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Advanced Characterization of Available not Conventional Mediterranean Biomass Solid Fuels for Ash Related Issues in Thermal Processes

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According to the European Biomass Association, bioenergy represents about 60% of the EU's total consumption of renewables. The EERA Bioenergy, section of the European Energy Research Alliance, indicates that agricultural residues and non-food crops should be used at farm- and village- scales, while low quality biomass and waste could be used for medium- and large- scale power and CHP plants. Among the barriers that hamper the efficient processing of solid fuels in thermal processes, such as combustion and gasification, ash related issues are still challenging for plant operators. These issues include agglomeration in fluidized bed combustion, slag formation, and fouling of convective heat exchangers. Furthermore, advanced characterization methods for solid biomass fuels, especially predictive approaches for ash related issues, are not fully developed. Consequently, the use of unconventional biomass solid fuels is limited because of operating risks. In addition, the availability of the detailed chemical analyses of unconventional fuels is often limited. In this investigation, a validated fuel characterization tool to define the agglomeration - slagging propensity of biomass fuels for their use in thermal processes, is applied to an advanced database of mediterranean (Greece, Italy, Spain) opportunity fuels. The database is built by means of an extensive literature review, including the detailed ash chemical compositions. The input of the tool is the specific fuel ash chemical composition, and the output is the agglomeration - slagging propensity computed as a parameter in the range (0 – 100). In this work it is shown that a high ash fusion temperature (from the Ash Fusion Test) is a necessary but not sufficient condition to low agglomeration and slagging in combustion applications. Among the fuels analyzed, wood, shrubs and citrus industry agro-residues evidenced a low-to-medium median propensity to agglomerate and slag, contrarily to the high propensity of agro-residues (various), wine industry residues, and crops. About 20 opportunity fuels, with low-to-medium agglomeration and slagging propensity and for which environmental, economic and social sustainability has to be further explored, are suggested for thermal applications. Some countermeasures to efficiently process the more challenging fuels are mentioned, including the use of specific combustion additives.

1. Introduction

Among the barriers that hamper the efficient processing of solid fuels in thermal processes such as combustion and gasification, ash related issues and the corresponding fuel predictive characterization are still very challenging. Agglomeration is due to chemical and mechanical interactions between the fuel ash and the bed materials. Slagging refers to the formation of semi-molten particles, impacting radiant heat exposed surfaces (e.g. boiler's walls, super heater sections) and residual matter formation in the bottom of the combustion chamber. The consequences of these mechanisms are disturbances of the combustion process, due to larger ash particles and hot spots creation, decreased system efficiency and increased energy costs, up to bed de-fluidization and boiler failure (Hupa, 2012).
Recent research evidences the possibility of predicting agglomeration and slagging for specific targeted fuels and boilers, if detailed combustion and thermochemical modelling is performed. However, thermochemical

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databases for the computations are not complete, showing different results depending on the selected database Billen et al., 2014). Simplified and flexible tools for the fuels screening and applicability criteria concerning the risk of ash related issues, are missing.
In this work, a fuel characterization approach to define the agglomeration - slagging propensity of biomass fuels in thermal processes has been applied to a database of available Mediterranean solid biomass fuels. Direct combustion is considered as the reference conversion process. Inorganic matter related issues in boilers are the result of complex interactions of fuel ash, additives and bed materials (if any) and are dependent on operating conditions, for example boiler temperature profile, combustion atmosphere, fluidization conditions and boiler design. In the approach presented, only the fuel composition is considered. Even though agglomeration and slagging are different physico-chemical 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. In Section 2, the fuel database is presented. In Section 3, the predictive capabilities of the tool are demonstrated for the entire fuel database.

2. Unconventional Mediterranean fuels database

There is still a considerable difference between the potential and available agro-fuels in South-Center Europe. The regions with the major differential available vs. potential [odt/ha/year], where investments could be concentrated, are: Auvergne, Rhône-Alpes and Midi-Pyrénées (France), Pais Vasco, La Rioja, Comunidad Foral de Navarra and Castilla y León (Spain), Emilia Romagna, Provincia Autonoma di Bolzano, Veneto and Friuli-Venezia Giulia (Italy), Dytiki Makedonia, Thessalia (Greece), Lisboa and Alentejo (Portugal) (Esteban et al., 2010).
Looking at the fuels, the availability of the detailed chemical analyses of unconventional fuels is often limited to specific samples. Recently, Molino et al. (Molino et al., 2014), characterized in a structured approach 12 biomass fuels from the southern Italy regions for their use in thermal processes. Within this investigation an updated list of available unconventional woody and agricultural Mediterranean biomass was built, including 74 samples with different origins (Fig. 1 a, b).

