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SINTERING REDUCTION OF HERBACEOUS BIOMASS WHEN BLENDED WITH WOODY BIOMASS: PREDICTION AND COMBUSTION TESTS

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ABSTRACT: The objective of this study was to predict and reduce the sintering behaviour of two herbaceous biofuels (triticale and corn straw) by the addition of three woody biofuels (poplar, pine and eucalyptus). Two CIEMAT laboratory in-house methods (disintegration and sieving methods) and the technical specification on ash melting behaviour (CEN/TS 15370-1) were used to predict ash sintering properties of the studied biomasses, and to determine the adequate blends to be used in subsequent combustion pilot plant tests to minimise ash sintering. Moreover, the mechanisms for reducing the slagging and fouling were evaluated and studied by analyses (e.g. ICP-OES and XRD) of biomass and ash collected from the combustion pilot plant (0.5 MWth).

Laboratory predictive methods were validated by comparing the information they provided with the results obtained by inspecting and analysing the ash collected in the pilot plant. The sieving and the disintegration methods can be used to predict ash melting behaviour and to select the optimal amount of woody biomass that should be blended with herbaceous biomass. The selected corn straw does not need to be blended with any woody biomass. In contrast, very high concentrations of woody biomass should be added to obtain significant results in reducing the sintering of triticale. These proportions of the woody biomass in the blend could

be even clearly higher than 50 wt.% (ash basis). The dilution effect seems to be the main mechanism for reducing the sintering.

Keywords: biomass, blending, slagging, sintering, chemical composition, combustion.

1 INTRODUCTION

The European Union is experiencing an important energy increase derived from biomass [1] and thus, the use of biomass is expected to increase in small and large-scale applications for producing heat, electricity, or for combined heat and power generation. The supply of traditional woody biomass to cover the expected future demand in those sectors makes the incorporation of new feedstocks to the market a promising alternative to cover the limited availability of high-quality woody biomass while reducing at the same time the costs of feedstock supply. In this context, increasing importance of herbaceous biomass from herbaceous agricultural residues and energy crops produced under sustainable conditions in the biomass feedstocks market [2] can be expected.

However, the introduction of herbaceous biomass to completely replace woody biomass leads to increased sintering and corrosion problems due to the high contents of alkaline compounds that are contained in the ash fraction of this type of biomass. The formation of slags can cause shutdowns of thermal plants and boilers and the formation of deposits of sintered ash on the surface of heat exchangers, which reduces heat exchange capacity and hinders the cleaning process of deposited ash, increasing maintenance costs.

There are several alternatives for reducing the formation of slags and sinters in herbaceous biomass combustion. Some of them are related to the combustion process conditions, as a

reduction of combustion temperature, but unfortunately a high amount of unburnt material could be generated, while others concern to the preparation of the biofuels prior to combustion or modification of their chemical properties. This is the case of herbaceous biomass leaching [3-5], biomass pyrolysis followed by combustion of the pyrolysis products [6] and the utilisation of mineral additives or the co-combustion with woody biomasses. [7-9].

To the authors' knowledge, co-combustion could be the most efficient process from an economic point of view. That latter process involves the addition of biofuels or fuels prior (co-combustion) or directly to combustion facilities (co-firing), with the aim of enhancing the melting temperature of the resulting ash, i.e. to mitigate the problems of slagging, fouling and even corrosion. Therefore, the co-combustion or co-firing of herbaceous biomass with woody biomass, which usually show higher ash melting temperatures, could be an optimum solution by generating an improved blend.

In the above context, the availability of suitable laboratory methods for predicting the ash sintering behaviour of biomass ash and ash blends is a key issue for obtaining reliable information on the appropriate blends to be used in combustion plants. At present no normalised method exists for solid biofuels to predict biomass ash sintering behaviour. There is a draft or technical specification (CEN/TS 15370-1), which often uses expensive instruments called optical heating microscopes. Moreover, some characteristic temperatures obtained following this technical specification [10] on ash melting behaviour cannot be always considered reliable temperatures [11], e.g. the initial sintering is not well-defined and its degree of sintering requires more research.

In this paper, the effect of adding woody biomasses (poplar, pine, eucalyptus) to two

herbaceous biofuels (corn straw and triticale) with the aim of reducing ash sintering in combustion facilities was studied at laboratory scale and in a 0.5 MWth pilot plant. Moreover, the suitability of three laboratory tests, two in-house methods and the procedure described in CEN/TS 15370-1 to predict the ash sintering behaviour of separate biofuels and their blends is comparatively discussed. Therefore, this work offers valuable information for planning and decision-making that may help optimise biomass blends in order to reduce ash sintering in combustion applications.

2 MATERIALS AND METHODS

2.1 Biomass and pre-treatment

Two different herbaceous biomasses, triticale (T) and corn straw (C) were selected for this work. Corn straw is one of the most traditional herbaceous biomasses, while triticale (aerial part, i.e. complete plant without root) is a crop sometimes used as fuel in biomass power plants.

The woody biomasses selected to improve the combustion performance of the aforementioned herbaceous fuels were poplar (PO), pine (PI) and eucalyptus (EU). Complete trees without roots of each woody biomass were cut for this work. Pine, poplar and eucalyptus are woody species well studied as energy crops. With the exception of corn straw, all biomasses utilised in this study came from experimental energy crop plantations.

Prior to testing, all biomasses were initially crushed in a 22 kW shredder and ground to pass a 50 mm sieve by means of a 30 kW knife mill. Only pine and eucalyptus needed pre-drying in a rotary drier up to reduce moisture content below 15% wet basis. Solid biofuels were finally stored in big-bags until further use.

2.2 Sample preparation and analytical methods

Sampling was performed according to ISO 18135. More than 20 elementary samples per biofuel were collected from different parts of all the big-bags where they were stored and mixed to form each laboratory sample. Samples were homogenized, divided, ground and dried, following the international standard ISO 14780 on sample preparation.

2.2.1 Solid biofuel analysis

Physical and chemical tests were performed according to the current ISO standards for solid biofuels. The following fuel properties were determined: moisture, ash content, volatile matter, calorific value, and chlorine, sulphur, carbon, hydrogen and nitrogen contents. Major elements were determined following ISO 16967 by digesting the ash, obtained from the fuel at 550 °C, in a microwave furnace and analysing the resulting solution by ICP-OES (Jarrell Ash, Thermo Fischer).

2.2.2 Ash analysis

On ash samples, similar analytical procedures to those used in biofuel samples were applied, with the exception of chlorine. Chlorine was determined in the ash following the American standard ASTM D-2361-66, based on the combustion of the sample with the Eschka mixture and subsequent quantification of the chloride by an indirect Volhard titration. Additionally, and to get the unburnt matter in ash, these samples were introduced in a laboratory furnace at 550 °C for 24 hours, and unburnt matter was calculated as a difference from 100%.

Particle size distribution of the ash collected in the combustion pilot plant (see Section 2.4) was performed for the purpose of determining the degree of sintering (see Section 3.2).

Total, organic, and inorganic carbon were determined by analysing the carbon content of the ash, before and after samples were treated with HCl, following ISO 10694 “Soil quality- Determination of organic and total carbon after dry combustion (elementary analysis)”. When samples are treated with HCl, the inorganic carbon is released as CO₂. The inorganic carbon was calculated as the difference between the total carbon initially present in the ash and the carbon present in the ash residue after HCl treatment (organic carbon).

