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ASH FUSIBILITY CHARACTERISTICS OF SOME BIOMASS FEEDSTOCKS AND EXAMINATION OF THE EFFECTS OF INORGANIC ADDITIVES

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1. Introduction

The interest in using agricultural waste, refuse and other biomass feedstocks as fuels for steam and power generation is growing steadily throughout the world, due to the high cost of fossil fuels in terms of purchase as well as of disposal in line with environmental regulations [Vamvuka 2003]. However, burning biomass for energy production induces varying degrees of ash agglomeration on the heat transfer surface of boilers, resulting in reduced energy efficiency, difficult cleaning of apparatuses from the ash deposits, and even mechanical failure of heat exchangers [Llorente Fernandez 2006]. The main cause of these problems is the high alkaline content, and consequently the low melting temperature, of the ash of some biomass feedstocks, particularly herbaceous materials, which also contain more ash than woody biomass [Llorente Fernandez 2005]. Biomass fuels contain several substances, including K, Na, S and Cl. During combustion these elements may give rise to molten phases which produce sticky ash particles that adhere to heat transfer surfaces [Werklin 2005]. This can lower the ash melting temperature, enhancing the adhesion efficiency of fly ash particles [Theis 2006]. It has been demonstrated that the addition of oxides and inorganic salts to the initial biomass can change its thermal behaviour and raise its melting temperature [Werther 2000; Zintl 1998; Van Ommen 2001; Vuthaluru 2001; Llorente Fernandez 2006]. Several works have explored the effect of feedstock supplementation with calcium and magnesium oxide, silica and limestone [Malte 2008; Fan 1984; Bhattacharya 2003]. After providing an overview of the characteristics of the inorganic fraction of some biomass types, we describe the effect on ash thermal behaviour with the addition of calcium oxide (CaO), silicon oxide (SiO_2), magnesium oxide (MgO), and calcium carbonate ($CaCO_3$) to corn grain (CG), sunflower cake (SC), and wheat straw (WS).

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2. Materials and methods

The experimental activity involved in this work was articulated in three phases.

2.1 *Determination of biomass ash characteristics*

In the first phase we determined the quantitative and qualitative characterisation of the inorganic fraction of 20 biomass materials (tab. 1), including agri-

No.	Biomass feedstock	Type
1	Wheat	Amylaceous biomass (AB)
2	Durum wheat (grains)	
3	Dent corn (grains)	
4	Flint corn (grains)	
5	Spruce	Woody biomass (WB)
6	Beech	
7	Wood (chips)	
8	Olive tree prunings	
9	Vine prunings	
10	Sawdust	
11	Corn (whole plant)	Herbaceous biomass (HB)
12	Sorghum (chips)	
13	Wheat (straw)	
14	Rice (straw)	
15	Olive residues	Agro-industrial residues (AR)
16	Grape residues	
17	Sunflower cake	
18	Rape cake	
19	Citrus residues	
20	Wheat bran	

Table 1 - Biomass feedstocks analysed.

cultural by-products and residues, forestry residue and crop discards, chosen as representative of the widely heterogeneous agro-industrial and forestry feedstocks, to provide a reference framework for the thermal behaviour of biomass ash.

The ash content (A_c) of the 20 biomass feedstocks was determined according to the CEN/TS 14775 standard; the materials were assigned to the CEN/TS 14961 classes on the basis of their A_c, expressed as a proportion of dry matter The A_c range of each class, defined using the general master table for the specification of the properties of other solid biofuels (CEN/TS 14961), is reported in table 2.

CEN/TS 14961 *classes*	***Ash content (A_c)range***
	(% d.m.)
A3	0 – 3
A6	3 – 6
A10	6 – 10
A>10	>10

TABLE 2 - Feedstock classification based on ash content.