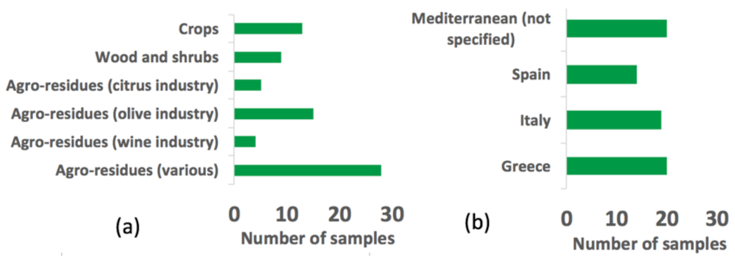

Figure 1: Fuels analysed with the predictive tool (a) type and (b) origin. Detailed compositions retrieved from Llorente et al., 2006; Fryda et al., 2007; Scala at al., 2008; O. Seneca, 2009; Vamvuka et al., 2009; Vamvuka et al., 2010; Karampinis et al., 2011; Viana et al., 2012; Wang et al., 2013; Díaz-Ramírez et al., 2014; Vamvuka et al., 2014; Molino et al., 2014; Garcia-Maraver et al., 2015; and Phyllis 2 (ecn.nl/phyllis2).

3. Predictive modelling approach

The model presented in this work is structured in an complex correlation and the outcome is a parameter in the range 0 - 100, which indicates the specific fuel propensity (low – very high) to induce agglomeration - slagging issues in combustion applications. The correlation should be considered as a first step of a three-step integrated approach, which includes the correlations, thermochemical modelling and specific pilot tests (e.g. Biagini et al. 2014). The input data for the computation of the fuel agglomeration - slagging propensity are parameters based on the concentration of inorganic species in the fuel: K, K_{pH3}, Na, Na_{pH3}, Ca, Ca_{pH1}, Mg, Mg_{pH1}, Si, non metallic Al, P, Fe, Cd, Zn, Pb [mg/kg d.b.]. The indication of pH follows the formulation at first proposed by Zabetta and co-authors (Zabetta et al., 2012). Further information on the predictive model is published in (De Fusco et al., 2015).

3.1 Validation of the modelling approach

The validation of the modelling approach is based on the comparison with experimental data from the literature (e.g. Figure 2, a) and with outcomes from other predictive models (e.g. Figure 2, b). For the fuels used for the validation, when the ash solubility results (chemical fractionation) were not available, approximations have been used (for example, all the potassium is leachable at pH = 3). Error bars presented

in the plots (Figure 2 and following) are computed as propagation errors considering a relative uncertainty in the fuel inorganic compositions of 10% (type B uncertainty), for each of the ash constituents.
In Figure 2 (a), the computed agglomeration - slagging propensity is compared with the experimentally derived de-fluidization temperature (DT), with the related uncertainty when available, for different fuels and mixtures. High DT indicates that the fuel can be processed at high operating temperatures before agglomeration occurs, therefore it is less prone to induce agglomeration. Alternative predictive models include thermochemical equilibrium computations (TEC) to compute the characteristic melting temperatures (e.g. the temperature at which 15% or 30% of the ash is molten, T15 or T30) and differential scanning calorimetry (DSC) of ashed samples to identify ash-melting peaks. The characteristic temperatures from TEC and DSC have been compared with the computed agglomeration - slagging propensity, for the fuels studied in the SciToBiCom Project (Frandsen et al., 2013) in Figure 2 (b). The computed trends are in good agreement with the outcomes from TEC, especially with respect to the computed temperature at which 30% of the ash is molten, T30 [°C].

