

REDUCTION OF ASH-RELATED PROBLEMS IN LARGE-SCALE BIOMASS COMBUSTION SYSTEMS VIA RESOURCE EFFICIENT LOW-COST FUEL ADDITIVES

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ABSTRACT: The incineration of waste wood is very often associated with ash-related problems (deposits, slagging and corrosion). This leads to short maintenance intervals, which result in significant power generation losses and high downtime costs. To avoid these problems, additives can be used, with particularly cost-effective additives being of great interest. Based on pre-evaluations, the addition of 2% gypsum and 3% coal fly ash was recommended, since an improved ash melting behaviour and reduced risk for high-temperature corrosion can be expected with addition of gypsum and coal fly ash. These additives with the recommended mixing rates were then investigated in a large-scale plant. Extensive investigations were carried out without additive (as a reference), and with the additives focusing on dust formation (aerosols and total dust), deposit formation and the corrosion behaviour of superheaters. These investigations were accompanied by fuel and ash analyses (grate, cyclone and filter). The addition of additives increased the amount of total dust in the flue gas up to 195% and 262% for gypsum and coal fly ash respectively. The chemical analysis of the total dust showed an enrichment of refractory species like Al for coal fly ash and Ca and Mg for gypsum which can positively influence the slagging behaviour. Aerosol measurements showed that the addition of coal fly ash minimised the amount of fine particulate matter, as less alkali metals (K and Na) were released into the gas phase. Gypsum addition increases the SO₂ concentrations in the gas phase due to the decomposition of gypsum, as in the combustion chamber about 900°C are present. Due to the preferred sulphation reactions (binding of S to alkali metals) less Cl is bound to alkali metals and therefore the Cl concentrations in the aerosols were lower compared to the reference case. This effect was also found in the deposits sampled at the position of the superheater. Based on the chemical composition of deposits the molar 2S/Cl ratios were determined, which can be used to predict the risk for high temperature corrosion. The analysis data showed that an improvement concerning the high temperature corrosion risk is possible by adding coal fly ash, whereas a significant improvement in case of gypsum additions seems very likely. The measurements carried out so far showed the influence (built-up rate, chemical composition etc.) of the additive application on ash fractions, deposits and dusts. By taking a closer look at the change in chemical compositions of dusts and deposits, additives with an appropriate additivation ratio can be suggested. In case of coal fly ash 3% and in case of gypsum 1% additive related to dry fuel seems to be adequate additive ratios to positively influence the risk of high temperature corrosion and reduce the slagging behaviour.

Keywords: biomass combustion; slagging fouling prevention, resource efficient additives,

1 INTRODUCTION AND OBJECTIVES

The incineration of waste wood is very often associated with ash-related problems (deposits, slagging and corrosion) [1, 2]. This leads to short maintenance intervals, which result in significant power generation losses and high downtime costs. To avoid these problems, additives can be used. A comprehensive review of different pure mineral additives can be found in Ref. [3]. Since these conventional additives are associated with relative high costs, cost-effective additives (from recycling material) are of great interest.

In previous work the combustion behaviour of 3 different waste wood mixtures without and with the addition of various low-cost additives such as recycled gypsum, coal fly ash and iron sulphide with two different addition ratios were investigated in a laboratory reactor. More detailed information about this system can be found in former work of the Authors [4, 5, 6]. Investigations in the laboratory reactor allowed the determination of suitable additives and ratios of additivation for further investigations in the large-scale plant. This approach represents a cost-effective and time-saving method for determining suitable additives and ratios of additivation. Based on the investigations carried out, the addition of 2% gypsum and 3% coal fly ash was recommended, since an improved ash melting behaviour can be expected with addition of gypsum and coal fly ash. Furthermore, an improved high temperature corrosion risk can be expected especially in case of gypsum application. Detailed information about this lab-scale evaluation can be found in Ref. [7].

The scope of this work was to investigate these additives with the recommended mixing rates in a large-scale plant. The investigations were accompanied by comprehensive measurements to determine the influence of the additive in the boiler.

