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Study of high–temperature interactions between ashes from cassava harvesting residues and inert materials via DTA/TG and SEM/EDS

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Abstract.*Agglomeration is a problem that is presented during biomass combustion in fluidized bed combustors (FBC) because of high–temperature interactions between alkali–compounds within biomass and the silica in the bed material. This problem is characterized by bed material sintering, inducing difficulties or loss of the fluidization state. In this study, samples composed by mixtures between ashes from cassava harvest residues with silica–sand and dolomite were analyzed via Differential Thermal Analysis coupled with Thermogravimetric Analysis (DTA/TG) aimed to determine the temperature to which agglomeration beginning and the effect of employing a bed material with low silica content in order to get a better comprehension of the structural composition of the samples prepared at chosen temperatures. The results showed the formation of two layers around sand particles at 910°C,in Ash-Sand samples, in accordance with coating–induced agglomeration route of formation. On the other hand, no interactions between ashes and dolomite were detected; however, high K–volatilization was identified between 580 and 900°C, demonstrating the dolomite utility as bed material during biomass combustion in FBC.*

Keywords: *Agglomeration, Agricultural residues, DTA/TG, SEM/EDS*

1. INTRODUCTION

There is a problem that is presented during the direct combustion of lignocellulosic biomass in FBC, and is related to interactions between the bed material and the alkalis content into biomass ashes. This problem is characterized by a continuous growth of the particle mean size of the bed and, in the most severe cases, may lead to bed defluidization (Chirone *et al.*, 2006; Bartels *et al.*, 2008; Visser *et al.*, 2008; Grimm *et al.*, 2011).

Studies developed around mechanisms of the formation of agglomerations, attribute as principally responsible for this phenomenon to alkalis silicates, which are formed due to high–temperature–reactions between the ash from the biomass and the silica of the bed material (Bartels *et al.*, 2008; Grimm *et al.*, 2011; Öhman *et al.*, 2000; Chirone *et al.*, 2000; Khan *et al.*, 2009; Mettanant *et al.*, 2009). Those compounds react forming eutectics of low melt temperatures and act as adherent media, leading to bed agglomeration (Öhman *et al.*, 2000).

This resear is aimed to evaluate the formation mechanism of agglomerations and the temperature at which they occur in samples composed by mixtures between silica–sand and dolomite with ashes from cassava harvest residues (Ash–Sand and Ash–Dolomite, respectively) by using DTA/TG and SEM/EDS.

Table 1: Characteristics of the materials used in this work.

Proximate Analysis [wt.%]				HHV[MJ/kg]$^{(1)}$
Moisture$^{(1)}$	**Vol. Matter**$^{(2)}$	**Ash**$^{(2)}$	**Fixed carbon** $^{(2)}$	
7.76	75.40	3.83	20.78	16.38

Elemental composition$^{(3)}$										
Component	**Na**	**K**	**Ca**	**Mg**	**Al**	**Fe**	**Si**	**S**	**Cl**	**P**
Ashes	0.81	64.25	20.88	4.44	–	–	0.41	3.89	–	5.34
Sand	–	–	–	–	0.77	1.85	97.38	–	–	–
Dolomite	–	0.445	47.05	28.43	2.01	1.68	20.38	–	–	–

$^{(1)}$ Wet based
$^{(2)}$ Dry based
$^{(3)}$Weight percent of dry matter free of oxygen

2. Experimental Procedure

Residual branches from cassava harvesting were directly collected from the ground and later mechanically ground and sieved to obtain samples with a particle size between 0.5 and 0.71 m.m. Silica–sand and dolomite of fine mean particle size were employed in this work.
Biomass characteristics along with the elemental content of its ashes and inert materials (silica–sand and dolomite) are shown at Tab. 1. Biomass ash revealed high–K content, with a agglomeration index value above 1.0 kg.GJ^{-1} (see Eq. (1)); indicating then, strong tendency to produce agglomeration according the criteria proposed by Hulkkonen *et al.* (2003).

$$\frac{K_2O + Na_2O}{HHV} \left[kg/GJ^{-1}\right] \quad (1)$$

In order to prepare the ashes from the biomass, it was followed the procedure described by Arvelakis *et al.* (2003):fine biomass particles were put into crucibles, then heated in muffle to 550°C at a rate of 2°C/min during 24 h.
The silica–sand and dolomite were calcined at 900°C during 8h so discarding any presence of organic material and moisture.
Each mixture was composed of over 20 times the minimal concentration of K to agglomerate 1 gr of silica–sand according with Chirone *et al.* (2006).
A Netzsch model STA 409 Thermal Analyzer was employed to observe the behaviour of the mixture samples at high temperatures. The experiments done obeyed the following parameters: Final temperature 1200°C; Heating Rate: 10°C/min; Atmosphere: O_2 with flow of 80 ml/min.