The mineral composition of the ash samples was determined by X-ray diffraction using a PANalytical X'pert-PRO diffractometer working at 45 KV and 45 mA. The identification of the mineral phases was made by using the Inorganic Crystal Structure Database (Fiz Karlsruhe, Germany). Rietveld analysis was used for semi-quantification.

2.3 Laboratory sintering methods

It is important to note that the predictions established in laboratory may not be really representative of deposit formation and its sintering in boilers due to several mechanisms such as particle transport (inertial impaction, Brownian diffusion or thermophoresis), phase changes and chemical reactions, which happen in a different extent within the different parts of the boilers.

As mentioned above and for the purpose of predicting the ash melting behaviour of biomasses and their blends in combustion plants, the herbaceous biofuels, triticale (T) and corn straw (C) were burned to ash at 550 °C and their ash blended at different proportions (25 wt.%, 50 wt.% and 75 wt.%) with woody biofuel ash. Afterwards three laboratory sintering assessment methods were used.

The first sintering assessment method was based on the changes in shape detected during the heating of a cylindrical biomass ash pellet (3 mm diameter and 3 mm height) from room temperature to 1400 °C in an atmosphere of air. The characteristic temperatures measured by an optical heating microscope were: deformation, hemisphere and fluid, following the CEN/TS 15370-1 pre-standard [10].

Two in-house methods were also used to predict the ash melting behaviour in the biofuel ash blends. One of them was a traditional method called the disintegration method, and the second (called sieving method) was an extension of the first one to try to quantify the results.

Both tests were performed by heating the biomass ashes and their ash blends, previously produced at 550° C, at different temperatures in a laboratory furnace: 800° C, 1000° C, 1200 °C and 1400° C. These temperatures cover a wide range of temperatures, which varied from the initial sintering to the complete melting. At each temperature selected, 0.5 g of loose ash, which had a grain size below 0.5 mm, was added to a porcelain capsule. Then, the capsules were rapidly heated at each temperature selected. The atmosphere was air.

Finally, the alterations produced in the resultant ash were observed such as the visual aspect and the easiness of manual ash disintegration. In regard to this last characteristic, four levels of difficulty were established:

Level 1: very easy disintegration of the ash: dust

Level 2: easy disintegration of the ash: weak agglomerates or sinters

Level 3: difficult disintegration of the ash: hard sinters

Level 4: very difficult disintegration of the ash: very hard sinters or slags

This method will be referred to as the “disintegration” method in this paper, and it was always performed by the same laboratory operator in order to obtain a good repeatability.

The sieving method was based on the measurement of ash particle size distribution. At the end of each heating process, the heated ash was placed in a small sieve (6 cm diameter) with a sieve aperture of 0.5 mm. The sieving process lasted 5 minutes by using a CISA device, model RP 15, where the level of vibration was about 60 cycles per second due to the alternating current. The vibration amplitude of each cycle was fixed at approximately 0.5 mm in the three dimensions by selecting level 5 in the sieving machine (the levels in the machine go from 1 to 15). Finally, the index was calculated as follows:

$$\text{Tendency to slag formation (TSF)} = \text{mass of sample remaining on the sieve} / \text{initial mass} \times 100$$

This in-house method (sieving) can also be used to predict the ash melting behaviour in other fuel ash blends using, e.g. coal, peat, municipal solid residues or residues of animal and human origin.

The following table shows the uncertainty associated with the pre-standard and sieving method for a sample of wheat straw utilised as a reference. The criteria established for determining the uncertainties was based on the ISO "Guide to the Expression of Uncertainty in Measurement" by applying analyses of variance. The combined uncertainty (u), which includes all sources of uncertainty, is expressed as standard deviation (SD). The relative combined uncertainty (ru) expressed in percentage as relative standard deviation (%RSD) is also included.

Table I: Combined uncertainty (U) and relative uncertainty (RU) of fusibility and sieving methods.

	Units	Mean	±U (SD)	±%RU (%RSD)
DT	°C	829	26	3.2
HT	°C	1072	2.0	0.18
FT	°C	1099	5.7	0.51
TSF at 700 °C	wt.%			
TSF at 750 °C	wt.%			
TSF at 800 °C	wt.%	99	1.5	1.5

DT: deformation temperature; HT: hemisphere temperature; FT: fluid temperature; TSF: Tendency to slag formation

2.4 Combustion pilot plant, combustion conditions and sampling

In order to compare the laboratory prediction results and so to perform a validation from the laboratory data to semi-industrial scale, several combustion tests (see Sections 3.2 and 3.3) were carried out in a grate of the combustion pilot plant (0.5 MWth).

A diagram of the combustion plant is shown in Fig. 1. The biomass supply system basically consisted of two bins with a screw conveyor of variable speed, where the woody biofuel was partially blended with the herbaceous biofuel and introduced into the boiler. The total biomass discharge was around 150 kg/h. The furnace contained a heat exchanger, where the flue gases and particles flowed downwards internally through three arrays of tubes. Combustion air was introduced into the furnace by three fans (one for primary air and two for secondary air, one in each side of the boiler) and fumes were forced to flow by another fan. In order to remove particles from exhaust gases, a multi-cyclone was used. The duration of each combustion test was approximately 6 hours under steady-state conditions, with a start up around 2 hours. Primary air (about 50% of the total air) was distributed through multiple holes placed in the moving grate. Secondary air was introduced by six orifices placed in the walls of the furnace. The air excess was around 60% in all combustion tests. The carbon conversion efficiency in the grate combustion pilot plant was higher than 95%.

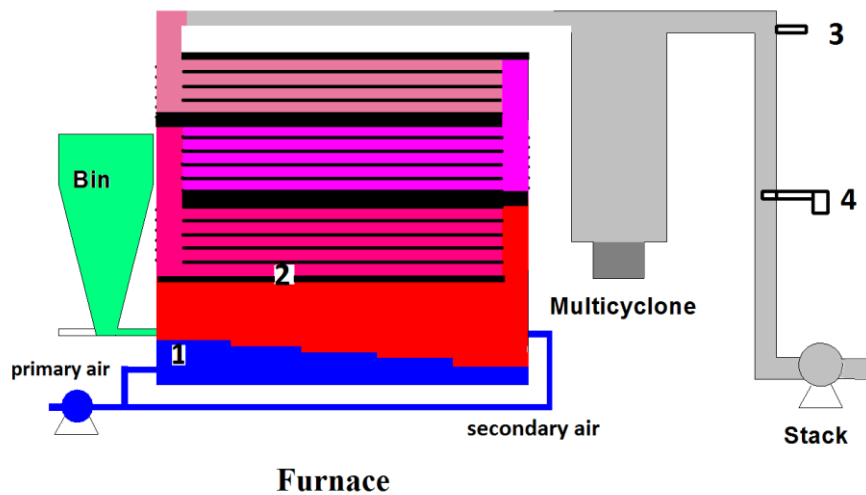


Figure 1: Diagram of the grate combustion pilot plant. 1: moving grate, 2: first heat exchanger, 3: outlet for continuous gas analyser, 4: TSP sampling.

The following ash locations were sampled after each combustion test for physical and chemical characterisation:

- Grate ash and slags: Grate ash was collected in the grate of the pilot plant after passing a screw conveyor. A representative laboratory sample was then extracted from all the material collected in the grate by coning and quartering. Slags, if any, were collected manually before passing through the screw conveyor to avoid losses by disintegration.
- Ash deposited on the first heat exchanger: An ash sample was taken by scrubbing the inner surface of the first heat exchanger. Sinters, if present, were collected manually to avoid disintegration losses.
- Total solid particles (TSP) in stack emissions: TSP were measured under isokinetic conditions following ISO 9096 “Stationary source emissions-Manual determination of mass concentration of particulate matter”.

