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Final report: Flexible use of biomass on PF Fired power plants

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Abstract

This report shortly describes the performed studies and the results of the project 'Flexible use of biomass on PF Fired power plants'. The research project was conducted in tight collaboration between Ørsted Bioenergy & Thermal Power and the CHEC research group at Department of Chemical Engineering at DTU. Three specific issues were investigated, that all are important for the optimal operation of pulverized fired biomass power plant boilers. Laboratory and model studies were conducted to improve the prediction of deposit formation in biomass pulverized fired boilers. A study on optimization of the use of coal ash and other additives to remove volatile alkali species from biomass-fired boilers was conducted. Additives are used to ensure a minimum concentration of harmful volatile alkali species in the furnace chamber. Inhibition of biomass wood mill fires while using a maximum air preheating temperature to the mills was also investigated. The main part of the work was performed in three PhD projects. The work has resulted in a range of research papers (documented in the appendix) and some practical recommendations provided in this report regarding biomass ash deposition, optimal use of additives and minimization of the risk of biomass mill fires.

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Appendixes

Journal publications

List of master and bachelor students connected to the project

Appendices – Contains the Journal publications

A. Laxminarayan Y., Jensen P.A., Wu H., Frandsen F.J., Sander B., Glarborg P. Deposit Shedding in Biomass-Fired Boilers: Shear Adhesion Strength Measurements. *Energy Fuels* 2017, 31, 8733–41.

B. Laxminarayan Y., Nair A.B., Jensen P.A., Wu H., Frandsen F.J., Sander B., Glarborg P. Tensile Adhesion Strength of Biomass Ash Deposits: Effect of Temperature Gradient and Ash Chemistry. *Energy Fuels* 2018, 32, 4432-4441.

C. Laxminarayan Y., Jensen P.A., Wu H., Frandsen F.J., Sander B., Glarborg P. Biomass fly ash deposition in an entrained flow reactor. *Proc. Combust. Inst* 2019. 37, 2689 - 2696.

D. Wang G., Jensen P.A., Wu H., Frandsen F.J., Sander B., Glarborg P. Potassium Capture by Kaolin, Part 1: KOH. *Energy & Fuel* 2018, 32, 1851-1862.

E. Wang G., Jensen P.A., Wu H., Frandsen F.J., Sander B., Glarborg P. Potassium Capture by Kaolin, Part 2: K_2CO_3 , KCl and K_2SO_4 . *Energy & Fuels* 2018, 32, 3566-3578.

F. Wang G., Jensen P.A., Wu H., Laxminarayan, Y., Frandsen F.J., Sander B., Glarborg P. KOH capture by Coal Fly Ash. *Fuel* 2019, 242, 828 – 836.

G. Wang G., Jensen P.A., Wu H., Laxminarayan, Y., Frandsen F.J., Sander B., Glarborg P. Potassium Capture by Coal Fly Ash: K_2CO_3 , KCl and K_2SO_4 . Accepted for publication in: *Fuel Processing Technology* 2019.

H. Schwarzer, L., Sárossy, Z., Jensen, P.A., Glarborg, P., Holm, J.K., Dam-Johansen, K.: Kinetic parameters for biomass at self-ignition conditions: Low-temperature oxidation and pyrolysis. Accepted for publication in *Energy & Fuels* 2019.

Schwarzer, L., Jensen, P.A., Glarborg, P., Wedel, S., Holm, J.K., Dam-Johansen, K.: Modelling of self-heating and thermal runaway of biomass (*manuscript in preparation, tentative title, not available in appendix*)

Appendix I . List of student projects

1.0 Introduction

The use of biomass on power plants are done to reduce Danish CO₂ emissions. The larger Danish pulverized fired power plants still have an important role to play in the electricity grid. The plants provide a large amount of the electricity load adaption capability that is needed, especially with a large contribution from wind power. Furthermore, the plants supply a large fraction of the district heating to major Danish cities.

The present project deals with important specific issues that are important for the efficient operation of pulverized fired biomass plants:

- Improved prediction of deposit formation in biomass pulverized fired boilers.
- Optimization of the use of coal ash and other additives in biomass fired boilers, in order to ensure a minimum use of coal ash, keeping a high superheater temperature and thereby a high boiler electrical efficiency.
- Inhibition of biomass wood mill fires while using a maximum air preheating temperature.

