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DEVELOPMENT OF A TOOL TO PREDICT BIOMASS FUELS AGGLOMERATION AND SLAGGING PROPENSITY IN COMBUSTION APPLICATIONS

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ABSTRACT: In the recent years, a growing interest for low - quality biomass fuels is observed, in both small- and large-scale combustion plants. Such fuels include wood mixtures and forest residues, short-rotation energy crops, herbaceous biomass (e.g. straws) and agricultural or fruit residues. The combustion of these fuels often portends technical operational issues, which include agglomeration of inorganic particles in fluidized beds and ash slag formation in combustors. A simplified fuel characterization approach has been developed in this work, with the objective to define the agglomeration and slagging propensity of biomass fuels for their use in combustion boilers. Among the variables that influence these complex mechanisms, the fuel inorganic composition is considered in this model. The outcome of the model is a parameter in the range 0 - 100 that indicates the specific fuel propensity to induce agglomeration and slagging issues in combustion applications. The model outcomes are validated with experimental results from literature and from laboratory tests in a pilot circulating fluidized bed reactor. The developed tool is build to be used for screening and preliminary selection of solid biomass fuels for combustion.

Keywords: characterization, agricultural residues, alkali, circulating fluidized bed, cofiring.

1 INTRODUCTION

In the recent years, a growing interest for low - quality and economically less expensive biomass fuels is observed, in both small and large-scale combustion plants. The combustion of these fuels often portends technical issues, which include agglomeration of inorganic particles in fluidized bed combustion and slag formation in combustors. The first mechanism is due to chemical and mechanical interactions between the fuel ash remaining in the bed and the bed materials. The use of alternative bed materials and additives, within specific temperature ranges, can mitigate both the coating-induced and melt-induced agglomeration [1]. The second mechanism refers to the formation of semi-molten phases particles, often inertially impacting radiant heat exposed surfaces (e.g. boiler's walls, superheater sections) and residual matter formation in the bottom of the combustion chamber. The consequences of agglomeration and slagging vary from disturbances of the combustion process, due to larger ash particles and hot spots creation, up to boiler failure, e.g. related to bed defluidization [2].

2 OBJECTIVES AND SCOPE

In this work, a simplified fuel characterization approach to define the agglomeration and slagging propensity of biomass fuels for their use in combustion boilers has been developed. Recent research evidences the possibility of predicting agglomeration and slagging for specific targeted fuels and boilers, if detailed combustion and thermochemical modelling is performed e.g. [3]. However, thermochemical databases are not complete, showing different results depending on the selected solution and solid phases [4], or simply not available. Therefore sophisticated models do not have wide use within the bioenergy plant operators. In fact, simplified and flexible tools for the fuels screening and applicability concerning the risk of ash issues, are missing.

Agglomeration and slagging in boilers are the result of complex interactions of fuel ash, additives and bed materials (if any) and are dependent on operating thermochemical conditions, for example boiler temperature profile, combustion atmosphere, fluidization conditions and boiler design. In the approach presented in this paper, only the fuel composition factor is considered: the framework of the investigation is the advanced biomass fuel characterization. In addition, well established that agglomeration and slagging are different mechanisms, the fuel inorganic constituents seem to act in a similar way in enhancing or reducing the sintering trends. For that reason, the computed propensity is associated to both agglomeration and slagging. The detailed modelling to predict quantitatively agglomeration and slagging, which depends on the operating conditions, is out of scope for this work.

Existing indices and correlations experimentally derived were reviewed and recent findings related to the fuel selective leaching are used to theoretically build the modelling approach. The model is structured as an improved correlation and the outcome is a parameter in the range 0 – 100, that indicates the specific fuel propensity to induce agglomeration and slagging issues in combustion. The modelling outcomes are validated with experimental results from the literature and with testing in a pilot circulating fluidized bed reactor. The key advantage of the developed tool is the possibility to be widely used for the fuels screening and preliminary selection. More advanced approaches such as thermochemical modelling and specific experimental testing can expand and complete the information obtained thanks to the proposed characterization strategy.

3 METHODOLOGY

3.1 Roles and associations of the ash constituents involved in agglomeration and slagging reactions

An advanced description of the content, association and fate of the biomass inorganic constituents is presented, as an example, in [5]. In the simplified approach developed, the inorganic constituents roles assumed are presented in the following paragraphs.