2 METHODOLOGICAL APPROACH

In Figure 1, the biomass boiler is shown schematically. Furthermore, the measurement points (GF, M1 - M3) and the position of the additive injection are indicated. The system is designed for a nominal thermal output of 40 MW_{th}. It consists of a grate fired boiler where mixtures of waste wood and bark are introduced on the grate. In addition, at 3 positions above the grate (left, centre, right) wood dust is blown into the furnace. The additive was introduced directly into the combustion chamber with an ejector nozzle. Actual operation suffers from slagging in the boiler in the 1st duct and by slagging, fouling and corrosion in the protective evaporator and the superheaters in the 3rd duct.

In Figure 2, a photo of the protective evaporator after a system operation of 9 weeks can be found. In the picture the solid deposits which are formed on the heat exchanger tubes can be seen. The deposits lead to a reduced heat transfer and result in higher flue gas temperatures at the chimney, which reduce the efficiency of the system. After a period of about 9 weeks, the plant must be shut down and these deposits must be removed with considerable effort.

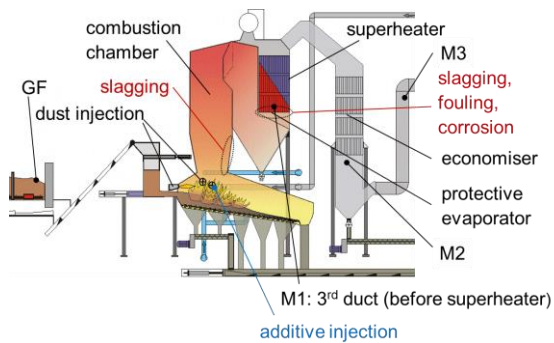


Figure 1: Scheme of the biomass boiler and indication of relevant measurement positions

Explanations: GF ... grate fuel sample position, M1 ... online-corrosion probe and deposit probe measurements position, M2 ... flue gas analysis position, M3 ... dust and aerosol measurement position



Figure 2: Protective evaporator from below (in the flow direction, luv) after a system operation of 9 weeks

To systematically investigate the problems prevailing in the boiler extensive investigations were carried out without additive (as a reference) and with the additives. The following measurements and analysis have been performed:

- Fuel sampling and analysis

Three fuel samples of grate fuel and dust were taken daily, of which a mixed sample was prepared per day. This mixed sample was analysed for water content, ash content and the elements S, Cl, Si, Ca, Mg, Al, Fe, Mn, P, K, Na, Zn and Pb.

- Ash sampling and analysis

Three ash samples of the individual ash fractions (grate, cyclone and filter ash) were taken daily, of which one mixed sample was produced per day. This mixed sample was analysed for the elements S, Cl, Si, Ca, Mg, Al, Fe, Mn, P, K, Na, Zn, Pb, TIC and TOC.

- Determination of total dust concentration

Determination of the total dust concentrations in the undiluted flue gas after the economiser by means of total dust measurement according to VDI 2066 with subsequent analysis of S, Cl, Si, Ca, Mg, Al, Fe, Mn, P, K, Na, Zn and Pb.

- Determination of aerosols in flue gas

The concentrations and particle size distributions of aerosols in the flue gas after the economiser were determined with a Dekati Gravimetric Impactor (DGI).

By means of the measurement the quantity of aerosols and the chemical composition (S, Cl, Si, Ca, Mg, Al, Fe, Mn, P, K, Na, Zn and Pb) of the aerosols was determined.

- Deposit probe measurements

With a deposit probe, deposit formation on heat exchanger tubes at the position M1 (see Figure 1) was investigated. The deposit probe, which simulates a heat exchanger tube, allows the determination of deposit build-up rates. The chemical composition of the deposits was determined by SEM-EDX.

- Analysis method for fuel, ash, total dust, aerosols concerning S, Cl, Si, Ca, Mg, Al, Fe, Mn, P, K, Na, Zn, Pb

The analysis method was in accordance with results of FP6 project BioNorm [7] which among other aspects also dealt with the definition of standards and best practice guidelines for biomass fuel analyses.

- Temperature measurement

At the position of the online corrosion probe, the flue gas temperature was continuously measured with a thermocouple.

