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THE STUDY OF WASTE WOOD BIOMASS AS A BIOFUEL IN THE CONTEXT OF BOILER OPERATIONAL PROBLEMS – SLAGGING AND HIGH-TEMPERATURE CORROSION

This paper presents the melting characteristics of ash from different residual forest biomass - wood pellets, oak chips, coniferous bark, deciduous tree bark, wet sawdust and non-sorted blueberries. The melting temperatures of ash in reducing and oxidizing atmospheres were similar and did not differ by more than 10°C to 30°C. These values were within a range of 1230°C to 1330°C, and for the blueberry it was more than 1500°C. Only ash pellets melted in a reducing atmosphere at a temperature of 1280°C, and in an oxidizing temperature at 1430°C. To compare, determination tests were also performed for ash from "agro" biomass waste. Ash melting temperatures for biomass composites of agricultural origin (made in an oxidizing atmosphere), turned out to be lower than the temperatures of ash from wood biomass. In the results of the presented elemental analysis, the share of chlorine and sulphur and the impact S/Cl on high temperature corrosion processes were indicated. On the basis of the results for all the tested types of biomass, the calculated ratio S/Cl was below the value of 2.0. This means that the tested biofuels do not meet the safe use of biofuels detailed in the energy sector criterium (from the point of view of boiler operation).

Keywords: wood waste, combustion, slagging, high-temperature corrosion

Introduction

The process of high-temperature thermal transition of fuel generates a solid mineral residue – ash. The amount of mineral substance in biomass is usually smaller than in coals. Although the amount of ash after the combustion of biofuel is smaller, its composition differs from the composition of the coal ash. This is the reason why boilers have many operational difficulties: on heat

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transfer surfaces deposits are formed, followed by their agglomeration and the phenomenon of high-temperature corrosion occurs.

The paper [Vassilev et al. 2013a, b, c] presented a series of excellent reviews on the composition and application of biomass ashes and their behaviour during co-combustion. Analysis of different kinds of ash, from wood biomass (eucalyptus, rockrose, pine, olive tree pruning, cork, and poplar), agro-industrial biomasses (almond shells, olive stones and another two by-products of the olive oil extraction industry called 'alperujo') and herbaceous biomasses (rice straw, wheat straw, sunflower, thistle and brassica) were conducted by [Fernández Llorentea and Carrasco García 2005, 2006]. To assess the degree of chloride corrosion risk based on the composition of the biomass, the fuel corrosion chloride rate (ICV) is used. It is set by determining the chlorine and sulphur content in biomass and potassium in the ash [Born 2005].

The small particle size of the fly ash produced from the combustion of biomass, means the biomass co-combustion with coal typically does not substantially increase the risk of erosion. If the biomass is contaminated with grains of sand, erosion may increase. With some simplification, it can be concluded, that the risk of slagging when burning a fuel depends on the characteristics of the melting ash, defined by three temperature values: softening – TD, melting – HT and flowing – FT. If, in case of biomass co-combustion with coal, the softening temperature of ash lowers (in comparison to the softening temperature of coal ash), this results in an increase in the speed of deposits build-up on boiler heating surfaces. In turn, this process causes a rise in the temperature of exhaust gas, and that reduces the gross efficiency of the boiler (compared to the efficiency obtained during the combustion of the coal). The study of ash changes, the building up of deposits on the heating surfaces during the combustion of wood and straw biomass and co-firing with coal was conducted by [Hansen et al. 1999; Robinson et al. 2002; Nordgren et al. 2013].

A relationship exists between the melting point of the ash and the content of chlorine, sulphur, silicon and alkali metals. Sticky fuel-derived ash may form in cases where fuel ash chemistry is governed by a high content of potassium and organically bound silicon, combined with a high content of chlorine and a low content of other ash-forming elements [Bartels et al. 2008; Brus et al. 2005]. Zheng et al. [2007] combusted bituminous coal, lignite coal and straw. They analysed fly ash, bottom ash and deposits, determining the concentration of Cl, S and K.

