile of the tested sample was scanned fluently, and deformation temperature (DT), sphere temperature (ST), hemisphere temperature (HT), and flow temperature (FT) were detected. The allowed temperature tolerance when defining the shape of the silhouette was $\pm 10^\circ\text{C}$ [31]. The ash fusibility index, indicating the temperature of ash agglomeration and clinkering, was calculated according to the equation $\text{AFI} = \frac{4\text{DT} + \text{HT}}{5}$ [3,10]. Values of DT and AFI were used to evaluate the ash inclination to slagging and fouling. The measured melting temperatures of ashes according to STN ISO 540 were assessed in relation to ash indices in Table 3.

Table 3. Characteristic temperatures of bio-ash fusion measured according to STN ISO 540 [31].

Sample	Initial Sintering Temperature T _{sin} [°C]	Deformation Temperature DT [°C]	Spherical Temperature ST [°C]	Hemisphere Temperature HT [°C]	Flow Temperature FT [°C]	Ash Fusibility Index AFI [°C]
S09	1226	1230	1235	1238	1242	1232
S10	1180	1205	1215	1215	1220	1207
T10	1160	1210	1220	1225	1250	1213
C09	1250	1305	1320	1345	1395	1313
C10	1300	1340	1385	1430	1470	1358
F09	1200	1405	1430	1432	1440	1410
F10	1200	1340	1450	1455	1460	1363
S09M	1250	1300	1305	1310	1320	1302
C09M	1250	1400	1440	1450	>1500	1410
F09M	1345	1445	1495	>1500	>1500	1466
S09L	1300	1395	1440	1460	1490	1408
C09L	1250	>1500	-	-	-	-

Table 3. Cont.

Sample	Initial Sintering Temperature T_{sin} [°C]	Deformation Temperature DT [°C]	Spherical Temperature ST [°C]	Hemisphere Temperature HT [°C]	Flow Temperature FT [°C]	Ash Fusibility Index AFI [°C]
F09L	1150	1350	1405	1410	1420	1362
S09A	1220	1305	1320	1325	1340	1309
S10A	1185	1230	1250	1255	1275	1235
T10A	1175	1375	1385	1390	1400	1378
C09A	1250	1395	1415	1415	1420	1399
C10A	1185	1425	1460	1460	1465	1432
F09A	1030	>1500	-	-	-	-
F10A	1050	>1500	-	-	-	-

Temperature ± 10 [°C].

3. Results

Composition and Fusibility Temperatures of Bio-Ash

Chemical compositions of basic ash and that modified with magnesite (M), limestone (L), and alumina (A) are summarized in Table 2. The classification of ashes according to the achieved indices values (Table 3) was compared with the measured temperature of deformation/softening point (DT) and ash fusibility index (AFI) in Table 4.

Table 4. Evaluation of indices of slagging, fouling and bio-ash fusibility [3,10].