Potassium (K) and sodium (Na) have a major role in the agglomeration and slagging mechanisms; their release is a temperature driven process [6]. The insoluble part of potassium (e.g. in silicate contaminations) is quite inert [7]. As assumed in other models ([8]), concerning agglomeration, K and Na soluble at pH = 3 (from the well established fuel selective leaching analysis) can be considered to be involved in the reactions, which are temperature dependent. Within this work, the same hypothesis is assumed for alkali metals involved in the slagging reactions. Reactive potassium (e.g. present in salts or organically bound) forms primary vapours (such as KOH(g), K(g), and KCl(g)), which react further (e.g. K_2CO_3). They can form with SiO_2 (e.g. from the bed material) potassium silicates, for example according to the Eq. (1) and low melting temperature mixed silicates with Ca, Na, see as an example Eq. (2) [5, 9].

$$SiO_2(s) + 2KCl(g) + H_2O(g) \rightarrow K_2SiO_3(s,l) + 2HCl(g) \quad (1)$$
$$K_2SiO_3(l) + CaO(s) \rightarrow K - Ca - Silicates\ (l) \quad (2)$$

Calcium (Ca) and magnesium (Mg) are supposed to increase the melting temperature of the formed compounds, within the secondary ash interactions. The Ca organically bound, the crystalline salts particles fraction, as well as the fraction added as additive, can be converted into solid CaO(s) during combustion [5]. Calcium in silicate minerals (such as feldspar) is insoluble and quite inert. In the proposed modelling approach, Ca and Mg soluble at pH = 1 (from the fuel selective leaching analysis) are assumed to be chemically reactive. Part of the calcium is involved in the sulphating reactions. Calcium concentration in alkali-phosphate compounds showed to increase the melting temperature by forming stable alkali-alkaline earths-phosphates phases [5]. However, calcium phosphate and sulphate may lead to low melting points compounds [5]. Mg is chemically similar to calcium but is present in much lower concentrations and its reactions take place at lower temperatures [5].

Phosphorus (P), in a very simplified description, forms low melting temperature alkali phosphates (see as an example Eq. (3) [10]) or can capture alkali in high melting temperature alkali-alkaline earths-phosphates (see as an example Eq. (4) [10])). Details of the phosphate chemistry are not fully understood.

$$P_2O_5(g) + 2KOH(g) \rightarrow 2KPO_3(l,g) + 2H_2O(g) \quad (3)$$
$$KPO_3(l,g) + CaO(s) \rightarrow K - Ca - Phosphates(s) \quad (4)$$

Silica (Si), when present as SiO_2 or in mineral form, is relatively inert. Metals connected to the silicate stay in the silicate matrix [5]. If present in the fuel organic matrix (e.g. agricultural residues) it reacts with alkali vapours to form low melting potassium silicate, see as an example Eq. (1). Aluminium (Al) present as silicates (e.g. clays) and organically bound may react with alkali vapours, trapping them by forming high melting point compounds: aluminium - silicates from the kaolinite group may counteract agglomeration (a proposed kaolin reaction in reported in Eq. (5) [9]) and slagging.

$$2KCl(g) + Al_2O_3 \cdot 2 \cdot SiO_2(s) + H_2O(g) \rightarrow K_2O \cdot Al_2O_3 \cdot 2 \cdot SiO_2(s) + 2HCl(g) \quad (5)$$

Heavy metals as zinc (Zn), lead (Pb) and cadmium (Cd) are released to the gas phase during combustion and are supposed to decrease the melting temperature of the formed alkali mixtures, or act as condensation nuclei for alkali species [7]. Manganese (Mn), titanium (Ti), copper (Cu) and other minor inorganic elements in the fuel are not considered in the proposed characterization approach.

3.2 Predictive indices and correlations from the literature

Some predictive correlations of the biomass ash fusion initial deformation temperatures have been developed with statistical analysis of databases see e.g. [11]. Nevertheless, the standardized Ash Fusion Test and the related ash fusion temperatures do not seem good indicators of the fuel propensity to agglomerate and slag due to the poor accuracy, uncertainties and repeatability concerns. Semi-empirical predictive indices available in the literature are mainly based on the alkali metals concentration in the fuel. Well known indicators are, for example: the alkali index: (K+Na)/(HHV) [mol/GJ]; the ash melting index: (Si+P+K)/(Ca+Mg) [mol/mol] [12]; the fine particulate emissions indicator: K+Na+Zn+Pb [mg/kg_f db] (kg of fuel, dry basis) [12].

3.3 Database definition and hypotheses

Fuels data used for the development of the modelling tool are selected from fuels handbooks (e.g. [7]) and the Phyllis 2 database (ecn.nl/phyllis2).