A continuous analyser was utilised to measure the emission levels of O₂, CO, CO₂, NO and SO₂. Measurement of the gaseous composition of exhaust gases during combustion tests was

carried out with a portable FTIR (Fourier transform infrared spectroscopy) analyser and a zirconium oxide cell to determine the concentration of O₂.

3 RESULTS AND DISCUSSION

3.1 Prediction of sintering reduction in laboratory applied to biomass blends

The average value of the main properties of the biofuels utilised in this study is shown in Table II. As expected, the two herbaceous biofuels (corn straw and triticale) presented higher contents of ash, nitrogen, chlorine and sulphur than woody solid biofuels.

Table II: Averaged values of physical and chemical characterisation of the herbaceous and woody biomass.

	Unit	Corn	Triticale	Poplar	Pine	Eucalyptus
<i>Calorific values</i>						
GCV	MJ/kg d.b.	17.11	17.89	19.75	20.04	18.60
NCV	MJ/kg d.b.	15.93	16.63	18.44	18.75	17.37
<i>Proximate analysis</i>						
Ash	wt.% d.b.	9.0	7.4	1.8	3.1	5.4
Volatile matter	wt.% d.b.	73.8	75.2	84.0	79.2	76.3
<i>Ultimate analysis</i>						
Carbon	wt.% d.b.	42.3	44.4	49.6	50.4	47.8
Hydrogen	wt.% d.b.	5.4	5.8	6.0	5.9	5.6
Nitrogen	wt.% d.b.	0.71	0.77	0.49	0.26	0.10
Sulphur	wt.% d.b.	0.09	0.08	0.07	0.03	0.02
Chlorine	wt.% d.b.	0.54	0.25	0.07	0.04	0.09
<i>Ash composition</i>						
Al ₂ O ₃	wt.% d.b.	5.6	2.3	1.2	5.7	4.0
BaO	wt.% d.b.	0.027	0.039	0.051	0.037	0.073
CaO	wt.% d.b.	4.7	5.2	38	18	33
Fe ₂ O ₃	wt.% d.b.	1.9	0.82	1.2	2.6	1.4
K ₂ O	wt.% d.b.	11	13	11	5.9	4.1
MgO	wt.% d.b.	4.0	2.4	6.6	7.1	2.7
Mn ₂ O ₃	wt.% d.b.	0.14	0.21	0.096	0.58	3.3
Na ₂ O	wt.% d.b.	1.7	6.2	1.0	2.3	2.4
P ₂ O ₅	wt.% d.b.	2.4	2.3	4.8	3.1	2.2
SO ₃	wt.% d.b.	2.0	2.5	3.4	2.2	1.1
SiO ₂	wt.% d.b.	53	54	6.1	38	24
SrO	wt.% d.b.	0.024	0.009	0.12	0.038	0.16
TiO ₂	wt.% d.b.	0.36	0.18	0.040	0.38	0.19
ZnO	wt.% d.b.	0.015	0.023	0.077	0.059	0.034
Sum		86.1	89.9	73.9	85.9	77.9
<i>Fusibility temperatures</i>						
Deformation	°C	1200	840	1390	1210	1260
Hemisphère	°C	1300	1120	nd	1250	1330
Fluid	°C	> 1400	1250	> 1400	1350	> 1400

w.b.: wet basis; d.b.: dry basis; GCV: gross calorific value; NCV: net calorific value; nd: non detected

The fusibility temperatures included in Table II were determined according to CEN/TS

15370-1. As can be seen, the characteristic fusibility temperatures of the two herbaceous biofuels studied were very different. The deformation temperature (DT), which marks the beginning of melting and is therefore frequently used as the temperature of reference in laboratories and thermochemical facilities [12-14], was much lower for triticale (840 °C) than corn (1200 °C), indicating the higher tendency of the former to form sinters and slags, probably because of their lower alkaline-earth (CaO+MgO) to alkaline oxide (K₂O+Na₂O) ratios (<0.7) [14]. A previous study demonstrated that biofuels with alkaline-earth to alkaline oxide ratios higher than 2 are not expected to cause sintering problems in power plants [14]. As expected, woody fuels exhibited higher alkaline-earth to alkaline oxide ratios (≥ 3) and DTs (≥ 1210 °C, Table II) and, therefore, the addition of these biofuels to the considered herbaceous biofuels is expected to improve the sintering behaviour of triticale in particular.

The ash fusibility temperatures (CEN/TS 15370-1) of the herbaceous and woody ash blends are shown in Table III.

Table III: Fusibility temperatures (CEN/TS 15370-1) of corn and triticale ash blends (25 wt.%, 50 wt.% and 75 wt.%) with woody biomass ash.

Blending	DT (°C)	HT (°C)	FT (°C)	Blending	DT (°C)	HT (°C)	FT (°C)
Corn 100%	1200	1300	> 1400	Triticale 100%	840	1120	1250
Corn + Poplar 25%	1280	1360	1380	Triticale + Poplar 25%	1050	1130	1190
Corn + Poplar 50%	1170	1220	1230	Triticale + Poplar 50%	1140	1160	1180
Corn + Poplar 75%	1320	1390	> 1400	Triticale + Poplar 75%	1190	1350	1400
Poplar 100%	1390	nd	> 1400	Poplar 100%	1390	nd	> 1400
Corn + Pine 25%	1210	1260	1320	Triticale + Pine 25%	930	1130	1240
Corn + Pine 50%	1230	1250	1310	Triticale + Pine 50%	1120	1240	1370
Corn + Pine 75%	1210	1250	1310	Triticale + Pine 75%	1310	1380	> 1400
Pine 100%	1210	1250	1350	Pine 100%	1210	1250	1350
Corn + Eucalyptus 25%	1180	1230	1300	Triticale + Eucalyptus 25%	1080	1170	1220
Corn + Eucalyptus 50%	1230	1230	1240	Triticale + Eucalyptus 50%	1180	1220	1230
Corn + Eucalyptus 75%	1250	1260	1270	Triticale + Eucalyptus 75%	1190	1220	1230
Eucalyptus 100%	1260	1330	> 1400	Eucalyptus 100%	1260	1330	> 1400

DT: deformation temperature; HT: hemisphere temperature; FT: fluid temperature; nd: non-detected

Taking the data of Table III into account, the sintering tendency following the addition of woody biofuels, mainly pine and eucalyptus, to the corn sample was practically negligible as reflected by the fact that the deformation temperature (DT) was maintained around 1200 °C. In contrast, DT increased from 840 °C to around 1100 °C when 50 wt.% of woody biomass ash was added to triticale ash.

However, there are several issues when the addition of woody biomass to triticale is considered, e.g. the fluid temperature (FT) hardly varied as a function of the eucalyptus ash addition. DT in eucalyptus addition did not practically increase at 75% addition either. The latter results cannot be explained from a technical point of view because the DT and FT should rise proportionally to the eucalyptus addition. Another unexpected finding was the higher DT of the 75% pine-triticale blend (1310 °C) related to DT of the pure wood biomass, i.e. pine 100% (1210 °C).