The second phase involved determination of the fusibility temperature of the ash of the 20 feedstocks. To do this ash was obtained by burning each biomass feedstock in a muffle incinerator at 550 °C and then subjected to granulometry reduction, to obtain a more homogeneous fine powder. Its fusibility temperature was determined in an oxidising atmosphere according to CEN/TS 15370, using an ash fusion analyser (IF 2000F, Sylab company) whose upper limit of detection was 1550 °C. The procedure involved preparation in a metal mould of a regular, cylindrical, solid test piece to be introduced into the ash fusion analyser. Fusibility analysis is based on detecting changes in the physical state (i.e. shape) of the test piece subjected to a rising temperature gradient, using an image recognition system made up of a video camera connected to a computer; an ad hoc software identifies sample geometry, where four main melting phases can be distinguished in relation to four characteristic temperatures, i.e. shrinkage, deformation (D_T), hemisphere and flow temperature (F_T) (CEN/TS 15370). D_T is the most informative parameter to understand the behaviour of ash in the boiler and the temperature at which agglomeration may arise. The fusibility test data allow a subdivision of the materials into quality categories in relation to the typical operating temperatures of biomass combustion plants.

The D_T range of each proposed category is listed in table 3. The operating temperature of large plants, where some of the biomass feedstocks considered are burned, generally ranges between 850°C and 1000°C [Sjaak 2008]. Ash deposits form on the surface of heat exchange banks at flue gas temperatures less than

Ash quality categories	***Range of deformation temperature (D_T)***
	(°C)
Low melting	< 1000
Medium melting	1000 - 1300
High melting	>1300

TABLE 3 - Classification of biomass in relation to ash melting temperatures.

1000ºC [Van Loo 2008]. The maximum fuel bed temperatures that apply in grate combustion of biomass materials are generally of the order of 1000-1200ºC, and the overall residence time on the grate is relatively long, usually several minutes [Van Loo 2008]. Fusion temperatures in excess of 1300°C are therefore believed not to cause problems.

2.2 *Measurement of data repeatability*

The method used to determine the ash melting temperature also envisages the possibility of determining measurement error. Preparation of the cylindrical test pieces is particularly critical, since the system's sensitivity in recognising their shape changes along the temperature gradient depends on their regular shape. Since current standards provide no indications on how to assess method accuracy or data repeatability, the tests of some ash samples, CG, WS and SC (selected for their low melting temperature), were run 6 times. Simple, descriptive statistics were applied to the results.

2.3 *Biomass material supplementation with mineral additives*

In the third phase of the work, known quantities of CaO, SiO_2, MgO and $CaCO_3$ mineral additives (> 90 % purity) were added to CG ash to examine to what extent it affected its melting temperature [Werther 2000; Zintl 1998; Van Ommen 2001; Llorente Fernandez 2006, Malte 2008, Fan 1984]. These minerals are already found in variable amounts in biomass ash and have a very high melting temperature. CG ash, ground in a hammer mill fitted with a 1 mm grid and dried on a stove at 105°C, was supplemented with 4 different additive concentrations (A_d): 0.25 %; 0.5 %; 0.75 %; 1 %. The 16 mixtures thus obtained were processed in the same way as the ash material (granulometry reduction and muffle incineration) and then subjected to fusibility analysis (CEN/TS 15370). Their fusibility temperatures were correlated with additive type and dose. The two additives inducing the strongest effects on D_T , with A_d equal to or less than 0.5 %, were added to WS and SC for a fusibility analysis by the same procedure.

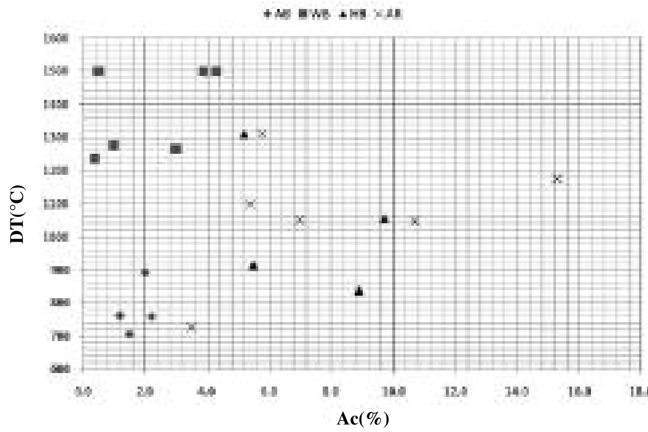
3. Results

The findings of the first two phases, i.e. the A_c and D_T of each sample, are reported in table 4. The A_c of the 20 biomass feedstocks ranged widely, from 0.5 % to ca. 15 %. D_T, the most informative parameter to understand the behaviour of ash in the boiler and the temperature at which agglomeration may arise, also showed widely different values that ranged from 800 °C up to more than 1500°C.

