SLAG FORMATION DURING COMBUSTION OF BIOMASS FUELS WITH LOW PHOSPHORUS CONTENT

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ABSTRACT: Slag and ash deposition problems have more than occasionally been observed in biomass fueled plants in general and especially in pellet fired plants. These problems can lead to reduced accessibility as well as performance of the combustion appliances. Slag formation including ash transformation mechanisms, measures for prevention and prediction during combustion of biomass fuels has been studied by the research groups at Lulea University of Technology, Umeå University and Energy Technology Center for over one decade now. Several (about 40) different biomass fuels/fuel mixtures have been studied and many different fuel additives/co-combustion fuels have been used to combat slag formation. About 20 scientific papers and 10 technical reports have been published by the research groups within the topic of slag formation during combustion of biomass fuels with low phosphorus content. The objective of the present work was to summarize the general experiences and conclusions of our research within the area of slag formation during combustion of fuels with low phosphorus and varying silicon content. Silicon rich fuels, i.e. fuel ash dominated by silicate-alkali chemistry (e.g. straw fuels), generally shows relatively high slagging tendencies. Exceptions to these general trends exist i.e. fuels with very high Si/K-ratios. Wood derived fuels with a relatively low inherent silicon content shows low or relatively moderate slagging tendencies. However, severe contamination of sand material to woody biomass fuels may greatly enhance the slagging tendencies. Fuel additive addition to problematic woody biomass and straw significantly reduces the slagging tendencies. When adding limestone and kaolin to the problematic wood and straw fuels the composition of the formed slag is changed from relatively low temperature melting silicates to high temperature melting silicates and oxides. The standard ash fusion tests and chemical equilibrium calculations give useful qualitatively information of the slagging tendencies. However, both methods must be further improved before quantitatively results can be used. The use of different fuel indexes to predict the slagging tendencies could be an interesting option. More research within this field is, however, needed.

Keywords: ashes, biomass, combustion, sintering

1 INTRODUCTION

An increasing interest in thermo-chemical biomass conversion processes including combustion has been seen during the last decades. Today several different biomass assortments are used for combustion and many new fuels are continuously entering the fuel market. Variations in ash forming matter between and within different biomass fuels/assortments are large. The behavior of the main ash forming elements (e.g. K, Ca, Mg, Fe, Al, Si, P, Cl and S) under combustion conditions is complex and exhibits rather large differences between different fuel (ash) compositions. After complete combustion of the biomass fuel particle a substantial part of the ash forming element will form a solid residue known as residual ash. This ash could form melted aggregates/sticky particles (> 1 μm) which further could form deposits (slag) on the furnace wall, in the burner (e.g. powder-pellet burners) or on the grate. Slag and ash deposition problems have more than occasionally been observed in biomass fueled plants in general and especially in pellet fired plants. These problems could lead to reduced accessibility as well as performance of the combustion appliances.

Slag formation including measures for prevention and prediction during combustion of biomass fuels has been studied by the research groups at Lulea University of Technology, Umeå University and Energy Technology Center for about one decade know. Several (about 40) different biomass fuels/fuel mixtures have been studied and many different fuel additives/co-combustion fuels have been used to combat slag formation. About 20 scientific papers and 10 technical reports have been published by the research groups within the topic of slag formation during combustion of biomass fuels.

The objective of the present work is to summarize the general experiences and conclusions of our research within the area of slag formation during combustion of biomass fuels with low phosphorus content.

2 RESULTS FROM PREVIOUS WORK ON SLAG FORMATION DURING COMBUSTION OF BIOMASS FUELS WITH LOW PHOSPHORUS CONTENT

2.1 Slagging characteristics during combustion of biomass fuels with low phosphorus content

After complete combustion of the fuel particles a major part of the ash forming elements will form a solid residue, known as residual ash. Previous work have shown that residual ash formation during biomass combustion depends on the amount and composition of ash forming elements as well as on actual process/fuel particle temperatures, the mixing between fuel and oxidizer and process residence time [1]. For several previous studied biomass parts of the residual ash has formed melted aggregates which not are transported out from the burner grate and or the furnace and therefore forms slag e.g. [2], [3], [4], [5].

Previous work in residential combustion appliances have shown that that the amounts of slag produced are affected both by the combustion appliance and the fuel type used whereas the composition and strength of the slag mostly are influenced of the fuel ash composition [2], [4]. The composition of the formed slag in combustion of seven different woody biomasses (e.g softwood bark fuels, - stem wood fuels and - logging residues) in different residential pellet appliances has been studied. The chemical composition of the produced
slag was identified as solid phases in a silicate melt. The results indicated also that the Si-content in the fuel correlated relatively well to the slagging tendencies of the different studied woody biomass ashes [4]. In another study, the critical levels of problematic ash components in stemwood pellets regarding slagging were determined [6], [7].