Figure 2 shows the results obtained when the same ash blends were analysed by the sintering and sieving methods, the two in-house predictive tests used in this study.

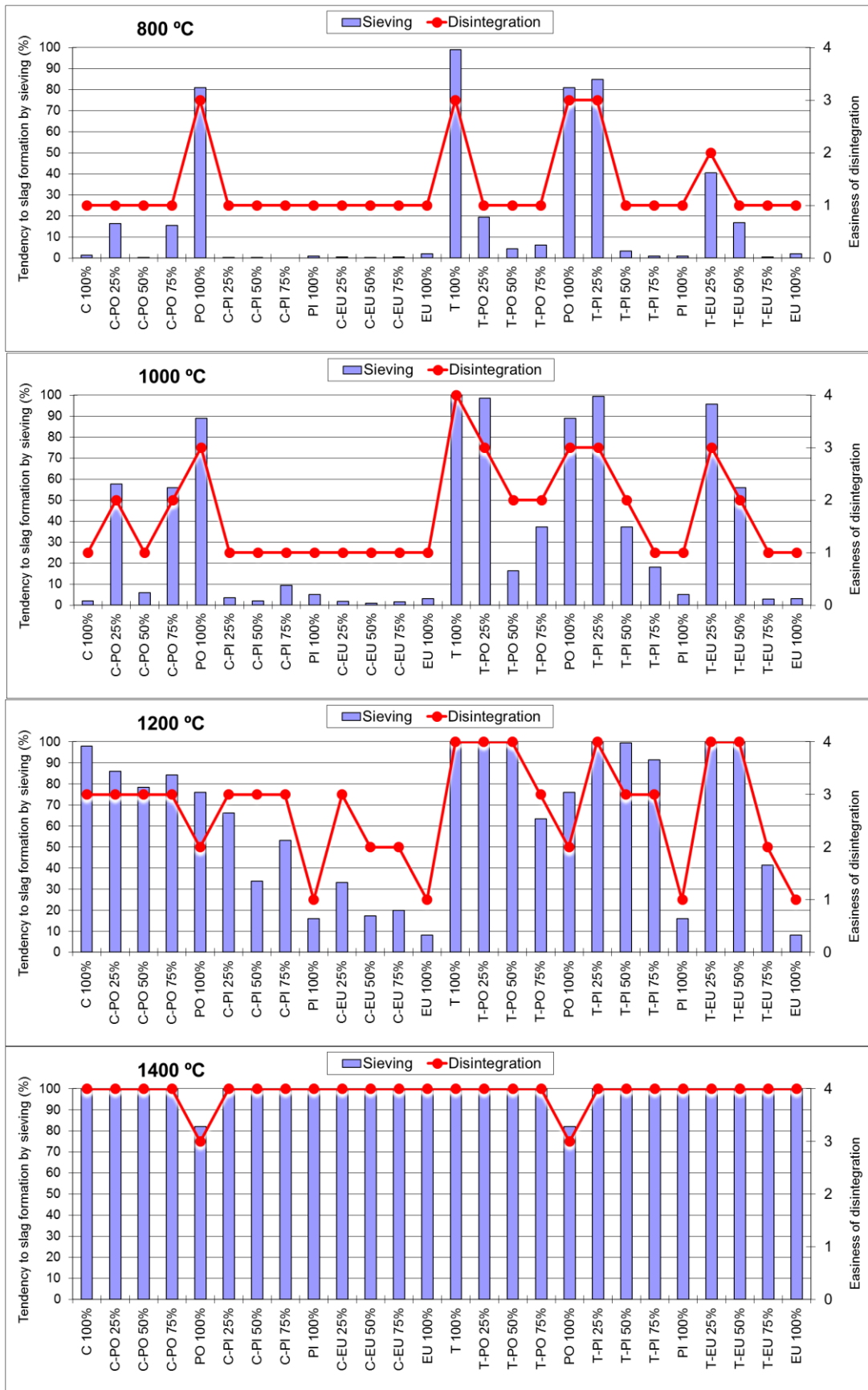


Figure 2: Results of sieving and disintegration methods of corn (C) and triticale (T) blends with woody biomass ash of poplar (PO), pine (PI) and eucalyptus (EU) at 800, 1000, 1200 and 1400 °C.

With the aim of comparing the sieving results to the disintegration results, the four levels of disintegration above (see Section 2.3 and Figure 2) can also be linked to other corresponding four levels of the sieving method by applying a simple regression model. Figure 3 shows the results of fitting a linear model to describe the relationship between the sieving results by applying the tendency to slag formation (TSF) and the disintegration results obtained in this study. The model explained 91% of the variability of the sieving method and the four levels of the sieving method were set as:

- Level 1: Ash as dust corresponds to a TSF below about 20%
- Level 2: Ash as weak agglomerates corresponds to a TSF between about 20% and 60%
- Level 3: Ash as hard sinters corresponds to a TSF between about 60% and 95%
- Level 4: Ash as slags corresponds to a TSF higher than about 95%

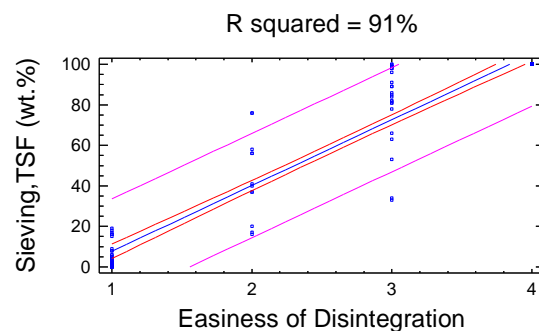


Figure 3: Correlation between sieving method as tendency to slag formation (TSP) and disintegration method.

In general and as can be seen in Figure 2, a disintegration level of 1 and 2 corresponded to TSF indices below 20% and 60%, respectively; a level of 3 was assigned to samples with TSF indices of about 80%, while a level of 4 was allocated those samples that showed TSF indices close to 100%. As mentioned, Figure 2 shows the overall good agreement between the disintegration method and the sieving method. Discrepancies between both methods were attributed to the qualitative nature of the results provided by the disintegration method, which

depends on the analyst's ability to perceive changes in ash texture.

Woody ash addition to corn straw did not generate any advantage at 800 °C and 1000 °C due to the fact that corn straw maintained, in general, a low sintering tendency with disintegration results of level 1 (very easy to disintegrate) and sieving results below 30%. In contrast, woody ash addition to the triticale ash was very positive because triticale had sieving results near 100% and disintegration results of level 3 (difficult to disintegrate) and level 4 (very difficult to disintegrate) at 800 °C and 1000 °C, respectively. As can be seen at 800 °C and 1000 °C, an ash addition of 25 and 50 wt.% of woody biomass respectively, was enough to maintain low levels of disintegration (1 and 2) and low levels of sieving index (below 60% as TSF). If the temperature was 1200 °C, an ash addition around or higher than 75 wt.% of woody biomass would be added to reduce triticale sinters. At very high temperatures such as 1400 °C, the effect of woody addition was negligible not only in triticale but also in corn straw.

Inspection of Figure 2 reveals that the woody addition to corn straw at 1200 °C had a positive effect when the wood was pine or eucalyptus. Poplar did not seem to reduce the sintering in corn straw, showing sieving indexes around 80% for all mixtures with poplar. Moreover, corn straw sintering at 1000 °C and 800 °C seemed to worsen with the poplar addition.