The quality and quantity findings are illustrated in diagram form in figure 1. The data are reported on a grid as the D_T to A_c ratio, which defines the quality category of each material. Their distribution shows that the different feedstocks tend to form separate groups: WB, which have low A_c and high D_T, cluster on the upper left side; HB are arranged in the middle; AB, which have low A_c but low melting temperature, cluster on the lower left side, whereas AR, which include materials of different origins and types, are scattered.

3.1 *Assessment of data repeatability*

Tables 5, 6 and 7 report the results of the fusibility analysis of CG, WS and SC, respectively, including the melting temperature of each of the 6 test pieces and their mean, standard deviation (SD), and coefficient of variability (CV). The variability of D_T was quite narrow ($CV < 1$ %).



WB: Woody biomass; HB: herbaceous biomass; AB: amylaceous biomass; AR: agro-industrial residues.

Fig. 1 - Qualitative and quantitative characterisation of the ash of the 20 biomass materials examined.

3.2 *Change in ash fusibility temperature after feedstock supplementation with the mineral additives*

The results of the fusibility tests of additive-supplemented ash are reported in table 8, where the mean ash fusibility temperatures of the six CG tests runs without additives (tab. 5) are used as the baseline.

The same data are reported in figure 2, where the increased deformation temperature is correlated with additive concentrations. MgO was the most effective

No.	Biomass feedstock	Type	A_c	D_T	F_T
			(%)	(°C)	(°C)
1	Wheat	Amylaceous biomass (AB)	2.2	760	819
2	Durum wheat (grains)		2.0	891	965
3	Dent corn (grains)		1.2	761	814
4	Flint corn (grains)		1.5	706	791
5	Spruce	Woody biomass (WB)	0.4	1236	1280
6	Beech		0.5	1500	>1500
7	Wood chips		3.0	1266	1350
8	Olive tree prunings		4.3	1500	>1500
9	Vine prunings		3.9	1500	>1500
10	Sawdust		1.0	1277	1356
11	Corn (whole plant)	Herbaceous biomass (HB)	5.2	1311	1373
12	Sorghum chips		5.5	914	1208
13	Wheat (straw)		8.9	839	1244
14	Rice (straw)		9.7	1057	1371
15	Olive residues	Agro-industrial residues (AR)	10.7	1046	1177
16	Grape residues		5.8	1310	1380
17	Sunflower cake		5.4	1098	1224
18	Rape cake		7.0	1051	1119
19	Citrus residues		15.3	1175	1196
20	Wheat bran		3.5	726	875

TABLE 4 - Combined biomass ash classification.

Test piece No.	Shrinkage temperature (°C)	Deformation temperature (°C)	Hemisphere temperature (°C)	Flow temperature (°C)
1	742	756	805	811
2	772	763	800	809
3	609	752	803	808
4	710	761	805	813
5	671	772	809	821
6	663	759	810	822
Mean	**695**	**761**	**805**	**814**
SD	58.9	6.8	3.7	6.1
CV (%)	8.5	0.9	0.5	0.8

TABLE 5 - Results of six test runs (corn grain).

Test piece No.	Shrinkage temperature (°C)	Deformation temperature (°C)	Hemisphere temperature (°C)	Flow temperature (°C)
1	745	844	1131	1215
2	743	830	1105	1258
3	748	845	1130	1251
4	752	828	1080	1250
5	753	848	1085	1258
6	749	841	1101	1233
Mean	**748**	**839**	**1105**	**1244**
SD	3.9	8.3	21.6	17.0
CV (%)	0.5	1.0	2.0	1.4

TABLE 6 - Results of six test runs (wheat straw).