3. RESULTS AND DISCUSSION

3.1 DTA/TG

The results obtained by the DTA/TG measurements for the mixture samples of cassava ashes with silica–sand and dolomite are shown in Figs. 1 and 2, respectively. In each graph, are highlighted the temperatures where endothermic peaks arose. For a better understanding of the thermal changes, the DTA–graphs were re–plotted and the corresponding DTA–graphs of the constituent materials of each sample were added (biomass–ash, silica–sand, and dolomite).

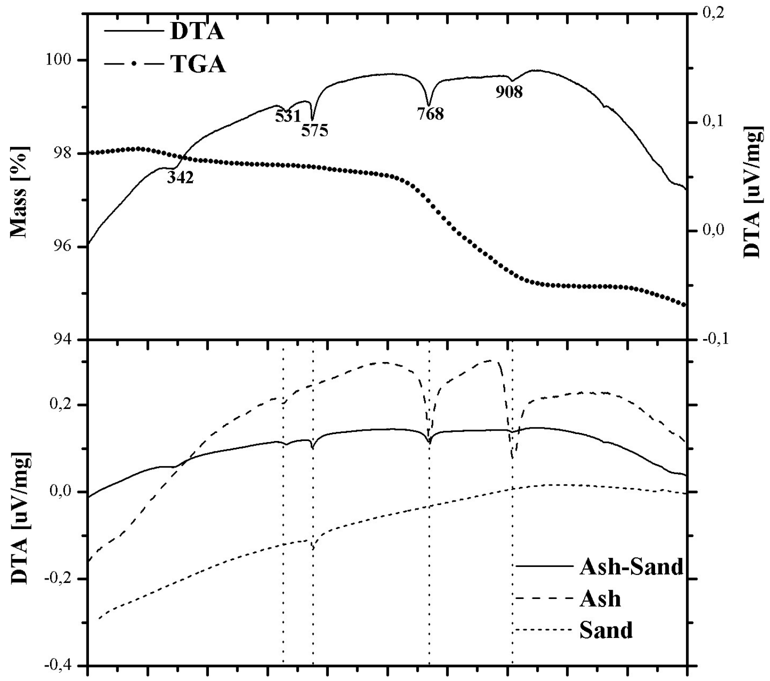


Figure 1: DTA/TG analysis for the Ash–Silica samples

In the Ash–Silica samples (Fig. 1), five endothermic peaks were identified at 342, 531, 575, 768, and 908°C. Vertical lines, corresponding with the minimum of every arose peak, cuts the three DTA–graphs. As is shown, each peak in the

mixture matches with some other on the component curve, indicating apparently the superposition of the reactions in each of the mixture components at the respective temperature.
The peak at 531°C, which matches with one in the ash sample, was not accompanied by any significant change of mass, suggesting the fusion of some compound contained in the ashes. The 575°C peak corresponds to the structural change from quartz–α to quartz–β in the silica–sand (Morey, 1964). Because of the high slope presented on th TGA curve, between 750 ans 900°C, it is not possible to identify the process carried out during the formation of the 750°C peak. Finally, there was not an appreciable change of mass around the endothermic peak at 900°C that is consistent with some fusion of material.