It is difficult to establish a level of sintering decrease among poplar, pine and eucalyptus but by considering, for example, the triticale blends at 1200 °C with 75% of poplar, pine and eucalyptus, it can be noted that addition of eucalyptus resulted in a lower disintegration index (2: easy to disintegrate) and sieving index (41%) compared to addition of pine and poplar (3: difficult to disintegrate and sieving index higher than 60%).

As opposed to the procedure described in CEN/TS 15370-1, the sieving and disintegration methods are simple procedures that do not require any expensive or specific instrumentation; only a laboratory furnace up to 1400 °C is needed, together with a balance and a sieve (in case of the sieving method), which are usually available in conventional laboratories performing basic analysis of solid biofuels. On the other hand, the analysis duration depends on the number of temperatures selected, and therefore, these can be time-consuming methods. The disintegration method is a more rudimentary procedure, and it highly depends on the analyst's judgement and ability to sense or perceive small changes in the consistency of the produced ash. A quantification of the ash sintering behaviour is possible by using the sieving method, as an index is obtained; the tendency to slag formation (TSF) expressed as a percentage.

3.2 Ash sintering study in the pilot plant combustion tests

According to results obtained in Section 3.1 and considering 1000 °C as the averaged reference temperature within the moving grate of the combustion pilot plant (0.5 MWth), an ash addition of woody biomass as high as 50 wt.% should be performed to decrease the sintering in the triticale. By recalculating this proportion (50 wt.%) from ash basis to biomass basis and taking the lower ash content of woody biomass compared to herbaceous biomass into account, woody biomass addition should be, in general, in the range from 50 wt.% to 90 wt.% to herbaceous biomass.

Three combustion tests were performed by blending 50% as weight percentage of triticale with poplar, pine and eucalyptus, respectively. By recalculating the cited percentage (50 wt.%) from biomass basis to ash basis and taking the ash content (Table II) of poplar, pine and eucalyptus into account, an ash addition about 20, 30 and 40 wt.%, respectively on triticale ash was obtained.

In order to validate the results of laboratory tests and to significantly decrease the slagging and fouling by the triticale biomass, a high dose of eucalyptus was also burnt by blending triticale with eucalyptus at 90 wt.% on ash basis, meaning the combustion test with a very high woody biomass dose. The combustion tests with 100 wt.% of triticale and 100 wt.% of corn straw were considered the reference tests for the purpose of completing the comparison with the laboratory tests of sintering prediction.

Relevant parameters measured during steady the state of each combustion test are shown in Table IV. The CO content was very high as a consequence of the poor distribution between the air and the loose biomass (without pelletising) fed to the plant. The total solid particles were also high because the pilot combustion plant only had a cyclone as the particle cleaning system. According to Tables I and IV, the results of particulate matter in the chimney were generally proportional to the ash content of the starting biofuels.

Table IV. Operating conditions and emission parameters during combustion tests

Biofuel	T_{inlet} (°C)	T_{outlet} (°C)	O_2 (v.% d.b.)	CO (mg/Nm ³ , d.b.)	TSP (mg/Nm ³ d.b.)
T	622	149	8.4	750	270
T EU 40%	636	161	8.4	660	220
T EU 90%	710	160	7.0	870	80
T PO 20%	606	150	9.3	1120	210
T PI 30%	653	155	8.4	470	170
C	593	146	8.8	1200	390

T_{inlet} is the temperature measured at the inlet of the heat exchanger; T_{outlet} is the temperature measured at the outlet of the heat exchanger; CO and total solid particles (TSP) are expressed at O_2 at 10 v.%; d.b.: dry basis. Triticale (T), eucalyptus (EU), poplar (PO), pine (PI) and corn (C).

Figure 4 shows the particle size distribution of the slags collected manually on the grate. The particle size measurement was carried out in order to evaluate the sintering tendency. It is very important to observe (Fig. 4) that the corn straw and the blending on ash basis of triticale with eucalyptus (90%) generated the lowest sintering due to the fact that the smaller the

particle size, the lower the sintering tendency. In contrast, the 100% triticale combustion test together with combustion tests of poplar, pine and eucalyptus blended with a 20%, 30% and 40% proportion, respectively, did not produce notable differences between them.

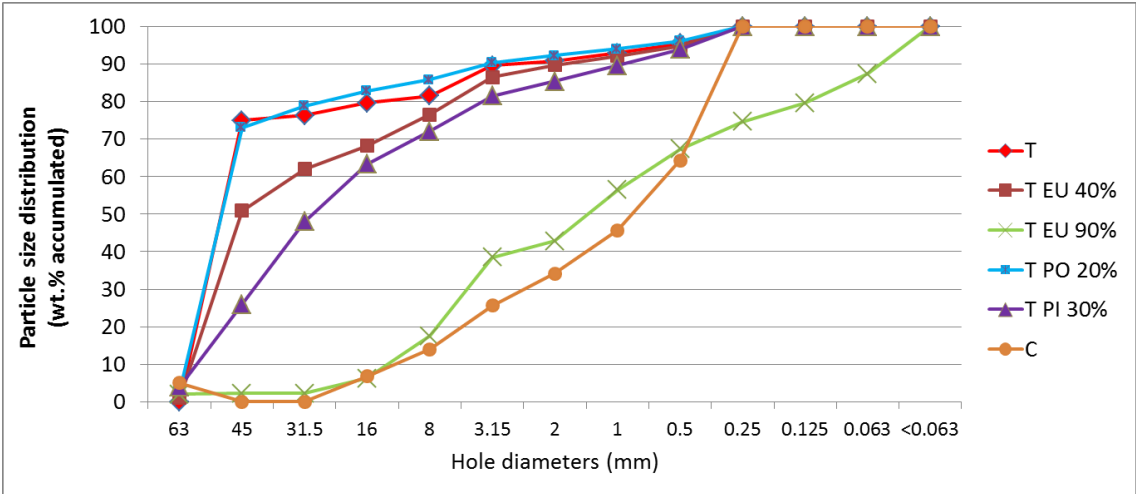


Figure 4: Particle size distribution of the slags collected manually on the grate of the pilot plant. Triticale (T), eucalyptus (EU), poplar (PO), pine (PI) and corn (C).

As was previously predicted in the laboratory tests, a reduction in sintering was obtained with high doses of woody biomass. Therefore, doses of eucalyptus, and very probably other woody biofuels, higher than 50 wt.% should be added to the triticale to almost completely reduce the slagging on the grate. Consequently, the experimental findings in the pilot plant are in agreement with the melting behaviour found in the sieving and disintegration laboratory tests. The corn straw combustion test produced very brittle slags similar to the triticale with eucalyptus (90%) combustion test, easily broken into little pieces, meaning that the corn straw did not generate any slagging problem, as was also forecasted in the laboratory tests of Section 3.1.

Concerning the ash deposited inside the tubes of the first heat exchanger (Fig. 5), it can be said that the size of the ash inside the 1st heat exchanger was similar in all combustion tests,

where some small and very brittle sinters were found but without substantial differences. One explanation of this result could be a lower temperature in that zone around 600 °C (Table IV), where the total or partial fusion of the alkaline compounds is less likely, compared to the bed zone (about 1000 °C as estimated). Although, it is important to note that the different composition of biofuel ash in the laboratory compared to the ash deposited on heat exchangers, where the alkaline compounds were enriched (see next Section 3.3) and therefore complicating the prediction of the sintering tendency in that convective zone.