The aim of the study was to determine (in reducing and oxidizing atmospheres) the characteristic melting temperatures of ash from forest residues. To compare, determination tests were also performed for ash from "agro" biomass waste [Król 2013]. Biomass as a fuel in the power industry, creates many operational difficulties. In order to avoid adverse agglomeration of the bed during the combustion process, (the formation of residues on the heating surfaces) the HT temperature of the ash should be higher than the temperature in

the furnace during combustion of the fuel. The aim of the study of chlorine and sulphur loads was to assess the slagging factors and corrosion of chloride for plant, wood and agriculture biomass.

Materials and methods

The subject of the study was forest biomass and agricultural waste. Forest biomass, which consisted of: wood pellets, wet sawdust, oak chips, bark coniferous, deciduous tree bark and unsorted blueberry came from TRAK a Timber Production Plant in Garbatka Długa, in the Mazowieckie province. The waste material is agricultural straw and oat bran (derived from individual agricultural crops, from the area of the Podlasie province) and potato pulp (waste from the manufacture of starch and potato starch, came from the Food Industry Enterprises PEPEES SA in Łomża). With agricultural waste two fuels were produced:
1. twenty percent from potato pulp plus eighty percent from oat bran;
2. twenty percent from potato pulp plus eighty percent from oat straw.

Characteristic ash melting temperatures in reducing and oxidizing atmospheres were determined using microscopic- photographic methods, according to CEN / TS 15370-1: 2007. The concentration of chlorine in the biomass was determined in accordance with ISO 587/2000. Sulphur was measured using CHNS elemental analyzer model 2400 series II Perkin Elmer.

Results and discussion

The results of determining the melting temperature of ash from forest biomass are shown in table 1.

SST shrinking temperature, determined in a reducing atmosphere (tab. 2), ranged from 740°C (wood pellets), 790°C (oak chips), 840°C (coniferous shoulder) and 1250°C, 1260°C (wet sawdust, deciduous tree bark) to > 1500°C (unsorted blueberry). In contrast, the SST determined in an oxidizing atmosphere was the lowest for ash from pellets – 720°C, the highest (> 1500°C) for ash from the unsorted blueberry sample, and for other materials it the value was between 1200 and 1270°C.

The first signs of shaped ash softening were visible at the deformation temperature called softening temperature TD. In a reducing atmosphere (as in the case of the shrinking temperature) the lowest TD was recorded for ash originating from the wood pellets (820°C) and the highest for unsorted blueberry ash (> 1500°C). The TD for the remaining biomass was contained within a range of 1240°C to 1290°C. The oxidizing atmosphere changed the TD value a little, and so: for wood pellets it was 1420°C, deciduous tree bark 1310°C, wet sawdust 1290°C, coniferous bark 1280°C and oak chips 1230°C. For unsorted blueberry, the softening temperature (as all characteristic ash temperatures

determined) regardless of the atmosphere (oxidizing or reducing), was higher than 1500°C.

Table 1. The characteristic melting temperatures of ash from forest residues

Type of forest biomass	Wood pellets	Wwet sawdust	Oak chips	Coniferous bark	Deciduous tree bark	Unsorted blueberry
SST°C, shrinking temperature atmosphere	reducing 740 720	reducing 1250 1270	reducing 790 1200	reducing 840 1260	reducing 1260 1260	reducing >1500 >1500
DT°C, deformation temperatutre atmosphere	reducing 820 oxidising 1420	reducing 1290 oxidising 1290	reducing 1240 oxidising 1230	reducing 1270 oxidising 1280	reducing 1290 oxidising 1310	reducing >1500 oxidising >1500
HT°C, hemisphere temperature atmosphere	reducing 1280 oxidising 1430	reducing 1290 oxidising 1300	reducing 1240 oxidising 1230	reducing 1280 oxidising 1290	reducing 1300 oxidising 1330	reducing >1500 oxidising >1500
FT°C, flowing temperature atmosphere	reducing 1300 oxidising 1440	reducing 1300 oxidising 1310	reducing 1250 oxidising 1240	reducing 1290 oxidising 1300	reducing 1320 oxidising 1340	reducing >1500 oxidising >1500