The results showed that the problematic wood-pellets had a significantly higher amount of Si in the fuel ash.

The critical level of Si (given as SiO2) was about 20-25 % weight-% of the fuel ash, i.e. pellets with levels in or over this range resulted in slagging problems in residential burners. In addition to this, the Si- and K content in the fuel were shown to be important indicators of ash sintering during combustion of several different agricultural fuels in different residential appliances [8].

The slag formation-characteristics have further been studied in residential combustion of twelve different woody and non-woody biomass fuels (different straw fuels) [9]. The results from that work suggest that during the char burnout and de-volatilization phase of the fuel particle high amounts of the potassium reacts with Si dispersed in the organic structure and/or mineral surfaces in the fuel. Sticky silicate melts are formed locally on these surfaces. Other residual ash forming elements such as calcium and magnesium which are frequently found in e.g. wood derived fuels could thereby be dissolved into the melt thereby enhance both the release of alkali from the melt and significantly reduce the amount of melt formed. According to the suggested chemical/physical slag formation process potassium containing biomass fuels relatively rich in silicon (either dispersed in the organic structure or contaminated with sand) with relatively low amounts of alkaline earth metals would retain a main part of the potassium forming a sticky alkali-silicate melt which are a prerequisite for the slag formation process.

The conclusions from this work [9] were that biomass fuel pellets rich in silicon (either inherent or contaminated with sand) and low content of alkaline earth metals the main part of the potassium reacted with the silicon rich ash-residue, forming sticky alkali-silicate particles that were not entrained from the burner but participated in the initiation of the slag formation process. Silicon rich fuels, i.e. fuels were the ash characteristics were dominated by silicate-alkali chemistry, generally showed relatively high slagging tendencies. Straw fuels have typically this ash composition but exceptions to these general trends exists (e.g. one of the hemp-fuels used in this work). Wood derived fuels with a relatively low inherent silicon content therefore showed low or relatively moderate slagging tendencies. However, severe contamination of sand material to these fuels may greatly enhance the slagging tendencies. In agreement with these results several studies [6], [10], [11] have shown that several other wood based/dervived fuels with low silicon content have had low slagging tendencies.

As discussed above previous investigations have suggested that sand contamination to woody biomass fuels enhance slag formation. To gain increased understanding in the ash and slag forming chemical processes the effect of soil contamination in different forestry assortments on the extent of slagging where therefore investigated [12]. The results from that work showed that melted bottom ash reacted with the admixed sand particles resulting in an increased amount of melt with an increased content of silicon. The results confirm earlier experiences that melted bottom ash from combustions of woody biomass, upon cooling, forms silicate phases. In the corresponding melted bottom ash, sand minerals as quartz, plagioclase and microcline are not thermodynamically stable, but will react and form a more silica rich melt. This melt has presumably lower liquidus temperature, explaining the increased amount of melted bottom ash observed in the combustion experiments of soil contaminated fuels.

In another study, the effect of peat addition to woody biomass on the slagging characteristics in residential combustion was investigated [13], [14]. When introducing a relatively silicon rich peat to the used woody biomasses (i.e. softwood stem wood and energy wood) the slagging tendency increased because high temperature melting Ca-Mg oxides reacts to form more low temperature melting Ca-Al-K silicates. When adding a ash poor peat, with relatively high CaSi ratio, there were still Ca-Mg oxides left in the bottom ash i.e. a less amount of sticky low temperature melting Ca-Al-K silicates were formed.

2.2 Measures for prevention of slag formation

Several authors have previously proposed the use of several various kinds of mineral additives mainly lime/dolomite based additives and/or clay or kaolinite based additives to combat ash related operational problems during combustion of biomass. Most of the work have been focused on fouling, bed agglomeration or corrosion and only very limited amount of work have been published on slag formation.

Adding limestone and kaolin suspension with additive-to-fuel ratio of 1 wt-% to a severely sand contaminated bark and cleaning assortment significantly reduced the slagging tendencies in residential pellet combustion [3]. Significantly higher Ca- and Al-concentrations in the slag were observed for limestone and kaolin addition, respectively. These changes resulted in a more favorable melting behavior (i.e. a higher solid phase to melt ratio).

By adding limestone with an additive-to-fuel ratio of 0.5 wt-% to a problematic softwood stemwood raw material (Si-enriched probably because of contamination of sand/soil), the severe slagging of the fuel could totally be eliminated [15]. Adding kaolin to the problematic raw material gave a minor decrease in slagging tendency of the problematic raw material and a major increase in slagging tendency of the problem-free stemwood raw material [15]. When adding limestone to the problematic raw material, the composition of the formed slag was changed from relatively low temperature melting silicates to high temperature melting silicates and oxides. On the other hand, kaolin addition to the problematic raw material changed the content of the slag from mainly Ca-Mg-silicates to be dominated by K-Al-silicates which have relatively low melting points. When introducing kaolin to a problem-free softwood stemwood raw material, the high temperature melting Ca-Mg oxides reacts to form lower temperature melting Ca-Al-K silicates.