3.4 Development of the fuel agglomeration and slagging propensity correlation

The input data for the computation of the fuel agglomeration and slagging propensity are parameters based on the concentration of inorganics in the fuel: total K, K_{pH3}, total Na, Na_{pH3}, total Ca, Ca_{pH1}, total Mg, Mg_{pH1}, Si_{pH1}, total Si, not metallic Al, total P, total Fe, total Cd, total Zn, total Pb, where the indication of pH follows the formulation at first proposed by Zabetta and co-authors [8].

4 RESULTS AND DISCUSSION

4.1 Validation of the fuel agglomeration and slagging propensity correlation and error propagation analysis

The validation of the modelling approach is based on the comparison of the predicted propensity with experimental data from the literature (selected data from Tab. I, Fig. 1 - 6). The experimental fuel characterization for agglomeration includes the evaluation of the temperature at which the bed defluidization is recorded (initial or total) [5] as well as the bottom ash and circulating material physical and chemical characterization. The experimental fuel characterization for slagging includes the slag or bottom ash physical and chemical characterization (e.g. PSD or granulometry, composition, hardness) and integrated evaluations such as the slagging "degree", based on semi-quantitative scales defined by the different authors. For all the fuels for which fuel chemical fractionation results were not available, some hypotheses have been set (K_{pH3} = total K; Na_{pH3} = total Na; Ca_{pH1} = total Ca; Mg_{pH1} = total Mg).

Error bars presented in the plots (Fig. 1 and following) are computed as propagation errors considering a relative uncertainty in the fuel inorganic composition, for each of the ash constituents (e.g. for calcium, $\Delta Ca/Ca$), of 10% (type B uncertainty). For most of the fuel data available, a single chemical composition measurement is available. In case more composition analyses are available for the same fuel, a statistical analysis should be performed in order to use as inputs for the tool a representative composition. The model sensitivity analysis is not detailed in this paper.

In Fig. 1 it is compared the computed agglomeration and slagging propensity and the experimentally derived defluidization temperature (initial or total, with the relative uncertainty when available) for different fuels and mixtures, within different experimental sets up. High defluidization temperatures indicate that the fuel is less prone to induce agglomeration. For the fuels and mixtures tested in the same experimental conditions, an agreement between the model results and the experimental trend is verified: increasing the propensity of agglomeration and slagging corresponds to a decrease in the maximum system operating temperature before agglomeration occurs. The tool should not be used to predict the defluidization temperatures, but to compare qualitatively different fuels.

If analysing the slagging behaviour of fuels, the most suitable experimental parameters to collect are the PSD of the slag collected and its hardness. In Fig. 2 it is reported the comparison between the computed agglomeration and slagging propensity and the experimentally derived fraction of fuel ash that forms slag (F_{Slag} [% ash]) and as a function of the degree of slag sintering D_{Slag} (from 1 to 5), for different fuels and mixtures and experimental sets up. Generally, for the fuels and mixtures tested in the same experimental conditions, an agreement between the degree of slag sintering and the experimental trend is verified. The predicted trends seem to be less correlated with the fraction of fuel ash that forms slag (Fig. 2).

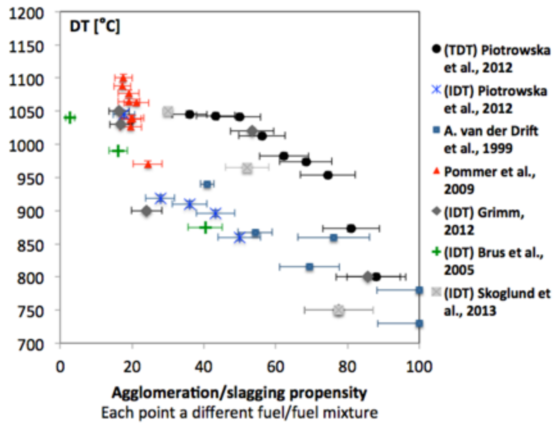

Figure 1: Agglomeration/slagging propensity as a function of the bed defluidization temperatures DT [°C] (I: initial defluidization; T: total defluidization), for different test campaigns.