In the boiler, unfavourable phenomena such as slagging or fouling of the heating surfaces (which is associated with the ash change temperature) are the result of insufficient values for their melting points HT (temperature of the hemisphere). Having the HT temperature higher than the temperature in the furnace during combustion of the fuel is preferred. The melting temperatures of ash in reducing and oxidizing atmospheres were similar and did not differ by more than 10°C to 30°C. These were the values in the range, from 1230°C to 1330°C, for unsorted blueberry, it was more than 1500°C. Only ash pellets melted in a reducing atmosphere at a temperature of 1280°C, and in an oxidizing temperature at 1430°C. The ability of sticking (adhesion) did have ashes already in the temperature range between the softening point and melting point. FT temperature of ash flow is the one at which the ash melts completely.

Ash melting characteristics determined by their melting temperatures based on laboratory tests alone, do not give all the information regarding the nature of the threat of slagging on heat exchange surfaces. Ash melting temperatures indicated by the laboratory tests do not include boiler design and operating conditions, which has a major impact on fouling and slagging. In the laboratory, melting temperatures are determined in a short time, heating up the ash with a several degree increase rate of the temperature per min., while deposits in the boiler accumulate over long periods and are subject to alternate heating and cooling processes in the environment of exhaust gases.

Melting temperatures of ash from biomass of agricultural origin composites (performed in an oxidizing atmosphere – table 2), proved to be lower than the temperatures of ash from wood biomass.

Table 2. Characteristic ash melting temperatures (in an oxidizing atmosphere) of agricultural biomass rolniczej [Król 2013]

Type of "agro" biomass	Shrinking temperature, SST (°C)	Deformation temperature, DT (°C)	Hemisphere temperature, HT (°C)	Flowing temperature, FT (°C)
80% oat bran + 20% potato pulp	700	990	1110	1180
80% oat straw + 20% potato pulp	580	990	1080	1110

FT temperatures, in which the ash melted, varied from 1110°C to 1180°C. These values are about 100°C to more than 500°C lower, than the value corresponding to the temperature of ash forest waste. Ash from "agro" biomass softened at DT = 990°C. With respect to ash from the forest biomass, they were lower in range from 240°C to more than 500°C. They melted at a temperature of HT 1000°C. In case of loading the biomass with chlorine, alkali and heavy metals (when forming eutectics), melting of the ash is already observed at around 250°C [Ferrer et al. 2005].

The melting and slagging of biomass is dependent on the concentrations of F, Cl, S, Al and Si in ash [Arvelakis and Frandsen 2007]. Chlorine in plant biomass is present predominantly in the form of chlorides and, in small quantities organic bindings. The direct burning of plant biomass may cause (because of the participation of chlorine) the occurrence of high temperature corrosion, slagging and the pollution of the heating surfaces of boilers. It is generally accepted, that if the share of chlorine does not exceed 0.3 percent, then the combustible has a low (Cl < 0.2%) or medium tendency to slagging. In contrast, when it is larger than 0.3 percent, this tendency is significant, or very large if the proportion of Cl > 0.5 percent.

On the basis of determining chlorine and sulfur in biofuels (tab. 3), the classification according to their propensity to form deposits, and the risk of high temperature chloride corrosion was shown. The molar ratio of S/Cl can be used as an indicator for the high-temperature corrosion risk [Sommersacher et al. 2012].