- Analysis of the flue gas

The flue gas after economiser was continuously analysed using a Fourier Transform Infrared Spectrometer (FT-IR) (Ansyco Series Dx-4000) and a flue gas analyser (ABB EL 3020)

- Corrosion measurements

Measurements were performed with an online corrosion probe.

Based on the investigations in the large scale plant the effect of the additives was determined and valuable insights into the operating behaviour of the plant with additives were generated.

3 RESULTS

3.1 Reaction of additives in the boiler

The fuel and ash analyses showed that the injected additives are not deposited on the grate but remain in the combustion chamber and are later deposited in the boiler or emitted as coarse or fine dust. This was confirmed by the measurements of SO₂ concentration, aerosols, total dust and deposits.

Figure 3 shows SO₂ and HCl concentrations in the raw gas as well as the feeding rate of wood dust to the boiler during the addition of gypsum.

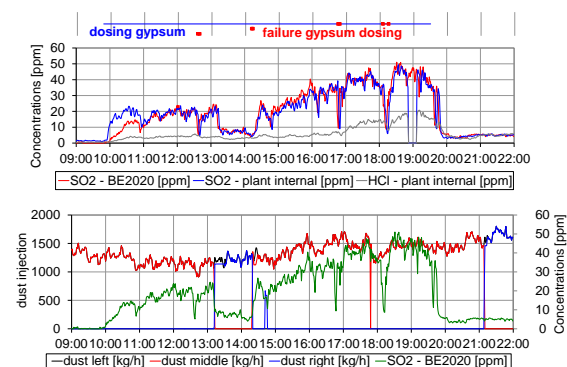


Figure 3: Influence of wood dust injection on precipitation of the additive based on SO₂ concentration

The addition of gypsum indicated increased in SO_2 concentration in the raw gas (see Figure 3) due to the decomposition of gypsum, as in the combustion chamber about 900°C were present. This increase was also dependent on the operation of the wood dust injection position (left, middle, right). It was found that when the wood dust injection is activated in the vicinity of the additive injection (right-hand injection of wood dust), the SO_2 concentration in the raw decreased which indicated that gypsum was not converted any more. It was visually confirmed, that the additive was largely deposited on the grate and only partial decomposition of the gypsum occurred. It could be shown that the point of injection has a significant influence on the effectiveness of the additive. If the additive shall be used in another boiler, first of all the conditions of the injection of the additive should be investigated.

3.2 Total dust concentration

In Figure 4, the total dust concentration (in the raw gas) for additive application and the reference case are shown.

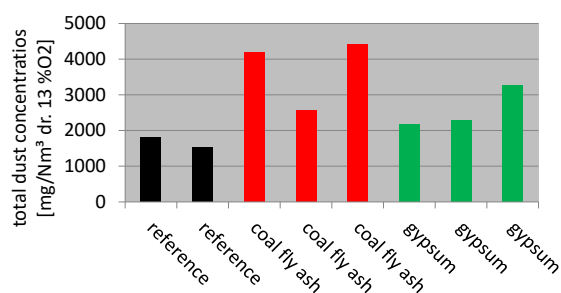


Figure 4: Total dust concentration for additive application and the reference case

Seen from Figure 4, the injection of additive increased the amount of total dust in the flue gas up to 195% and 262% for gypsum and coal fly ash respectively compared to the reference case.

The chemical analysis of the dust showed that elements which have high concentrations in the additive can be found in the total dust, which is basically consistent with the dust precipitated in the cyclone. This implies that refractory species such as Al (in the case of coal fly ash) and Ca and Mg (in the case of gypsum) occur in higher concentrations than in the reference case. It can also be assumed that increased concentrations of these aforementioned elements occur in the deposits and therefore the tendency to slag formation is minimized.

3.3 Aerosol concentrations

The aerosol concentrations (in the raw gas) for additive application and the reference case can be found in Figure 5.