Sample	SiO ₂	B/A	Indices of Slagging, Fouling and Ash Fusibility vs. DT Temperature, Index AFI, and T_{sin}						DT [°C]	AFI [°C]	T_{sin} [°C]
			R _s	F _u	S _R	TA	S/A	BAI			
S09	25	2.0	6.9	7.3	30.9	3.7	4.5	0.84	1230	1232	1226
	+++	++++	++++	++	+++	++++	+	+	+		
S10	35.6	1.08	3.13	9.9	50.5	9.2	6.0	0.3	1205	1207	1180
	++++	++	++++	++	+++	++++	+	+	+	+++	
T10	48.9	0.64	1.79	8.5	64.6	7.9	7.4	0.35	1210	1213	1160
	++++	+	++	++	++	++++	+	+	+	+++	
C09	17.2	2.83	7.9	11.3	24.2	4.0	5.4	0.62	1305	1313	1250
	++		++++	++	+++	++++	+	+	+	++	
C10	21.7	1.99	4.18	15.3	33.3	7.7	4.8	0.27	1340	1358	1300
	+++	++++	++++	++	+++	++++	+	+	+	+	
F09	3.2	16.25	27.6	250.2	5.4	15.4	2.7	0.1	1405	1410	1200
	+	++++	++++	++++	++++	++++	+++	+++	+	+	
F10	4.6	9.63	7.74	186.8	11.2	19.4	3.5	0.04	1340	1363	1200
	+	++++	++++	++++	++++	++++	++	+++	+	+	
S09M	18.5	2.64	10.57	8.7	24.5	3.3	3.9	1.09	1300	1302	1250
	++	++++	++++	++	+++	++++	+++	+	+	++	
C09M	12.8	3.7	13.13	13.3	18.7	3.6	4.0	0.9	1400	1410	1250
	++		++	++	++	++++	++	+	+	+	
F09M	3.3	13.33	32.0	149.3	5.5	11.2	1.8	0.2	1445	1466	1345
	+	++++	++++	++++	++++	++++	+++	++	+	+	
S09L	16.9	2.8	6.82	7.2	23.6	2.6	4.4	0.85	1395	1408	1300
	++	++++	++++	++	++++	++++	++	+	+	+	
C09L	11.7	4.04	8.03	6.8	18.0	2.8	5.1	0.64	>1500	-	1250
	++	++++	++++	++	++++	++++	+	+	+		
F09L	2.3	20.0	22.0	208.0	4.0	10.4	2.3	0.1	1350	1362	1150
	+	++++	++++	++++	++++	++++	+++	+++	+	+	
S09A	16.7	0.74	1.55	1.8	31.1	2.5	0.45	0.84	1305	1309	1220
	++	++	++	++	++++	++++	+++	+	+	++	
S10A	23.7	0.49	0.93	3.0	50.5	6.2	0.6	0.3	1230	1235	1185
	+++	+	++	++	+++	++++	+++	+	+	+++	
T10A	32.6	0.34	0.65	1.8	64.4	5.3	0.86	0.36	1375	1378	1175
	++++	+	++	++	++	++++	+++	+	+	+	
C09A	11.5	0.82	1.4	2.2	24.3	2.9	0.3	0.63	1395	1399	1250
	++	++	++	++	++++	++++	+++	+	+	+	
C10A	14.5	0.68	0.95	3.5	33.3	5.2	0.4	0.27	1425	1432	1185
	++	+	++	++	++++	++++	+++	+	+	+	
F09A	2.1	1.31	1.31	13.4	5.4	10.9	0.06	0.09	>1500	-	1030
	+	+++	++	++	++++	++++	+	+++	+		
F10A	3.1	1.02	0.51	13.3	11.3	13.0	0.09	0.04	>1500	-	1050
	+	++	+	++	++++	++++	+	+++	+		

(+)—low; (++)—medium. (+++)—high and (++++)—extremely high probability of slagging/fouling.

The results of X-ray analyses of the investigated ash samples show significant differences in the phase composition of bio-ash fractions. The ash-slag on the grate (S) had the character of glassy porous agglomerates. In addition to the amorphous phase, calcium silicates, calcite, and anorthite were detected. Calcium silicates ($2\text{CaO} \cdot \text{SiO}_2$), SiO_2 , and

carbonates (CaCO_3 , and spurrite ($\text{Ca}_5(\text{SiO}_4)_2\text{CO}_3$) were identified in the sandy ash (T) from the flue channel. The ash trapped in the cyclone (C) contained mainly calcium silicates ($2\text{CaO} \cdot \text{SiO}_2$), SiO_2 , and calcite. The fine fraction from the fabric filter (F) was formed predominantly of arcanite, calcite, and spurrite (K_2SO_4 , CaCO_3 , $\text{Ca}_5(\text{SiO}_4)_2\text{CO}_3$). It cannot be ignored that other complex (Ca/K) carbonates and silicates were also present in the ash fractions.

4. Discussion

During the combustion of dendromass in the atmosphere of flue gases (CO_2 , N_2 , water vapour with a minor content of gaseous K, S, P, and Cl components) the fine sticky ash particles are generated. Even low concentrations of alkali metals in the atmosphere of combustion chamber can have a significant impact on the ash fusibility, slagging, melting and grate clogging, and fouling of the furnace and other parts of the boilers. These accretions react intensively with the lining refractory materials. The values of the slagging and fouling indices of ash are determined by their chemical composition. It follows that reducing the reactivity and the stickiness of ash particles can be achieved by changing the chemical composition of the ash, e.g., by adding minor amounts of inhibitors to the fuel [26]. The effect of increasing MgO , CaO , and Al_2O_3 content in bio-ashes on the change in the values of some indices determining the inclination to ash slagging and fouling has been verified.

Although S09, S10, T10, C09, and C10 ashes contained much more SiO_2 than F09 and F10 ashes (Table 2), their measured sintering temperatures were comparable. T10 ash, which contained the most SiO_2 , had the lowest sintering temperature. SiO_2 content is crucial to sintering and melting of bio-ash. The measured ash fusibility temperatures of S, T, and C ashes were lower ($\text{AFI} = 1207\text{--}1313\text{ }^\circ\text{C}$) than the index for F09 and F10 ash ($\text{AFI} = 1410\text{ }^\circ\text{C}$ and $1363\text{ }^\circ\text{C}$) (Table 3). If the SiO_2 content in the ash is low and the K_2O content is higher, as in the case of F ash, more intense evaporation of alkali occurs [33].