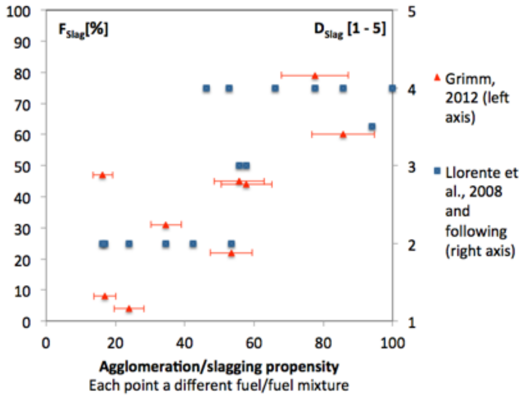

Figure 2: Agglomeration/slagging propensity as a function of the fraction of fuel ash that forms slag (F_{Slag} [% ash]) and of the degree of slag sintering D_{Slag} (from 1 to 5) from different experimental test campaigns.

The modelling approach developed is tested for the fuels analyzed within the AshMelT project (ashmelt.eu), for which a large quantity of data is available (fuels data [13], return of experience [14]). The comparison between the predicted propensity and the experimental results are presented in Fig. 3, 4 and 5. In Fig. 3 it is possible to verify that different experimental combustion tests correspond to different results concerning the PSD of the slag (e.g. F15 and F13; F11 and F10; F04 and F03). Their comparison with the outcome of the modelling approach shows a good agreement. High alkali metals, phosphorus and organically bound silica fuels show high propensity towards slag formation. Stem wood pellets generally have a lower slagging propensity.

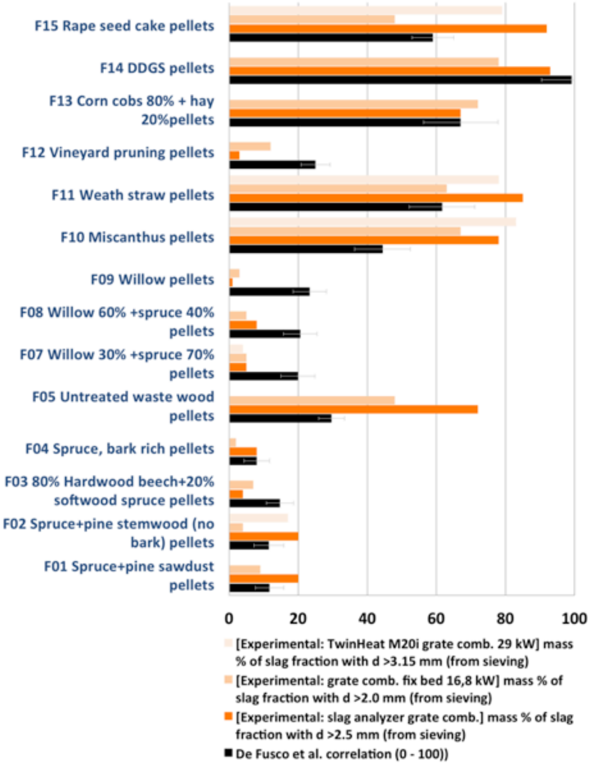

Figure 3: Agglomeration/slagging propensity compared to synthetic results from slagging test for the fuels from the AshMelT project, in different combustion facilities.

4.2 Results and discussion of case studies

In a recent test campaign, two woody fuels of different quality have been tested in a pilot reactor with circulating fluidized bed (0.1 MW), at the typical combustion conditions of a fluidized bed utility boiler (about 850°C).

The characterization tool has been applied to for the three fuels analysed and a comparison with experimental results is reported in Tab. III. Also within this case study, the prediction approach is useful to assess the agglomeration propensity of the fuels (in this case associated to the mass median diameter $D_{p,50}$ of bottom ash and circulating material, since defluidization regimes were not investigated).

Table I: Comparison between the predicted agglomeration/slagging propensity and experimental testing in a pilot reactor with CFB. BA Bottom ash, CM circulating material.

Fuel name	**Computed propensity (0-100)**	**BA ($D_{p,50}$)** [microm]	**CM ($D_{p,50}$)** [microm]
Wood 1	17	323	250
Wood 2	4	249	203

4.3 Comparison with the standardized ash fusion temperature (IDT) from the Ash Fusion Test

The comparison between the computed agglomeration and slagging propensity and the standardized ash fusion temperature (IDT) from the Ash Fusion Test, for different fuels, is presented in Fig. 4. Interestingly, all the fuels with an agglomeration and slagging propensity lower than 20, have an Ash Fusion Temperature (SST) higher than 1000°C. Moreover, the results show that a high Ash Fusion Temperature (SST) is a necessary but not sufficient condition to expect low agglomeration and slagging.