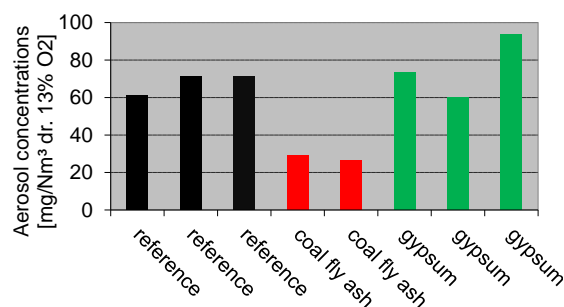


Figure 5: Aerosol concentrations for additive application and the reference case

The aerosol concentration (particles $<1 \mu\text{m}$) was on average 27.7 mg/Nm^3 during the coal fly ash dosing. This is lower than for the other cases (reference and gypsum addition) and can be explained by the reduced release of alkali metals K and Na, which is achieved by binding alkali metals in Al-silicates contained in the coal fly ash. A similar mechanism was also described in Ref. [3, 5]. For the reference case (no additive) the averaged aerosol concentrations were 67.8 mg/Nm^3 and during the dosing of gypsum averaged aerosol concentrations of 75.6 mg/Nm^3 were determined. The aerosol measurements prove that by addition of coal fly ash the amount of aerosol concentrations and the chemical composition can be influenced. Lower release rates of alkali metals from the fuel to the gas phase also mean that less alkali metals are available for binding S and Cl to aerosols. Therefore, an influence of the deposits formed is very likely which can further influence other problems which prevail in the boiler e.g. high temperature corrosion (see section 3.5) and slagging tendency.

3.4 Deposit formation

Figure 6, shows the deposit built-up rate for additive application and the reference case

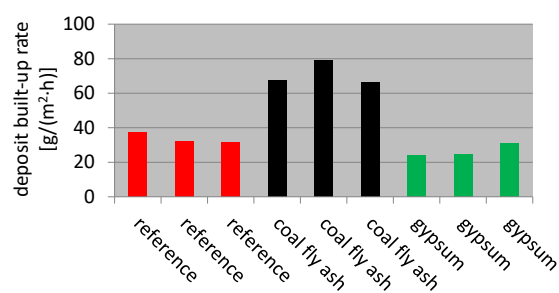


Figure 6: Deposit built-up rate for additive application and the reference case

Deposit probe measurements showed that the addition of coal fly ash resulted in the highest deposit build-up rates (66 to $79 \text{ [g/(m}^2\cdot\text{h)]}$). Without additive, significantly lower deposit build-up rates were determined (31 and $38 \text{ [g/(m}^2\cdot\text{h)]}$), with the lowest deposit build-up rates (between 24 and $31 \text{ [g/(m}^2\cdot\text{h)]}$) being determined for the addition of gypsum.

As part of the BIOASH project [7], deposit probe measurements were carried out in the second duct (empty pass) in a waste wood biomass combustion system (grate firing). In these measurements, deposit built-up rates of $9.2 \text{ g/(m}^2\cdot\text{h)}$ for a probe temperature of 450°C were found for 2 h measurements. During the deposit probe

measurements in the current project (see Figure 6), the lowest measured build-up rate was 24 g/(m² h). The higher deposit formation rates compared to the measurements performed within BIOASH are most likely caused by the wood dust injection, since ash resulting from the wood dust injection is transported with the flue gas and not precipitated on the grate.

Figure 7 shows 2 selected SEM-EDX analyses per operating state (related to the additive).

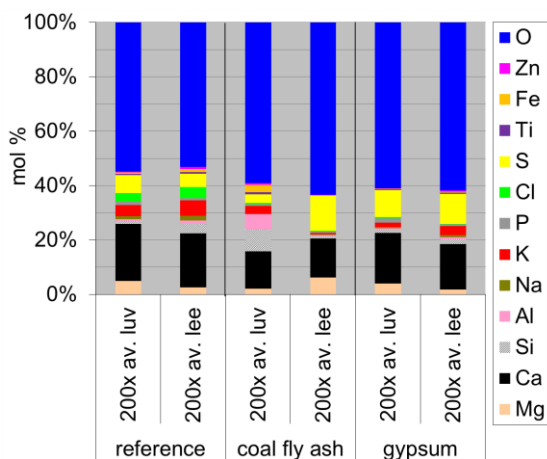


Figure 7: SEM-EDX analyses of deposit samples
Explanation: av. ... average for the whole analysis area

Deposits on the windward side (luv) consist mainly of elements which are typically found in coarse fly ash particles (Ca, Si, Mg). Further, K, Na, S and Cl are found, suggesting alkali metal sulphates and chlorides.