The knowledge that SiO_2 in the presence of K_2O , Na_2O forms low-meltable glassy phases predetermines the ratio of basic to acid oxides in ash for their categorisation. The ashes were graded in categories of probability of slagging and fouling. The classification of ash based on the values of B/A, R_s , and S_R indices does not correspond to the relatively high measured deformation temperature and the fusibility index (Table 4).

The addition of MgCO_3 to the F ash had a positive effect: the sintering and deformation temperatures increased. However, the addition of Al_2O_3 promoted sintering (Table 3, Figure 1). This can be explained by the high affinity of K_2O to Al_2O_3 and their interactions. Nevertheless, Al_2O_3 caused an extreme increase in the deformation temperature.

The T_{sin} temperatures of S, T, C ashes and modified ashes were $\geq 1150\text{ }^\circ\text{C}$ (Table 3). The addition of MgCO_3 or CaCO_3 to S, T, and C ashes increased the values of T_{sin} , but not as significantly as values of AFI and DT (Figure 1). The MgO and CaO concentration were directly included in the definitions of B/A, R_s , F_U , and S_R [3]. By definition, an increase in the basic oxide content cannot move the ash into better categories. The deformation temperatures (DT) of ash and the AFI indexes were slightly increased by Al_2O_3 addition.

The addition of Al_2O_3 to the bio-ash resulted in a decrease in the B/A, R_s , and F_U indices and in a shift of the ashes into categories with less inclination to slagging and fouling. However, the added amount of Al_2O_3 was not enough to shift the modified ashes into the better categories of S/A. It should be pointed out that Al_2O_3 is implied only in definition in the B/A, R_s , F_U , and S/A indices. As can be seen from the data in Table 4, the prediction of the bio-ashes' behaviour at a higher temperature given by these indices is ambiguous, often even contradictory. Conformity of categorization according to indices with measured fusibility temperatures is minimal.

The measured T_{sin} and DT temperatures were not consistent with the ash classification by slag viscosity indices (S_R) but correlated relatively well with the categorization by the bed agglomeration index (BAI). It seems that the sintering temperature (T_{sin}) was the best predicting indicator of bio-ash fouling and bed agglomeration from the measured

temperatures of ash fusibility (STN ISO 540). The same value of temperature regions as used for the initial deformation temperature (DT, Table 1) could be used to categorize the bio-ash using the sintering temperature (T_{sin}) [31].

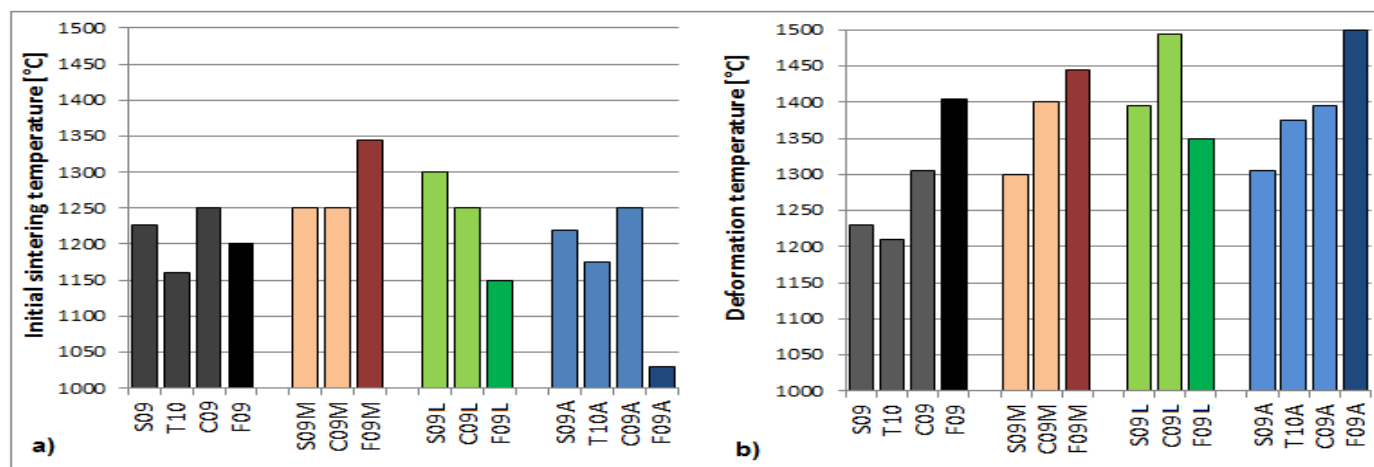


Figure 1. Effect of magnesite, limestone, and Al_2O_3 addition to S, C, T, and F ash on (a) sintering temperature (T_{sin}); (b) deformation temperature (DT).