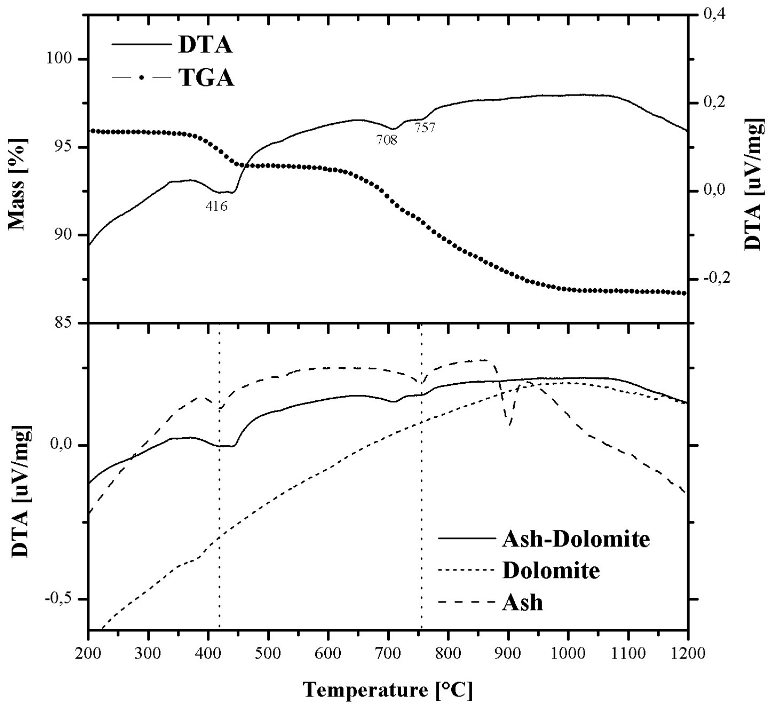
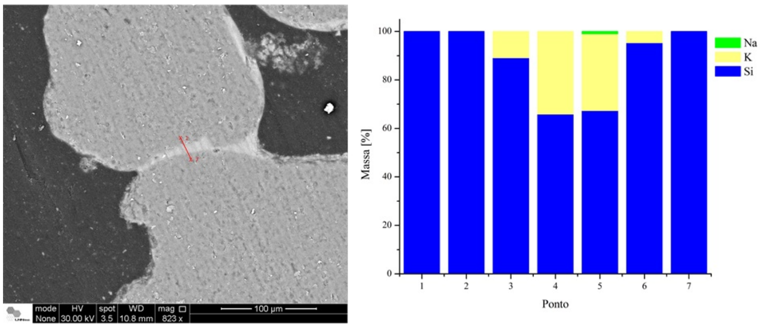


Figure 2: DTA/TG analysis for the Ash–Dolomite samples

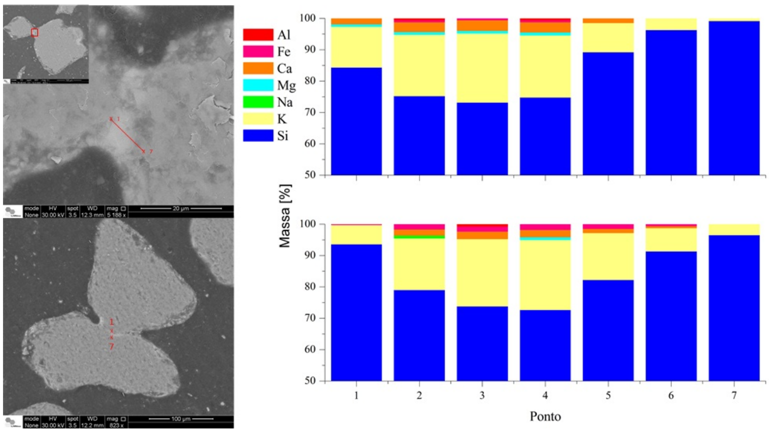
In the Ash–Dolomite samples, the DTA graph (Fig. 2) shows three endothermic peaks occurred at 416, 708 and 757°C, all of them matching with those on the DTA–curve of the ashes around the same temperatures. These peaks appear in regions with high loss of mass, not allowing to determine the principal cause of these effects.