On the downstream side (lee) significantly lower concentrations of Ca, Si and Mg are found. The proportion of the alkali metals and S and Cl is higher. These results are consistent with experiences from other wood firing systems [1]. Coarse fly ash particles are typically deposited by impaction and therefore found mainly on the upstream side. Alkali metal chlorides and sulphates form deposits by condensation from the gas phase and by thermophoresis. These processes also occur on the downstream side.

By adding coal fly ash, the concentrations of Si, Al and Fe are increased compared to the reference case, (see Figure 7 200x av. luv) which most likely result from direct impaction of coarse fly ash particles. Especially Al and Fe are known as refractory species and thus can minimise the slagging tendency of deposits. For 200x av. lee higher S and lower K, Na and Cl concentrations are obvious compared to the reference case. Similar to the aerosol measurements (see section 3.3) a reduced release of alkali metals from the fuel to the gas seems plausible for the deposit probe measurements. The higher S concentrations are an indication of preferable sulphation reactions which can positively influence the high temperature corrosion behaviour (see section 3.5). When adding gypsum, higher S concentrations can be seen in comparison to the reference sample. Sulphation of the alkali metal chlorides occurs as a result of these high S concentrations in the gas phase by gypsum addition, and as a result almost no Cl was found in deposits, which is evident from the SEM-EDX analyses. Hereby, a reduction of the corrosion rates (see section 3.5) of superheater tubes should be achievable.

3.5 Corrosion

The online corrosion probe measurement showed a dependence between corrosion rate and flue gas temperature. Due to the process of soot blowing in the boiler, the flue gas temperatures and also the corrosion conductance decreased. However, the measurements showed that neither the addition of coal fly ash nor the addition of gypsum has a significant influence on the corrosion rate. Nevertheless, an indication of a reduction in the corrosion rate was evident after the addition of gypsum. The most likely reason is, that gypsum and coal fly ash was only added for 10 hours and changes in the ash chemistry of already formed deposits, that influence the corrosion rate, most likely take some time.

In former work it was shown that a link between the 2S/Cl ratio in the fuel and in the aerosols respectively deposits formed prevails. For fuels with high 2S/Cl ratios a protective sulphate layer is formed at the tube surfaces and thus reduces active Cl induced corrosion [4]. Hence, adding S or an additive that releases S during its decomposition should increase the 2S/Cl ratio in deposits.

According to literature [11] only minor corrosion risks have to be expected for 2S/Cl ratios in the fuel of > 4. It is additionally suggested that the molar 2S/Cl ratio in the fuel should be at least 8 to achieve negligible chlorine levels in boiler deposits, and thereby reduce corrosion from this source. Table I shows the molar 2S/Cl ratios of the deposits sampled at position M1 (see Figure 1). For this evaluation the chemical composition of deposits like described in Ref. [8] was, additionally to the SEM/EDX analysis, determined. In case of the deposits the molar 2S/Cl ratio is only slightly above 4 for the reference case, thus high temperature corrosion cannot be neglected. In case of additive application a significant increase of the molar 2S/Cl ratio of the deposits is obvious. It can be assumed that even with an additive ratio of 1 % (half additive ratio like in the investigations performed) a satisfying improvement concerning high temperature corrosion can be achieved.