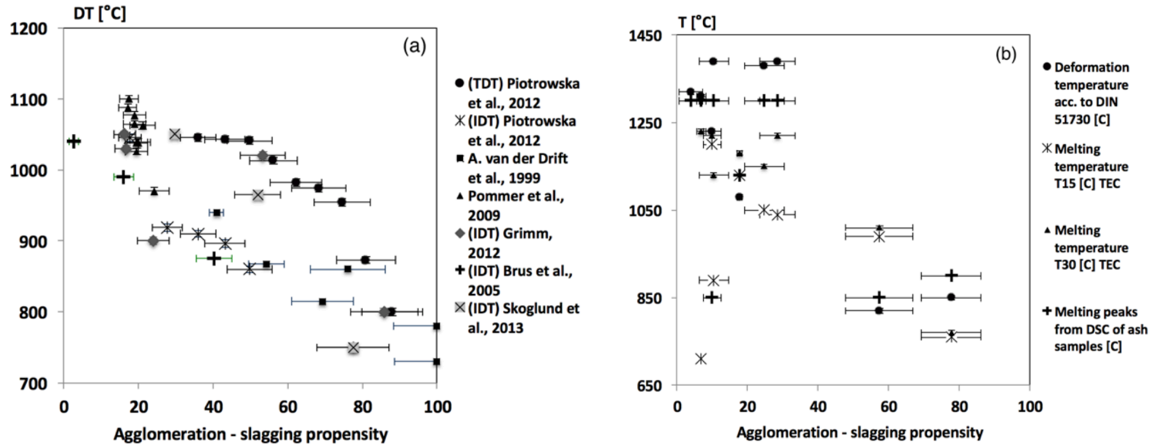

Figure 2: (a) DT [°C] (I: initial; T: total de-fluidization), for different test campaigns. (b) Agglomeration - slagging propensity compared with TEC, ash melting peak temperatures from DSC and standard AFT according to DIN 5130. Each point is a different fuel or fuel mixture.

The comparison between the computed propensity and the shrinkage starting temperature (SST) from the Ash Fusion Test (AFT) is presented in Figure 3 for different fuels. A high SST is necessary but not sufficient condition to low agglomeration and slagging in combustion.

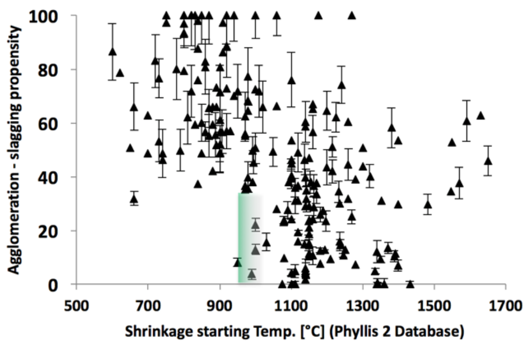

Figure 3: Computed propensity and the related SST from the standard AFT.

4. Results and discussion

The fuels presented in Section 2 are analysed. The propensity of agglomeration and slagging is plotted as a function of the fuel type in Figure 4 (a) and sorted in Table 1. As expected, the behavior of the fuels is largely varying from 0 to 100. When multiple analyses of the same fuel type are available, a median value for each of the ash constituent is computed, and the propensity is computed for the median fuel. Figure 4 and Table 1 evidence that the predicted agglomeration - slagging propensity is the highest for some agro-residues (olive kernels, corn cobs) and crops (e.g. miscanthus wood). On the contrary, for some residual fuels (e.g. grain straw), woody species (poplar, olive and citrus prunings), and fibrous matter (such as olive leaves and vine branches), the computed propensity is low-to-medium. Generally, husks and straws are in the medium-to-very high range. Median propensities for the different classes, based on the collected information, are: agro-residues (various): 54; wine industry residues: 47; crops: 46; olive industry residues: 37; citrus industry residues: 28; wood and shrubs: 21. The extension of the database is likely to cause an alteration of the median values. Fuels of the same class can behave very differently depending on the specific ash chemical composition. This is the case, for example, for the olive industry agro-residues. Samples from Spain evidence a lower propensity than samples from Greece and Italy. Olive tree pruning seems to have a slightly higher agglomeration and slagging propensity than the tree stem wood and leaves. Olive bagasse and pressing residues evidence a medium-to-high propensity. Within this class, olive kernels and husks are the opportunity fuels with the highest propensity to slag and agglomerate in combustion. Such information is particularly valuable for the selection of a fuel mixture.