Test piece No.	Shrinkage temperature (°C)	Deformation temperature (°C)	Hemisphere temperature (°C)	Flow temperature (°C)
1	927	1099	1131	1228
2	925	1094	1127	1222
3	932	1092	1152	1212
4	925	1098	1145	1264
5	912	1100	1142	1204
6	919	1103	1155	1213
Mean	**923**	**1098**	**1142**	**1224**
SD	6.9	4.0	11.2	21.4
CV (%)	0.8	0.4	1.0	1.7

TABLE 7 - Results of six test runs (sunflower cake).

Additive concentration (%)	Shrinkage temperature (°C)	Deformation temperature (°C)	Hemisphere temperature (°C)	Flow temperature (°C)
0	695	761	805	814
		SiO_2		
0.25	764	986	1236	1315
0.5	800	1260	1382	1425
0.75	874	1419	>1500	>1500
1	858	1457	>1500	>1500
		MgO		
0.25	1163	1329	1458	1464
0.5	1347	1406	1477	>1500
0.75	1329	1456	>1500	>1500
1	1406	1463	>1500	>1500
		CaO		
0.25	978	1072	1140	1170
0.5	1209	1441	1459	>1500
0.75	1308	>1500	>1500	>1500
1	>1500	>1500	>1500	>1500
		$CaCO_3$		
0.25	743	1020	1032	1040
0.5	1007	1134	1186	1199
0.75	1155	1225	1301	1358
1	1230	1447	1466	>1500

TABLE 8 - Ash melting temperatures of corn grain supplemented with mineral additives.

additive in raising the D_T of CG ash. In particular, the addition of 0.25% MgO raised it from 756°C (CG without additives) to > 1400°C. CaO was slightly less effective. Finally, 0.8% SiO_2 and 1% $CaCO_3$ were required to achieve a D_T > 1400°C.

Figures 3 and 4 describe the effect on ash thermal behaviour of WS and SC supplementation with MgO and CaO, the two additives that proved to be the most effective in the tests with CG. D_T increased in both feedstocks, but not as much as it did with CG. The increase was between 250°C and 350°C in the case of WS, and was greater using MgO, especially at A_d less than 0.5 %, whereas when 1 % of MgO was added to SC the gain was barely 200°C.

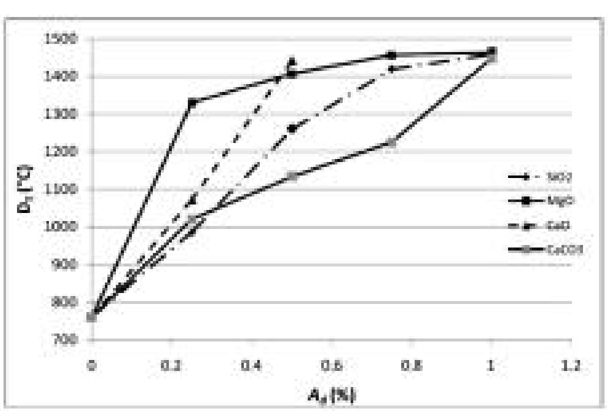


Fig. 2 - Deformation temperature (D_T) of corn grain ash as a function of additive concentration (A_d).

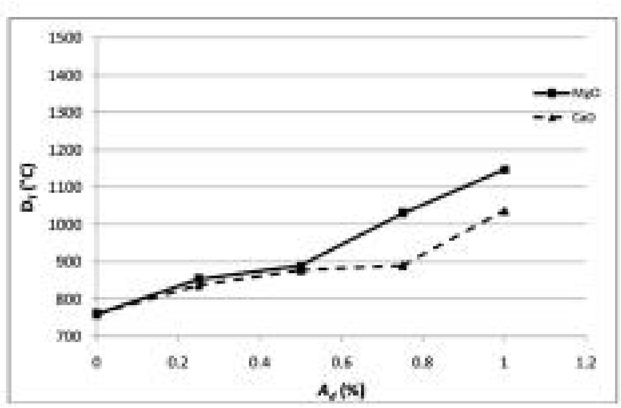


Fig. 3 - Deformation temperature (D_T) of wheat straw ash as a function of additive concentration (A_d).