4.4 Further applications considering the bed material in fluidized bed combustion and the presence of additives

As an application, the correlation could be applied considering the total inorganic material in the combustion reactor for example, fuel ash, make up of the bed material (in fluidized bed combustion) and additives. Additional computations and the comparison with experimental data from the literature are reported in Fig. 5 – 6. However, given the complexity of the thermo-chemical system and the simplifications considered in the model, the results are only qualitative indication of possible trends. Despite the results are coherent with the expected trends when including different bed materials make up (comparison of the influence of quartz sand and olivine bed in Fig. 5), additives (kaolin, Fig. 6), the tool is not build for the bed materials or additives selection.

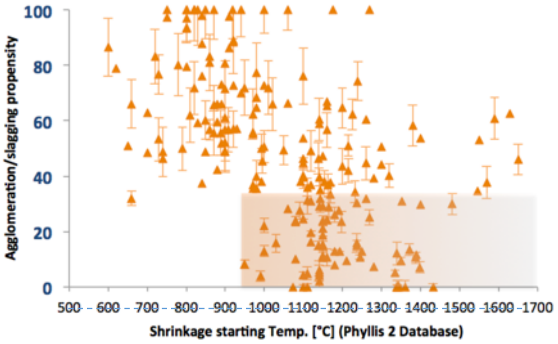

Figure 4: Computed agglomeration and slagging propensity and their related shrinkage starting temperature SST from the standard Ash Fusion Test.

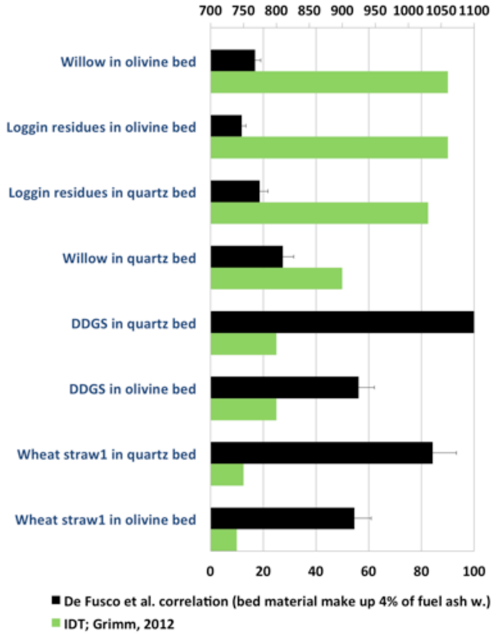

Figure 5: Agglomeration/slagging propensity computed including the composition of the bed material make up. IDT: Initial defluidization temperature [°C], top axis.

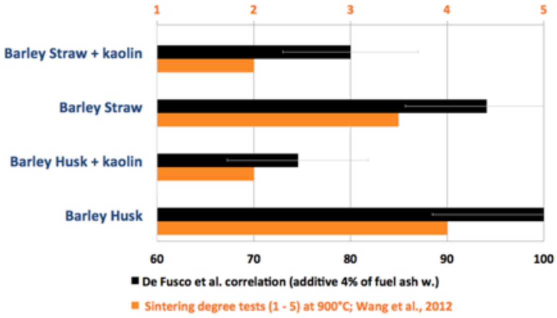

Figure 6: Agglomeration/slagging propensity computed including the composition of additives. Sintering degree (1 – 5), top axis.

5 CONCLUSIONS

Lower quality biomass fuels, with a wider range of chemical composition and combustion characteristics with respect to traditional high quality biomass, are more and more exploited in combustion applications. Current problems associated to fuel selection and with fuel quality variation are, for example, ash related issues. The combustion process is particular influenced by agglomeration and slagging of biomass ash (and bed material in fluidized bed combustion). This work presents the results of a model to compute the fuels propensity to induce agglomeration and slagging issues as a function of the detailed fuel composition, in order to preliminarily assess the impact of fuel quality variation on combustion applications. The developed tool, rather than being an agglomeration and slagging mechanisms prediction, is build to be used for screening and selection of solid biomass fuels for combustion, with a focus on the agglomeration and slagging propensity.

The comparison with literature data and experimental testing in a pilot CFB reactor shows that the integrated correlation can be used for a first evaluation of the specific fuel agglomeration and slagging propensity. When including the bed material make up and the additives composition, despite the results are coherent with the experimentally verified trends, the tool should be coupled with detailed thermochemical modelling and ad-hoc testing. Future research includes the development of a simplified strategy for the prediction of the biomass fuels fouling propensity.

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