Table I: Molar 2S/Cl ratios of the deposits

Explanation: Chemical composition of S and Cl determined by methods described in [8]

		reference	coal fly ash	gypsum
2S/Cl depositions	mol/mol	4.2	19.3	75.6

3.6 Costs of the additive

Besides the effect of the additives in the boiler, also the costs related to the additives were estimated. The price of the additive depends on the current market situation and the supply and demand of the additive. The price to receive the coal fly ash from a coal fired plant is about 20 €/t. The transport costs were identified to be about 25 €/t, resulting in total costs of 45 €/t

The price for used plasterboard from building enterprises have a negative value of < -30 €/t since the disposal costs are 30 – 40 €/t. The costs for shredding and milling of used plasterboard are in the range of ~ 40-45 €/t. With the addition of transport cost of about 25 €/t (similar to coal fly ash) total costs of 35 – 40 €/t was estimated for used plasterboard. The prices estimated is clearly above the price of e.g. kaolin which was estimated with 220 €/ton [12] from factory excl. shipping (supplier: Thiele Nordic grain size: <2 µm).

For a suitable evaluation of the use of the additive, long-term tests with the additives are recommended. Based on these tests, the costs and benefits of the additives could best be evaluated and an optimal rate of addition determined.

3.7 Suggestion of appropriate additives and ratios

The short term injection of the additives indicate that 3% of coal fly ash (related to dry fuel) are necessary to reduce the release of alkali metals from the fuel to the gas phase and to positively influence the chemical compositions of deposits. The addition of 2% gypsum cause a significant increase in gaseous SO₂ concentrations (see Figure 3) and a clear improvement concerning the high temperature corrosion risk (see Table I). This high SO₂ concentrations indicates that 2% of gypsum represent an overdosing. It is suggested that half of tested additive amount is enough to positively influence problems in the boiler (e.g. slagging and high temperature corrosion). As already mentioned, for a fine tuning of the amount of additive, long term tests with the recommended additive ratio should be performed.

4 SUMMARY AND CONCLUSIONS

The incineration of waste wood is very often associated with ash-related problems (deposits, slagging and corrosion). This leads to short maintenance intervals, which result in significant power generation losses and high downtime costs. To avoid these problems, additives can be used, with particularly cost-effective additives being of great interest.

In previous work the combustion behaviour of 3 different waste wood mixtures without and with the addition of various low-cost additives such as recycled gypsum, coal fly ash and iron sulphide with two different addition ratios were investigated in a laboratory reactor. Based on the investigations carried out, the addition of 2% gypsum and 3% coal fly ash was recommended. These additives with the recommended mixing rates were then investigated in a large-scale plant (a 40 MW_{th} grate furnace with additional injection (position: left, centre, right) of wood dust above the grate). Extensive investigations were carried out without additive (as a reference), and with the additives focusing on dust formation (aerosols and total dust), deposit formation and the corrosion behaviour of superheaters. These investigations were accompanied by fuel and ash analyses (grate, cyclone and filter ash).

The additives increased the amount of total dust in the raw gas up to 15% and 262% for gypsum and coal fly ash respectively. The chemical analysis of the total dust also showed that elements which have high concentrations in the additive can be found in the total dust. Especially the enrichment of refractory species like Al for coal fly ash and Ca and Mg for gypsum can positively influence the slagging behaviour. Aerosol measurements showed that the addition of coal fly ash minimised the amount of fine particulate matter, as less alkali metals (K and Na) were released into the gas phase. Gypsum addition increases the SO₂ concentrations in the gas phase due to the decomposition of gypsum, as in the combustion chamber about 900°C are present. Due to the preferred sulphation reactions (binding of S to alkali metals) less Cl is bound to alkali metals and therefore the Cl concentrations in the aerosols were lower compared to

the reference case.

This effect was also found in the deposits sampled at the position of the superheater. Without additives, the deposits contained significant amounts of Cl. With the addition of coal fly ash the Cl concentration in the deposits was reduced but the built-up rate strongly increased due to the larger total dust concentration in the flue gas. For the addition of gypsum, almost no Cl was found in deposits due to the sulphation of alkali metal chlorides. The deposit build-up rates were similar for the reference case and for gypsum addition.

By using the chemical composition of the deposits the molar 2S/Cl ratios were determined, which can be used to predict the risk for high temperature corrosion. The analysis data show that an improvement concerning the high temperature corrosion risk is possible by adding coal fly ash, whereas a significant improvement in case of gypsum additions seems very likely.