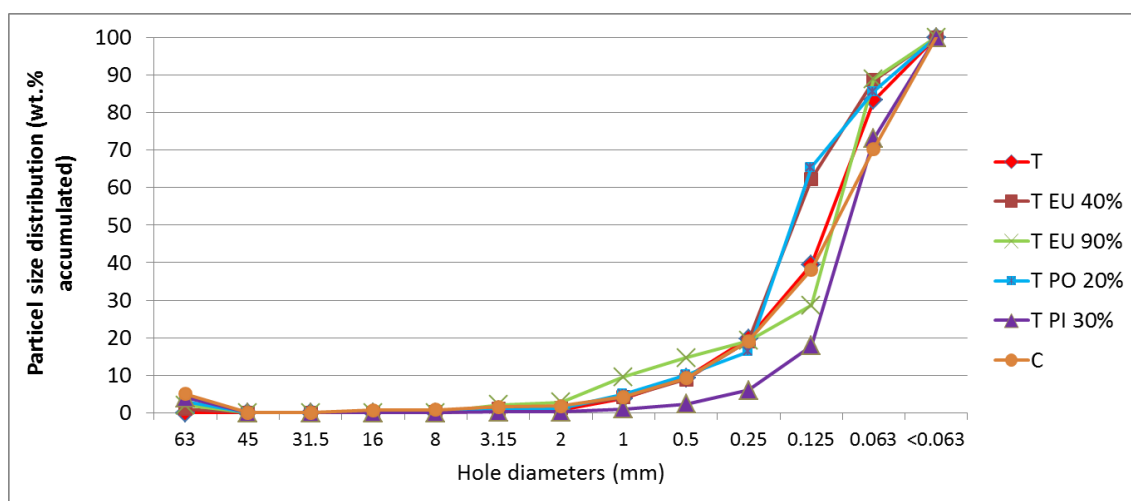


Figure 5: Particle size distribution of the ash collected from the tubes of the first heat exchanger. Triticale (T), eucalyptus (EU), poplar (PO), pine (PI) and corn (C).

3.3 Ash composition study in the pilot plant combustion tests

Figures 6-7 and 9-10 show the chemical and mineral composition of the different types of collected ash after feeding the combustion pilot plant separately with the herbaceous biofuels, and afterwards with blends of triticale and eucalyptus at different doses. The different types of collected samples were described in section 2.4. For comparison reasons, the ash composition of the biofuels used in combustion tests, ash that was produced in the laboratory at 550 °C, were also included in these figures. For all samples, the sum of major elements (expressed as oxides), chlorine, and carbon dioxide was ≥ 95 wt.% (unburnt material was negligible in all

ash samples). Iron contents were generally low, with the exception of some sinter deposits and ash collected on the inner surface of the heat exchanger as a result of the corrosion of the metal tubes. To remove this effect and facilitate the comparison of the samples, all the ash compositions shown in the aforementioned figures were recalculated to be iron-free and then normalized at 100 wt.%.

As shown in Figures 6-7, the ash and sinters collected from the heat exchanger were enriched in K, Cl, and S, compared to the ash directly produced at 550 °C from their corresponding biofuels, owing to the high volatility of alkaline compounds such as KCl and K₂SO₄. As a consequence, the slag and ash samples collected in the grate, before and after the conveyor screw, exhibited comparatively lower K, Cl, and S contents. This corroborates the known fact that alkaline compounds are directly condensed on the cool surfaces of the metal tubes or on the particles (nucleation), which are subsequently deposited on the tube surfaces by thermophoresis [15].

Corn straw and triticale biofuels behaved very differently as was mentioned in Section 3.1 and 3.2, without relevant or breakable slags in the corn combustion test. The main difference between corn and triticale was the higher alkaline content of triticale ash in the laboratory tests (see Table II and Fig. 6-7) compared to the corn ash. The difference was not very high but the effect on slag production was very significant. Inspection of Fig. 7 revealed the generation of alkaline silicates (yellow in the lower part of Figure 7), which can be considered low fusion point compounds, in the grate ash of the triticale combustion test. In contrast, no potassium silicates were detected in the grate ash of the corn combustion test (lower part of Fig. 6). The formation of alkaline aluminosilicates such as orthoclase (KAlSi₃O₈), leucite (KAlSi₂O₆) and albite (NaAlSi₃O₈) in case of triticale, as shown in Figure 8, could also be an

indication of the chemical reaction between the silica or Al-silicates, and K-Na compounds (red in the lower part of Figure 6) such as KCl , K_2SO_4 and $NaCl$ contained in the triticale.

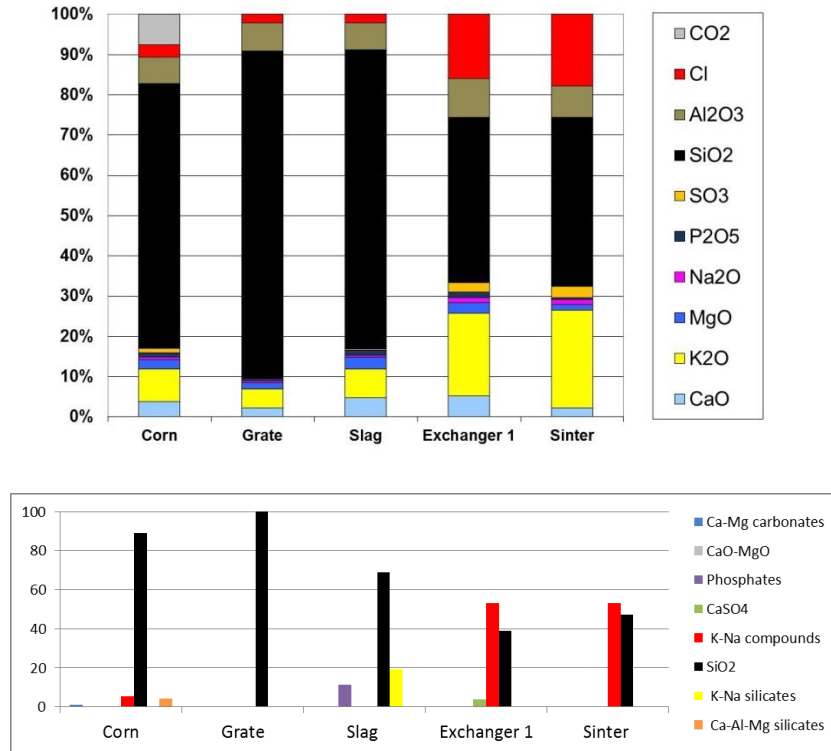


Figure 6: Ash composition of samples collected from the **Corn** combustion test. Elements: upper figure; Compounds: lower figure.