Forest biomass and agricultural biomass composites are characterized by a low tendency to slagging (CI < 0.2%), in contradiction to oak chips. In oak chips, the chlorine content is within a range of 0.3 < 0.26 > 0.2, and therefore, the tendency of slagging is at an average level. As mentioned above, chlorine is present in the biomass in the form of chlorides, the presence of which (especially potassium chloride) is important due to the high temperature corrosion. These

Table 3. The size of slagging and chloride corrosion factors for plant biomass

Type of biomass	Chlorine Cl	Slagging tendency	Sulfur S	S/Cl	Chloride corrosion preponderance S/Cl < 2
wood pellets	0.10	<0.2% small	0.02	0.20	very high
wet sawdust	0.16	<0.2% small	0.01	0.06	very high
oak chips	0.26	<0.3% average	0.02	0.08	very high
coniferous bark	0.12	<0.2% small	0.03	0.25	very high
deciduous tree bark	0.09	<0.2% small	0.05	0.56	very high
unsorted blueberry	0.07	<0.2% small	0.03	0.43	very high
oat bran + potato pulp	0.08	<0.2% small	0.13	1.63	yes
oat straw + potato pulp	0.17	<0.2% small	0.01	0.06	very high

chlorides, residing in sediments forming on the boiler heating surfaces, can cause intense chloride corrosion. The presence of sulfur in biofuel reduces the risk of chloride corrosion by replacing the chloride ion in potassium chlorides or sodium in sulfate ion, determining higher stability of the sulfates of chlorides. Salmenoia [2000] reports that only when the state in which the ratio of the weight fractions of the S/Cl in the fuel falls below 2.0, is it dangerous. In [Aho and Ferrer 2005], this value is given as 2.2. From the results of the research presented in table 4 for all the examined types of biomass, the S/Cl is below the value of 2.0. This means that the tested biofuels do not meet the safe use of biofuels detailed in the energy sector criterium (from the point of view of the boiler operation).

Conclusions

In the processes of energy use of biomass waste, we can observe unfavourable events in the form of slagging or build-up of deposits on the heat transfer surfaces. This is related to the ash temperature changes, which are usually lower than the corresponding temperatures of the ashes from bituminous coals. This is particularly true for insufficient HT melting temperatures (hemisphere temperatures) which for carbon, is somewhere around 1500°C.

For the ash from wood waste, HT temperatures defined under reducing and oxidizing conditions, ranged from 1240°C to 1440°C. Only another forest biomass (unsorted blueberry), was characterized by a HT temperature value as in case of coal, i.e. more than 1500°C. In technical terms these values are acceptable.

Agriculture biomass, due to a very different quantitative composition of ash (in terms of low melting components) compared with the ash from coal, generates ash during combustion with lower values of temperature change. This was confirmed by studies of fuel formed from "agro" waste. Melting of ash was observed at 1000°C. These temperatures were lower than for wood ash, by several hundred degrees Celsius. Typical agricultural biomass, however, for

example in the form of wheat straw, is characterized by significantly lower ash melting temperatures, around 772°C. In practice, if agro biomass is combusted, the combustion temperature is allowed to be at 700°C to750°C. Under these thermal conditions, ash rich in alkali chlorides does not readily lend itself to the softening process, thus preventing corrosion and slagging of boilers. All tested biomass materials were characterized by a low tendency to slagging (Cl < 0.2%).

The sulphur and chlorine introduced into the furnace boiler with fuel, especially such as straw or wood, play a key role both in corrosion processes, which, in the high temperature atmosphere of the steam boiler constitute a threat to its structural steel materials, screens, superheater or evaporator and in staining (fly ash) and the slag on heat transfer surfaces. The criterion of safety for boiler corrosion processes is the ratio of sulfur to chlorine S/Cl 0> 2. The biofuels tested do not meet the safe use in energy industry criterium (from the point of view of the boiler operation). The S/Cl is less than two.

Plant biomass fuel is such a difficult fuel, because its combustion or co-combustion with coal requires the prevention of these undesirable processes, which significantly hinders ensuring trouble-free operation of boilers.

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