The cost estimate shows that recycling materials such as recycling gypsum cost only a fraction of minerals such as kaolin. This circumstance makes such recycling materials to a great extent extremely interesting for use in large-scale facilities.

The measurements carried out so far showed the influence (built-up rate, chemical composition etc.) of the additive application on ash fractions, deposits and dusts. By taking a closer look at the change in chemical compositions of dusts and deposits, additives with an appropriate addition ratio can be suggested. In case of coal fly ash 3% and in case of gypsum 1% additive related to dry fuel seems to be adequate additive ratios to positively influence the risk of high temperature corrosion and reduce the slagging behaviour. However, in order to proof the positive influence of additives, the addition would have to take place over a longer time period (at least weeks).

5 REFERENCES

- [1] Jenkins B.M.; Baxter L.L.; Miles T.R. Jr.; Miles T.R. Combustion properties of biomass; *Fuel Processing Technology* 54; 1998; 17–46
- [2] Niu Y.; Tan H.; Hui S. Ash-related issues during biomass combustion: Alkali-induced slagging, silicate melt-induced slagging (ash fusion), agglomeration, corrosion, ash utilization, and related countermeasures. *Progress in Energy and Combustion Science* 52; 2016; 1–61
- [3] Wang L.; Hustad J. E.; Skreiberg O.; Skjevraak G.; Gronli M. A Critical Review on Additives to Reduce Ash Related Operation Problems in Biomass Combustion Applications; *Energy Procedia* 20; 2012; 20-29
- [4] Sommersacher, P.; Brunner, T.; Obernberger, I. Fuel indexes – a novel method for the evaluation of relevant combustion properties of new biomass fuels. *Energy Fuels* 2012, 26, 380-390
- [5] Sommersacher, P.; Brunner, T.; Obernberger, I.; Kienzl, N.; Kanzian, W. Application of novel and advanced fuel characterization tools for the combustion related characterization of different wood/Kaolin and straw/Kaolin mixtures. *Energy Fuels* 2013, 27 (9), 5192–5206
- [6] Sommersacher, P.; Brunner, T.; Obernberger, I.; Kienzl, N.; Kanzian, W. Combustion related characterisation of Miscanthus peat blends applying

- novel fuel characterisation tools. *Fuel* 2015, 158, 253–262
- [7] Sommersacher P. REFAWOOD - Resource-efficient fuel additives for reducing ash related operational problems in waste wood combustion “REFAWOOD”; Presentations of the 5th Central European Biomass Conference
- [8] Bärenthaler G.; Zischka M.; Hanraldsson C.; Obernberger I.; Determination of major and minor ash-forming elements in solid biofuels. *Biomass and Bioenergy*; 2006; 983-997
- [9] STANDARDKESSEL LENTJES GMBH., 2007: Project no. SES-CT-2033-502679, BIOASH, Ash and aerosol related problems in biomass combustion and co-firing, Deliverable D16, Evaluation of test runs at the large-scale combustion unit of SKG at Elsterwerda, 2007
- [10] Retschitzegger S.; Brunner T.; Obernberger I.; Waldmann B. Assessment of Online Corrosion Measurements in Combination with Fuel Analyses and Aerosol and Deposit Measurements in a Biomass Combined Heat and Power Plant; *Energy & fuels*. 27 (10); 2013; 5670-5683
- [11] Salmenoja K.; Field and laboratory studies on chlorine-induced superheater corrosion in boilers fired with Biofuels. *PhD-Thesis 2000*, Abo Akademi, Faculty of Chemical Engineering, Abo/Turku, Finland
- [12] Boman C.; Fuel additives and blending as primary measures for reduction of fine ash particle emissions – state of the art; ERA-NET FutureBioTec, <[http://futurebiotec.bioenergy2020.eu/files/FutureBioTec-Additives and fuel blending-state of the art report.pdf](http://futurebiotec.bioenergy2020.eu/files/FutureBioTec-Additives%20and%20fuel%20blending-state%20of%20the%20art%20report.pdf)>

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7 LOGO SPACE

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