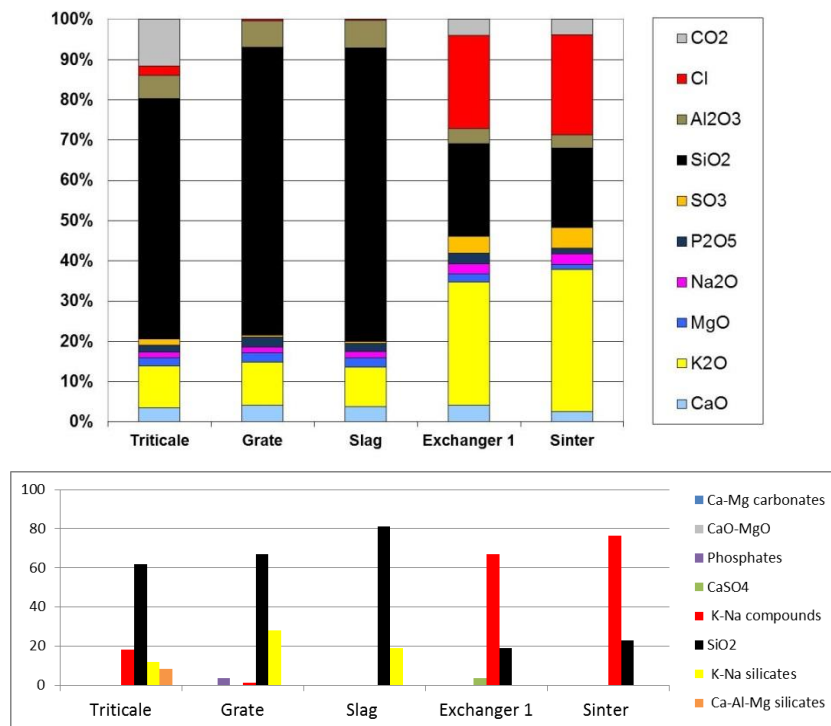


Figure 7: Ash composition of samples collected from the **Triticale** combustion test. Elements: upper figure; Compounds: lower figure.

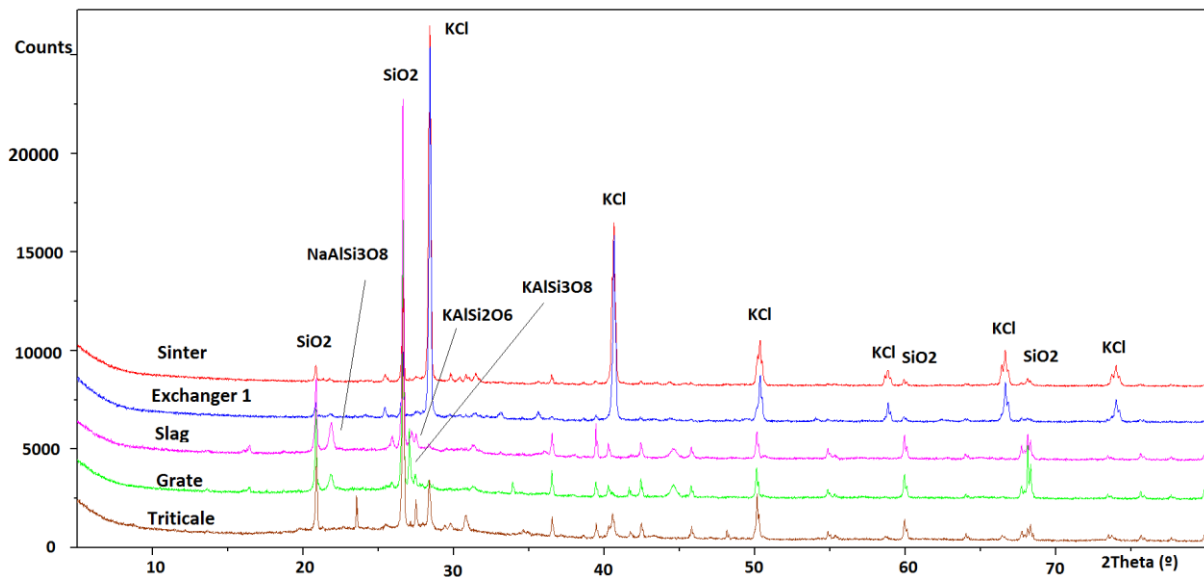


Figure 8: XRD patterns of samples collected from the **Triticale** combustion test.

An increase in calcium in the triticale ash when blended with eucalyptus at 40 wt.% and 90 wt.% ash doses is depicted in Figures 9 and 10, respectively. The formation of potassium silicates in the grate ash occurred in triticale plus eucalyptus (40%) combustion test (yellow of the lower part of Fig. 9). It is very important to comment that the appearance of potassium silicates in the grate ash also occurred in the other combustion tests with the addition of woody biomass, not only with 40 wt.% of eucalyptus biomass addition but also with 30 wt.% pine and 20 wt.% poplar combustion tests (results not shown). Inspection of Fig. 10 (triticale plus eucalyptus 90%) reveals the absence of formation of potassium silicates and a similar result also obtained in the corn straw combustion test (lower part of Fig. 6). Therefore, the absence of chemical reactions between the silica and potassium compounds and the absence of low melting compounds could be explained as a consequence of a dilution effect of the alkaline compounds by silica in the corn straw combustion test and by limestone in the triticale-eucalyptus (90%) combustion test.

Regarding the ash composition as a function of the ash sample location from the grate sample to sinter sample, similar comments can be made to those of the second paragraph of this

Section 3.3. However, the effect of the calcium is notorious in all samples, especially with eucalyptus at 90 wt.% ash dose (lower part of Fig. 10), where CaO was detected in the grate, slag and first heat exchanger. This increase in calcium can be the cause of the good behaviour of the eucalyptus in reducing the slagging. One possible explanation would be a dilution effect [16] which could be caused not only by the excess of calcium carbonate addition but also by adsorption of alkaline salts on the surface of the pores of calcium compounds such as lime (CaO) and portlandite (Ca(OH)₂). This explanation could also be applied to ash deposits, considering the highest particle flow of CaCO₃, CaO and Ca(OH)₂ that could escape from the moving grate to the heat exchangers, compared to combustion tests without woody biomass addition. However, and as commented in Section 3.2, the temperature seems to be too low (around 600 °C) to form hard sinters and the effect of calcium addition on heat exchangers cannot be finally validated.

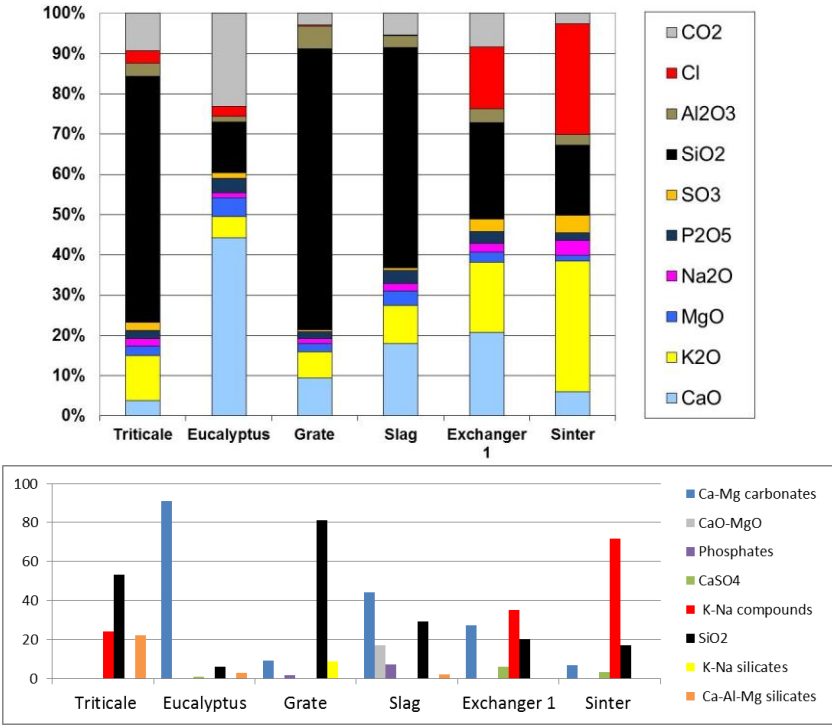


Figure 9: Ash composition of samples collected from the **Triticale plus Eucalyptus (40%)** combustion test. Elements: upper figure; Compounds: lower figure.