The shape and dimension changes of the sample profile vs. temperature were observed from low temperatures during the ash fusibility measurement. In the literature [32], the sintering temperature is characterised as the temperature of dimensional change—shrinkage between 2–5% without observation of external phenomena of melting. The solid-state sintering can take place in the presence of a liquid phase, or without a liquid phase. Due to the rate of bio-ash sintering, the presence of a liquid phase is clear [34]. Nordgern, in [35], states that the softening / deformation point (DT) of ash is related to the melting of minerals containing K_2O . In this case, there was a change in the dimensions of the sample, but no change in shape.

It should be noted that the chemical analyses, as well as the ash fusibility measurements, are carried out on the post-mortem bio-ash samples. During the fuel combustion, the conditions in the combustion chamber are different, and therefore the results of ash indices and ash fusibility are considered only as indicative. The temperature and atmosphere in the combustion chamber affects the interactions of ash particles, melting, slag, sticking, fouling of ash, etc.

As it is mentioned in works [11,12] the mechanism of ash formation in the solid fuel combustion process (coal, biomass/dendromass in form of wood chips, pellets) should be divided into two temperature zones: the combustion zone and the cooling zone. The temperature in the combustion zone reaches up to 1100 °C (extreme case 1200 °C) and in the cooling zone it is below 900 °C. The processes occurring in the combustion zone are mainly oxidation, fragmentation, evaporation, and melting. In the cooling zone, agglomeration, condensation, and solidification occur.

The wood chips are scattered in the flame. The ash formation during biomass combustion can be described as a fast, consistent transformation—decomposition of organic mass due to the heat which is released when carbon burns. Hot flue gasses contain volatilized alkali (K, Na) and less S, Cl. These components attack the ash micro-particles (CaO-SiO_2) and form low-melting slag on their surface. Ashes become sticky and agglomerate; their size grows. The flue gases with ash proceed into the colder zone, where the bigger ash particles are captured and solidify. The bio-fuel composition strongly influences the progress of agglomeration. The composition variability of biofuels and combustion conditions are the cause of the heterogeneous deposits and ash accretions. Some volatilised components later condense to form (K, Ca) sulphates and carbonates in cooler parts of the power equipment [2]. The slag on the grate and ash from flue channels contains less alkali due to the

condensation of alkali in the colder parts (cyclone, filter). Since the alkaline vapours in the combustion zone greatly influence the ash slagging, fouling, and agglomeration, this phenomenon should be taken into account in the categorisation and selection of proper indices, and the range of indices changes for the assessment of the behaviour of biofuels [36].

From the results presented in Table 4, it is clear that the indices in their current form and with the classification ranges are not reliable to characterize bio-ash slagging, fouling, and agglomeration. Results from the measurement of ash fusibility according to ISO 540 are more relevant for the evaluation of bio-ash fusibility. The temperatures of sintering (T_{sin}) and softening (DT) seem to be most suitable for evaluation of ash tendency to slagging and fouling. This work confirmed the results of observation by other authors [3,14,22,24,37] who searched for relevant indicators to predict behaviour of the bio-ash in combustion chambers and grates.

5. Conclusions

Behaviour of bio-ash and modified bio-ash with magnesite, limestone, and alumina at combustion temperatures were characterized using indices derived for coal ash. The use of these indices has been shown as unsatisfactory for the assessment of bio-ash slagging, fouling, and agglomeration. In the case of biofuels, in addition to the chemical composition, which is highly variable in the case of biomass/dendromass fuel, the furnace atmosphere has an important influence on the formation of slag and its melting in the combustion chamber. The combustion conditions and variability of biomass/dendromass fuels should be taken into account when deriving new indices and/or adjusting the ranges of classification values.

Results of ash fusibility measured on a high-temperature microscope (ISO 540) seem to be more suitable for predicting slagging and agglomeration of bio-ash. The initial sintering temperature (T_{sin}) is probably the most suitable indicator of ash slagging. Measured results of ash fusibility confirmed the beneficial effect of magnesite and limestone addition to the dendromass ash (increase in MgO, CaO, and Al_2O_3 concentration in the ash) on the increase in temperatures defined by the points: DT, HT, and FT.

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