This research project has mainly been conducted in PhD projects that dealt with the three work packets:

- WP1. Prediction of boiler deposit formation – fundamental data needed for deposit modelling
- WP2. Using coal ash and other additives – optimization of additive use
- WP3. Optimization of efficient mill operation – understanding low temperature biomass particle ignition

The project work was conducted from 2014 to 2018 in tight collaboration between Ørsted Bioenergy & Thermal power and the CHEC research group at Department of Chemical Engineering at DTU. Chapter 2 to 4 in this report provide an overview of the conducted work and the obtained results. For a more in depth information on the project results, one can consult the published research papers seen in appendix A to H.

Besides the project results, the project has contributed to the education of the three PhDs Yashasvi Laxminarayan, Guoliang Wang and Lars Schwarzer. 4 project students have also been connected to the project and a list with their projects can be found in appendix I.

2.0 Formation, sintering and removal of biomass ash deposits

Biomass combustion in PF boilers may lead to several ash related operational problems. Biomass typically contains a high amount of volatile and chemically aggressive ash species containing K, Cl, and S, which may form troublesome deposits on boiler surfaces, especially on superheater tubes. Ash deposits hinder heat transfer to the steam cycle, thereby reducing boiler efficiency, and may completely block flue gas channels in severe cases, causing unscheduled boiler shutdowns. Moreover, biomass ash deposits may cause severe corrosion of boiler surfaces. Therefore, reducing deposit formation and timely deposit removal are essential for optimal boiler operation.

The formation, sintering and removal of boiler deposits has been investigated, by simulating boiler conditions in laboratory-scale setups. Deposit formation was simulated in an Entrained Flow Reactor, to investigate the effect of operating conditions and ash chemistry on the rate of deposit formation. Deposit removal were

investigated in specially designed ovens where the adherence strength of deposits towards boilers tubes could be studied. The studies provided information on the buildup and shedding of deposits as a function of ash chemistry and local conditions.

For the biomass ash deposit study an modified Entrained Flow Reactor (EFR) was applied. The Reactor was mounted with a deposit probe as shown in Figure 1. The deposit build up could be monitored with a camera. The probe surface temperature was kept constant by an air cooling system and the deposit weight was registered by measuring the probe weight after the experiments.

To understand the forces needed to remove biomass ash deposits and course shedding both shear and tensile adhesion tests were conducted. Model deposits was made and adhered to a metal surface and the force needed to remove the deposits was measured. A system with deposits on a superheater tube placed in an oven, and with the deposit samples connected to arms to measure tensile force, was developed. An image of the inner part of the experimental set up can be seen in Figure 2.

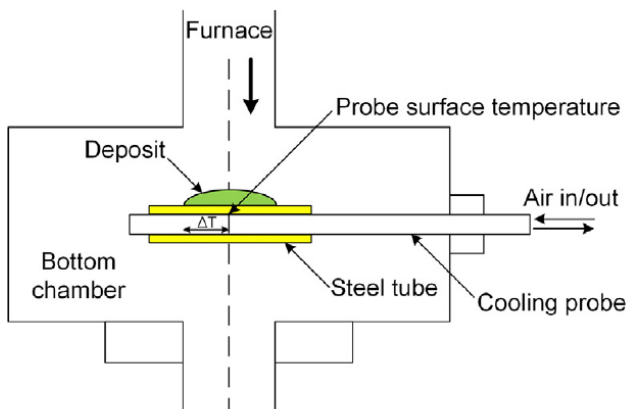


Figure 1. Bottom Chamber of the EFR. Deposits are formed on the steel tube mounted on the probe [from paper, appendix C].

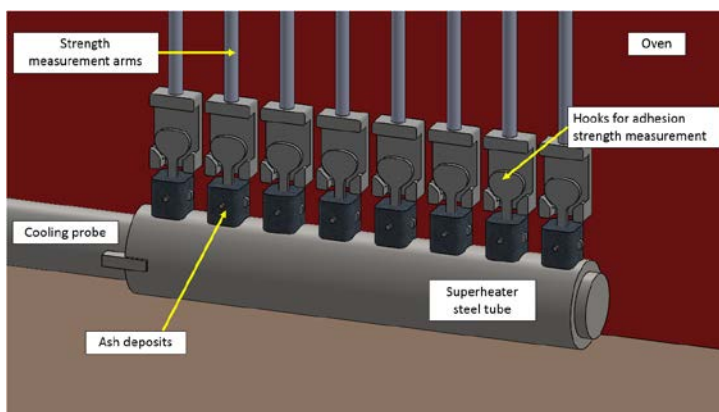


Figure 2. System inside oven used to measure deposits tensile strength.