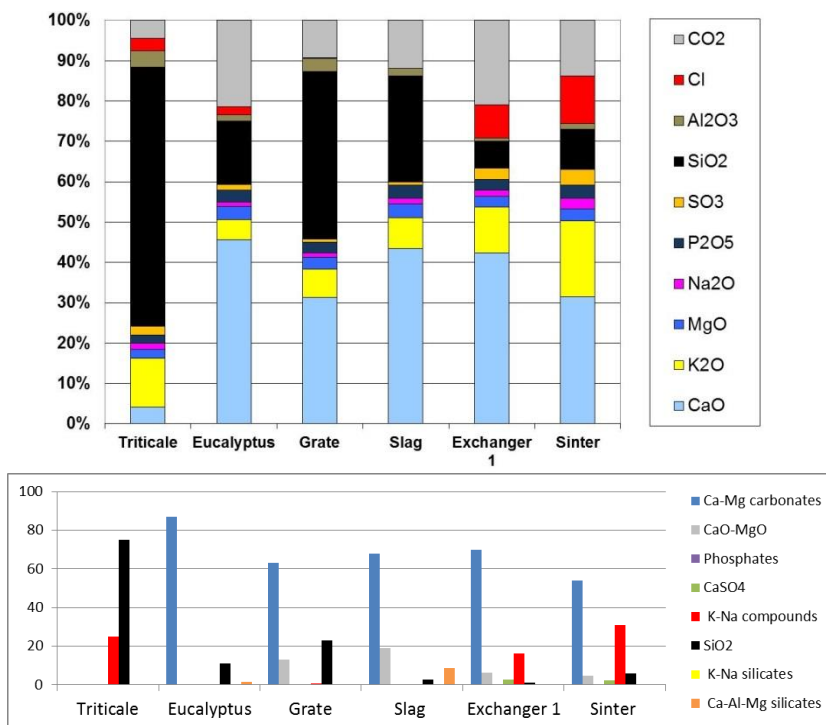


Figure 10: Ash composition of samples collected from the **Triticale plus Eucalyptus (90%)** combustion test. Elements: upper figure; Compounds: lower figure.

4 CONCLUSIONS

This work leads to the following conclusions:

Herbaceous biomass can behave very differently on sintering depending on its chemical composition. According to the laboratory results and the combustion tests, the corn straw, although a herbaceous biomass, presented a low sintering tendency and the addition of woody material was not required. In contrast, high concentrations of woody biomass should be added to triticale to obtain a significant reduction of its sintering behaviour, i.e. these proportions could be around 50 wt.% (ash basis) or even higher than 50 wt.% (ash basis).

The sintering prediction laboratory results were well correlated with the results from the 0.5 MWth combustion pilot plant tests. Consequently, this fact validates the sintering prediction tests performed in the laboratory. However, the technical specification on ash melting

behaviour (CEN/TS 15370-1) needs complementary predictive methods.

The sieving and the disintegration methods can be used to predict ash melting behaviour and to select the optimal amount of woody biomass that should be blended with herbaceous biomass to improve the ash sintering of herbaceous fuels. The sieving method was found to provide reliable results. The disintegration method also provides useful information, but it is subjected to the analyst's ability to perceive changes in ash consistency.

According to the disintegration and sieving predictive tests, eucalyptus may be the most suitable material for improving the sintering behaviour of triticale, followed by pine and poplar. Combustion tests in the pilot plant revealed that calcium compounds such as lime or portlandite were responsible for the good behaviour of eucalyptus in reducing the slagging of triticale biomass. A simple dilution effect seemed to be the main mechanism for reducing the sintering of triticale biomass when utilised as fuel blended with eucalyptus.

When corn was combusted, the ash collected in the grate of the plant did not contain potassium silicates and alkaline aluminosilicates, compounds with low melting points. The dilution effect could also be the main mechanism of sintering reduction due to the corn ash itself, which possessed a very high silica content compared to the content of alkaline compounds such as KCl and K₂SO₄.

5 REFERENCES

[1] Communication from the Commission. Green paper: A 2030 framework for climate and energy policies. Brussels: European Commission COM; 2013, <https://eur-lex.europa.eu/legal->

<content/EN/TXT/PDF/?uri=CELEX:52013DC0169&from=EN>; 2018 [accessed 3 August 2016].

- [2] De Laporte AV, Weersink AJ, McKenney DW. Effects of supply chain structure and biomass prices on bioenergy feedstock supply. *Applied Energy* 2016;183:1053–64.
- [3] Jenkins BM, Bakker RR, Wei JB. On the properties of washed straw, *Biomass and Bioenergy* 1996;10:177-200.
- [4] Allica JH, Mitre AJ, Bustamante JA, Itoiz C, Blanco F, Alkorta I, Garbisu C. Straw quality for its combustion in a straw-fired power plant. *Biomass and Bioenergy* 2001;21:249-58.
- [5] Yanqing N, Houzhang T, Shi'en H. Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. *Combustion of agricultural residues. Progress in Energy and Combustion Science* 2016;52:1-61.
- [6] Jensen PA, Sander B, Dam-Johansen K. Pretreatment of straw for power production by pyrolysis and char wash. *Biomass and Bioenergy* 2001;20:431-46.
- [7] Miles TR (Jr) and Miles TR. Alkali deposits found in biomass power plants. Summary report for National Renewable Energy Laboratory. NREL Subcontract TZ-2-11226-1; 1994.
- [8] Werther J, Saenger M, Hartge EU, Ogada T, Siagi Z. Combustion of agricultural residues. *Progress in Energy and Combustion Science* 2000;26:1-27.
- [9] Fernández MJ, Escalada R, Murillo JM, Carrasco JE. Combustion in bubbling fluidised bed with bed material of limestone to reduce the biomass ash agglomeration and sintering. *Fuel* 2006;85:2081-92.
- [10] CEN/TS 15370-1:2006, Solid Biofuels — Determination of ash melting behaviour – Part 1: Characteristic temperatures method. CEN European Committee for Standardization.

- [11] De Fusco L, Jeanmart H, Blondeau J, Contino F. Development of a tool to predict biomass fuels agglomeration and slagging propensity in combustion applications, In: Proceedings of the 23rd European Biomass Conference & Exhibition (Vienna); 2015, p. 1782-86. ETA-Florence and WIP-Munich Pub.
- [12] Wilén C, Moilanen A, Kurkela E. Biomass feedstock analyses. Espoo (Finland): VTT Publications 282; 1996.
- [13] Skrifvars BJ, Öhman M, Nordin A, Hupa M. Predicting bed agglomeration tendencies for biomass fuels fired in FBC boilers: a comparison of three different methods. *Energy and Fuels* 1999;13:359-63.
- [14] Fernández MJ, Carrasco JE. Comparing methods for predicting the sintering of biomass ash in combustion. *Fuel* 2005;84:1893-1900.
- [15] Rosner DE. Transport processes in chemically reacting flow systems. New York: Dover Publications Inc; 2000.
- [16] Steenari BM, Lindqvist O. High-temperature reactions of straw ash and the anti-sintering additives kaolin and dolomite. *Biomass and Bioenergy* 1998;14,67:76.

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