In another work, the slagging characteristics during combustion of corner stovers with and without kaolin and calcite were investigated [16]. A 3% kaolin and calcite addition increased ash melting temperature (TT) by about 100-200 °C. By adding the 3% kaolin or calcite to the corn stover raw material, the severe slagging tendency of the fuel was considerably reduced. Also in this study the
reduction of slagging when using additives was attributed to a change from relatively low melting temperature silicates to more high melting temperature silicates. For the corn stove without additives the low melting fractions of the slag were assumed to mainly consist of potassium calcium silicate, indirectly observed as a glass.

When kaolin was added a depletion of potassium was observed due to the extensive formation of leucite (KAlSi2O6) and the glass became dominated by calcium, aluminium and silicon. This process was accompanied by a considerable reduction of glass amount. In the case of CaCO3 addition, however, calcium magnesium silicates formed in an extent that the glass (low melting material) finally became dominated by potassium silicate. This process was also accompanied by a substantial reduction of the amount of glass [16].

2.3 Predicting slagging tendencies of biomass fuels with low phosphorus content

As mentioned in the introduction, slag formation could lead to reduced accessibility as well as performance of the combustion appliances. The slagging behavior could also be rather different between various fuels. Examples of potential problematic fuels are "new" more ash rich biomass fuels (e.g. agricultural residues/derived fuels). It would therefore be of considerable interest to predict the slagging tendencies for different biomass assortments.

Many ash behavior prediction techniques are available. Most of these have however been developed for addressing fouling and slagging during coal combustion. The standard ash fusion tests (AFT; ISO 540; BS 1016.15-1970; GOST 2057-1982; SABS 932; ASTM D1857, 1987; DIN 517 30, 1984; AS 1038.15, 1987; GE 219-74) are the most commonly used laboratory methods and also the only standardized approach to predicting the behavior of ashes in different processes.

In a previous study [17] a comparison between four different types (both empirical and theoretical) techniques to predict the slagging tendencies in residential pellet combustion appliances was performed. The four techniques used were the standard ash fusion test (SS ISO 540), thermal analysis (TGA/DTA), thermochemical model calculations and a lab-scale sintering test. The tests were performed with twelve pelletized biomass raw materials and the results were compared with actual slagging tendency results obtained from controlled combustion experiments. The results showed significant differences in the predicting slagging tendencies between different predicting techniques and fuels. The method based on thermal analysis (TGA/DTA) of produced slag's must be further developed before useful information could be provided of the slagging behavior of different fuels. The used sintering method must also be further improved before the slagging tendency of fuels forming slags extremely rich in silicon (e.g. some grasses) can be predicted. Relatively good agreement was obtained between results from chemical equilibrium calculations and the actual slagging tendencies from the combustion tests. However, the model calculations must be further improved before quantitatively results can be used. The results from the standard ash fusion test (SS ISO 540) showed in general relatively high deformation temperatures, therefore predicting a less problematic behavior of the fuels in comparison to the actual slagging tendencies obtained from controlled combustion experiments in commercial pellet burner equipments. Nevertheless, the method predicted in most cases the same fuel specific slagging (qualitatively) trends as the corresponding combustion behavior.

3 CONCLUSIONS

- Silicon rich fuels, i.e. fuel ash dominated by silicate-alkali chemistry (e.g. straw fuels), generally showed relatively high slagging tendencies. Exceptions to these general trends exists i.e. fuels with high Si/K-ratios.
- Wood derived fuels with a relatively low inherent silicon content showed low or relatively moderate slagging tendencies.
- Severe contamination of sand material to woody biomass fuels may greatly enhance the slagging tendencies.
- Fuel additive addition to problematic woody biomass and straw significantly reduce the slagging tendencies.
- When adding limestone and kaolin to the problematic fuels the composition of the formed slag was changed from relatively low temperature melting silicates to high temperature melting silicates and oxides.
- The standard ash fusion tests and chemical equilibrium calculations gives useful qualitatively information of the slagging tendencies. However, both methods must be further improved before quantitatively results can be used.
- The use of different fuel index to predict the slagging tendencies could be an interesting option. More research is needed.

4 ACKNOWLEDGEMENTS

The financial support from the Swedish Energy Agency (STEM), EU Objective 1 Södra Skogsland region, the counties of Västernorrland, Västerbotten and Norrbotten, the Kempe Foundations, the Swedish University of Agricultural Science (SLU), NEQVA, Torvörska, the Swedish pellet production industry (PIR) and several industrial companies is gratefully acknowledged. Additional funding from the National Technology Agency of Finland through the research project ChemCom at Åbo Akademi University (RB) is also acknowledged.

5 REFERENCES

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