3.2 SEM/EDS

Aimed to get a better comprehension about the responsible effects of the endothermic–peaks in the mixtures, samples from each mixture were prepared by muffle at selected temperatures and analyzed by SEM/EDS, following the procedure of Ergudenler and Ghaly (1993). For Ash–Sand samples, there were chosen two temperatures where changes in the mass and followed with a endothermic peak were observed, at 768 and 908°C. After the preparation by muffle, as consequence of the total sintering of each sample into the crucible, they were mounted in epoxy resin, polished and analyzed by SEM. For the other hand, the ash–dolomite samples were put in muffle at 580 and 900 °C, matching with the region where there were high loss of mass. After the thermal treatment, the samples were attached to the sample holder by using a carbon tape.
The elemental composition of the Ash–Sand sample along seven points on a line traced is shown at Fig. 3. For the sample prepared at 768°C, which presented a weaker sintering than the sample at 908°, the composition on the nearest points to sand particle surface was principally dominated by K ans Si being this latter of smaller proportion as the measurements were taken further from the sand particle surface. The exclusively presence of K in the neck formed between the sand particles indicate this element as the principal responsible of the beginning of sample sintering according with the literature. A similar tendency was showed in the sample prepared at 908°C, but with presence of other elements not revealed at the previous temperature on further points from the inert particle surface. Those elements there were detected initially in the biomass ashes. This indicates the formation of two layers, one inner and other outer, around the sand particle, what agrees with coating–induced agglomeration route of formation (Öhman *et al.*, 2000; Visser *et al.*, 2008; Gatternig and Karl, 2015)



(a) 768°C sample



(b) 908°C sample

Figure 3: SEM/EDS analysis in prepared Ash–Sand samples

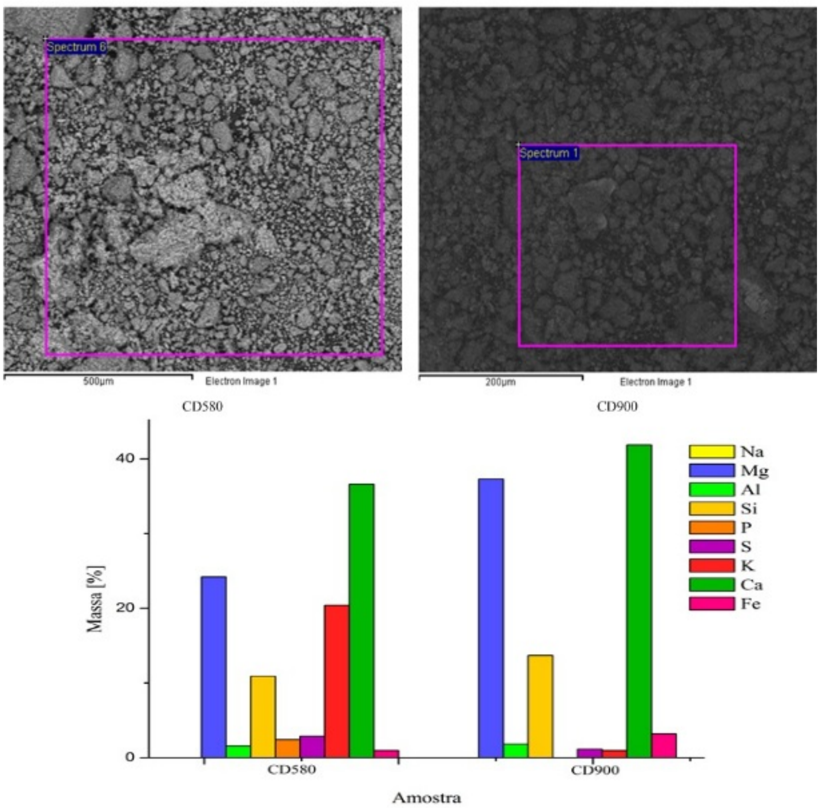


Figure 4: XXX

The first layer was formed by the deposition of K–compounds particles on the sand surface. This deposition, along with the high temperatures, led the formation of eutectics from the K_2O–SiO_2 system of low melting temperature; therefore, initiating the agglomeration. As the first layer grew, a second one governed by either K_2O–SiO_2–CaO or K_2O–SiO_2–MgO system were formed followed by the attaching of the others compounds from the ashes. This explain the hardness of the sintered sample after its preparation by muffle.

Figure 4 shows the results from SEM/EDS applied to Ash–Dolomite mixtures. Comparing the elemental composition of the both samples is evident the reduction around 95% in the K–content, indicating that the presence of Ca and Mg promotes the K-compounds volatilization, so decreasing the agglomeration tendency during biomass combustion.

4. CONCLUSIONS

For the Ash–Sand samples, the results obtained by DTA/TG and supported via SEM/EDS showed that agglomeration were induced by the deposition of K–compounds over the sand particles, promoting the formation of alkali silicates, and therefore low melting temperatures.

Despite the fact of cassava residues has high tendency to form agglomerations because of its high K–content, the use of dolomite inhibited this tendency; therefore, proving its importance as bed material during biomass combustion in FBC.

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