EFR deposit experiments were performed using model biomass fly ash, prepared from mixtures of $K_2Si_4O_9$, KCl , K_2SO_4 , CaO , SiO_2 and KOH , as well as three different boiler fly ashes: a wood fly ash, a straw fly ash, and a straw + wood co-fired fly ash. The chosen model species are all appearing in the ash formed from wood

and straw combustion. The model fly ash particles were mixed with air, and injected into the EFR reactor, to form deposits on an air-cooled probe. The influence of flue gas temperature (589 – 968 °C), probe surface temperature (300 – 550 °C), flue gas velocity (0.7 – 3.5 m/s), fly ash composition, fly ash flux (10000 – 40000 g/m²/h), fly ash particle size (3.5 – 90 µm) and probe residence time (up to 60 min) were investigated.

The results of the EFR tests revealed that increasing flue gas temperature and probe surface temperature increased the sticking probability of the fly ash particles/deposit surface, thereby increasing the rate of deposit formation. However, increasing flue gas velocity resulted in a decrease in the deposit formation rate, due to increased particle rebound. Furthermore, it was observed that the deposit formation rate increased with time, fly ash flux and fly ash particle size. A mechanistic model was developed for predicting deposit formation on the laboratory probe. Deposit formation by condensation, thermophoresis and inertial impaction was incorporated into the model, and the sticking probability of the ash particles was estimated by accounting for energy dissipation due to particle deformation. The model reasonably predicted the influence of flue gas temperature and fly ash flux on the deposit formation rate.

The deposit formation rates of the investigated species are shown in Figure 3, and they decreased in the following order: KOH > K₂SO₄ > KCl > K₂Si₄O₉ > SiO₂ > CaO, at the applied conditions. Addition of KCl to K₂Si₄O₉, SiO₂, CaO, and K₂SO₄ in the model fly ash mixture resulted in an increased deposit formation rate, and induced rapid deposit sintering. Furthermore, addition of KOH to K₂Si₄O₉ in the model fly ash mixture resulted in a large increase in the deposit formation rate. The relative deposit formation rates of the investigated boiler fly ashes were observed to increase in the following order: wood fly ash, followed by straw + wood co-fired fly ash and straw fly ash. Inertial impaction was the primary mechanism of deposit formation on the upstream side of the steel tube, when the model fly ash was present as solid or semi-molten particles. However, presence of vapor species or submicron ash particles in the flue gas resulted in the formation of deposits on both sides of the steel tube via condensation or thermophoresis.

The developed numerical deposit model could calculate the amount of deposits as a function of ash type, and local conditions. The model was able to reasonably predict the influence of flue gas temperature and fly ash flux, suggesting that accounting for energy dissipation due to particle deformation, for predicting the sticking probability of incoming ash particles, seems to be fairly successful in predicting the influence of changes in local conditions on the deposit formation process. However, the model was unable to accurately predict the influence of probe surface temperature, gas velocity and probe residence time.