Additives convert vaporized inorganic species to less harmful forms or retain in specific ash fractions dangerous compounds, for example binding potassium (K) in high melting temperature structures. For the fuels with high and very high computed propensities, additives should be used to lower the risk of agglomeration and slagging. They are classed as Al-Si-based (e.g. kaolinite, bauxite, clays, zeolites, halloysite, coal ash) (Wang et al., 2013), S-based (e.g. ammonium sulfate, aluminum sulfate), P-based (e.g. phosphoric acid), and Ca-based (e.g. calcium carbonate, ca-phosphates etc. (De Fusco et al., 2016)) according to the major elements present. Their specific effectiveness is still the subject of research.

The comparison between the computed propensity and the SST from the AFT (in oxidizing conditions), for some of the fuels analysed, is presented in Figure 4 (b). It is confirmed that a high SST is necessary but not sufficient condition to expect a low agglomeration and slagging. Moreover, the comparison between the computed agglomeration - slagging propensity and an index such as the alkaline ratio, defined here as (K+Na)/LHV in [mg/MJ d.b.], for some of the fuels analysed, is presented in Figure 4 (c). The alkali metals concentration, alone, should not be considered as the ultimate indication for agglomeration and slagging.

Table 1: Classification of selected biomass fuels based on the computed agglomeration-slagging propensity.

Aggl. - slag. propensity	**Fuels (examples)**
Low (<10)	Orange tree, prunings (GR); Virgin pomace (IT); Cofee grounds (Phyllis 2/1769); Poplar pellets (ES).
Medium (10 - 30)	Grain straw (IT); Poplar (IT); Cytisus multiflorus sweet shrub (ES); Wood chips (IT); Apricot kernels (IT); Pine sawmill waste (IT); Corn straw (IT); Olive tree (ES); Pine branches (Not specified); Olive leaves (ES); Vine branches (IT); Olive tree, pruning (ES); Eucalyptus wood (Phyllis 2/3291); Carragean waste (MixBioPells); Citrus tree (GR) [ashed at 600C]; Willow (GR); Citrus tree, pruning (GR); Poplar (GR).
High (30 - 50)	Olive tree (GR) (ashed 600C); Cerris (IT); Brassica pellets (ES); Olive tree, pruning (GR) and others.
Very high (>50)	Olive kernel (GR); Thistle (ES); Almond shells (IT); Corn stalks (MixBioPells) and others.

5. Conclusions

In the recent years, a growing interest for low-quality and economically less expensive biomass fuels is observed, in both small and large-scale thermal processing plants. Among the barriers that hamper the efficient processing of these fuels, agglomeration in fluidized bed combustion, slag formation, and fouling of convective heat exchangers are still challenging for plant operators. In this work, a fuel characterization approach to define the agglomeration - slagging propensity of biomass fuels in thermal processes has been applied to a database of available Mediterranean solid biomass. Among the fuels analyzed, wood, shrubs and citrus industry agro-residues evidenced a low-to-medium median propensity to agglomerate and slag, contrarily to the high propensity of various agro-residues, wine industry residues, and crops. The thermal processing of some agro-fuels such as straws, husks and corn cobs is expected to be challenging due to ash issues. Since technical applicability is a major constraint in the use of new fuels in thermal plants, about 20 opportunity fuels, with low-to-medium agglomeration and slagging propensity and for which environmental, economic and social sustainability has to be further explored, are suggested for thermal applications. For the fuels with a high computed agglomeration and slagging propensity, use of additives should be investigated. In this work, it is evidenced that a high Ash Fusion Temperature (SST) and a low alkali metal concentration in the ash (often identified as the root of sintering issues, for example computed as (K+Na)/LHV [mg/MJ d.b.]) are necessary but not sufficient conditions to preliminarily expect a low agglomeration and slagging. Finally, it is important to bear in mind that biomass composition can vary considerably depending on its biological origin, location, seasonality, farming and harvesting practices, and ultimately the fuel preprocessing: the predicted values reported in the plots in this investigation cannot be applied generally, but are dependent on the specific composition of the samples collected in the database.

Figure 4: (a) Agglomeration - slagging propensity (bottom axis, bars) computed for the fuels in the database; (b) compared with the the SST from the Ash Fusion Test (in oxidizing conditions) (top axis, bullets); (c) compared with the alkaline ratio defined as (K+Na)/LHV in [mg/MJ] (top axis, bullets).

Acknowledgments

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