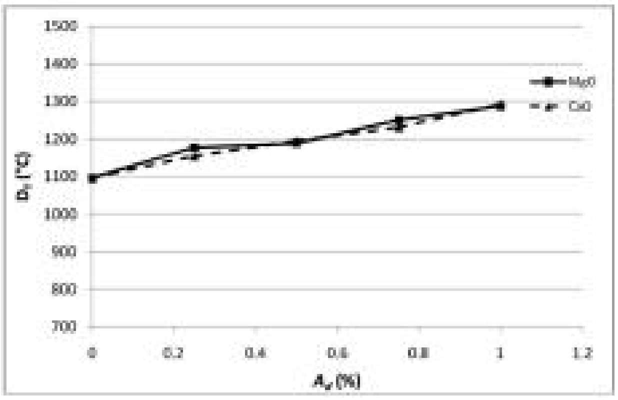


Fig. 4 - Deformation temperature (D_T) of sunflower cake ash as a function of additive concentration (A_d).

4. Conclusions

Analysis of biomass feedstocks based on their inorganic fraction demonstrated a very broad range of values of ash content and deformation temperature. Since materials with similar origin were seen to have comparable quality, it is conceivable that feedstocks that were not analysed here will be found to contain similar inorganic fractions as tested feedstocks having similar quality. Nevertheless, supplementation with inorganic additives was able to change the thermal behaviour of some feedstock and to improve their ash melting temperature, though negatively affecting their A_C. In the materials exhibiting a linear D_T response to the additive, it seems possible to calculate the amount of additive, to be added to the initial biomass, that will achieve a stable temperature range. MgO and CaO were the most effective of the additives tested, since small amounts exerted a strong effect on D_T. In particular, ca. 0.2 % of MgO or CaO were seen to be required to raise the D_T of CG to a temperature greater than 1300 °C, to achieve a relative A_c increase of 12-15 % compared with pure CG, since its value would increase from 1.5 % to approximately 1.7 %.

Whereas supplementation with additives was very effective in the case of CG, it did not raise the ash melting temperature of SC and WS to a sufficient extent, possibly due to their different ash content. In other words, the lower the A_c content of the additive-supplemented feedstock, the greater the additive's effect in raising D_T. Achieving the same effect (D_T = 1300 °C) with WS using MgO would require an A_d of about 1.6 %. In such case the additive mixture would raise the A_c of the biomass feedstock from ca. 8.9 % to ca. 10.5 %, whereas achieving the same result with SC would require an A_d of 1%, resulting in an increase in the A_c of the mixture from 5.4 % to 6.4 %.

If these processes can be extended to other biomass types (on which work is now in progress in our laboratory) and, especially, if the effects obtained with the analyser can be reproduced in the actual combustion plant, the decision to use additives and their amount would be dictated by economic factors (cost of purchase and disposal).

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SUMMARY

The increased consumption of solid biomass for energy production has raised a number of technical problems that are mainly related to the variability of the chemical-physical characteristics of feedstocks. The low melting temperature of their inorganic fraction is the main cause of these problems. In this work analysis and comparison of the thermal behaviour of ash from 20 different feedstocks highlighted that biomass materials with the same origin share similar qualitative and quantitative characteristics. A feedstock from a starch group, corn grain, was tested for the effects of four mineral additives (MgO, CaO, $CaCO_3$, and SiO_2) on ash deformation temperature. MgO and CaO seemed to be the most effective, raising ash melting temperature and enhancing the thermal behaviour of the feedstock. The results of supplementation of the initial corn grain, wheat straw and sunflower cake biomass demonstrated that the amount of additive to be used is a function of biomass type and can depend on its ash content.

Keywords: biomass, ash behaviour, melting temperature, inorganic additive.

List of symbols

A_c	ash content with reference to dry weight (%)
A_d	additive content with reference to dry weight (%)
CG	corn grain
WS	wheat straw
SC	sunflower cake
CV	coefficient of variability (%)
D_T	deformation temperature (°C)
F_T	flow temperature (°C)
AB	amylaceous biomass
WB	woody biomass
HB	herbaceous biomass
AR	agro-industrial residues