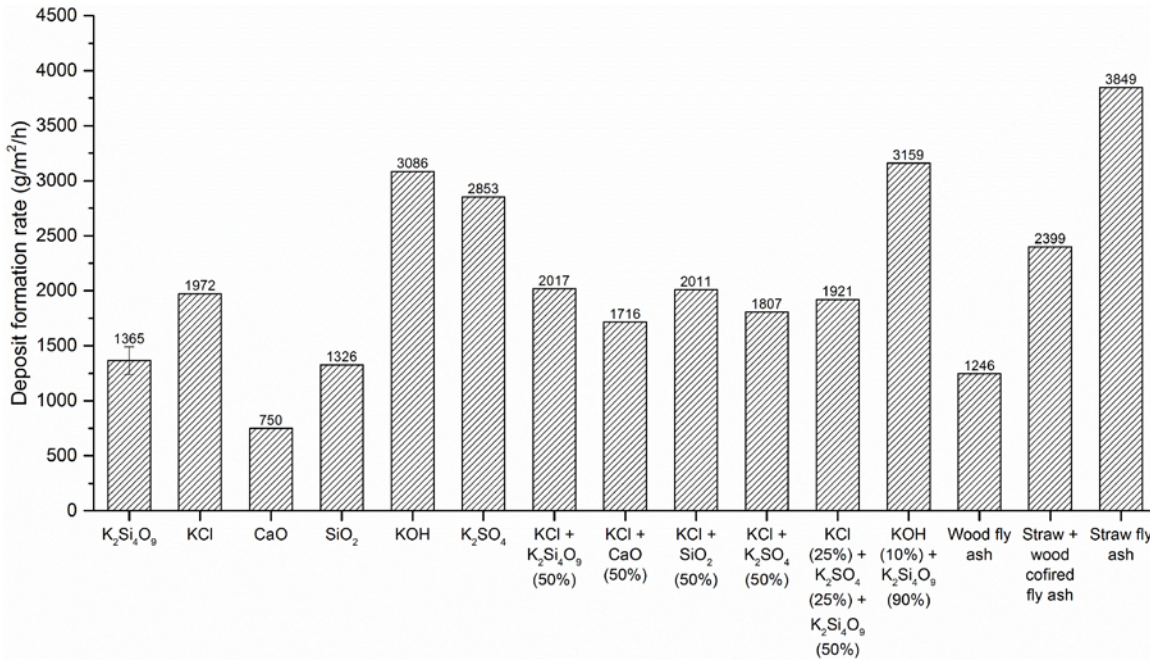


Figure 3. Effect of fly ash composition on the deposit formation rate. Experiments performed with a furnace temperature of 1450 °C, a flue gas temperature of 968 °C, probe surface temperature of 475 °C, gas velocity of 1 m/s, fly ash flux of 20412 g/m²/h for 15 min. K₂Si₄O₉ has a median particle size of 13.2 μm, whereas all other compounds have particle sizes lower than 32 μm. All compositions in wt %.

In order to understand deposit shedding in boilers, the shear adhesion strength of biomass ash deposits on a metal surface was quantified by laboratory experiments. Artificial deposits were prepared using biomass fly ash from full-scale boilers, as well as from mixtures of KCl, K₂SO₄, CaO, CaSO₄, SiO₂, K₂CO₃, Fe₂O₃, K₂Si₄O₉, and KOH. The deposits were prepared on superheater steel tubes and sintered in an oven. Subsequently, the deposits were sheared off by an electrically controlled arm, and the corresponding adhesion strength was measured. The effects of sintering temperature (500 – 1000 °C), sintering time (0 – 24 h), deposit composition, thermal shocks on the deposit, and steel type were investigated. The results revealed that the adhesion strength of ash deposits was dependent on two factors: the ash melt fraction, and corrosion occurring at the deposit–tube interface. Adhesion strength increased with increasing sintering temperature, sharply increasing at the ash deformation temperature. However, sintering time, as well as the type of steel used, did not have a significant effect on the adhesion strength, under the investigated conditions. Addition of compounds which increased the melt fraction of the ash deposit, typically by forming a eutectic system, increased the adhesion strength, whereas addition of inert compounds with a high melting point decreased the adhesion strength. Furthermore, the study indicated that sulfation of ash deposits might lead to an increase in the adhesion strength, while cooling down the deposits after sintering decreased the adhesion strength. Finally, it was observed that adhesion strength data displayed a significant degree of scatter, following a log-normal distribution.

Additionally, the tensile adhesion strength of biomass ash deposits was investigated under the influence of a temperature gradient across the deposit. Model biomass ash deposits, containing mixtures of KCl, K₂SO₄, CaO, CaSO₄ and K₂Si₄O₉, were prepared on superheater steel tubes, and sintered in an oven. The superheater steel tube was cooled by air, incorporating a temperature gradient across the deposits. After sintering, the

deposits were removed using an electrically controlled arm, and the corresponding tensile adhesion strength was measured. The effects of flue gas temperature (500 – 700 °C), steel surface temperature (500 – 650 °C) and deposit composition were investigated. The results revealed that increasing the flue gas temperature, as well as the steel surface temperature, led to a sharp increase in the tensile adhesion strength of the model deposits. The sharp increase was typically observed near the melting temperature (or deformation temperature) of the investigated model deposits. A large temperature gradient across the deposits induced migration of molten/vapor species from the outer layer of the deposit to the deposit–tube interface, causing liquid state sintering, and thereby increasing the tensile adhesion strength. Varying the ash chemistry of the model deposits revealed that the melt fraction of the deposit was highly influential in determining deposit adhesion strength. The tensile adhesion strength data qualitatively and quantitatively agreed with the shear adhesion strength data. Corrosion occurring at the interface between deposit and tube metal may increase the adhesion strength of the deposits, since most corrosion products form a eutectic system with the inner layer of deposit and thereby increase the local melt fraction.

Finally, heterogeneous sulfation of model biomass ash deposits was simulated in three different experimental setups. The effect of sulfation time (0 – 24 h), SO₂ concentration (0 – 600 ppm) and sintering temperature (500 – 650 °C) on the shear/tensile adhesion strength of the deposits was investigated. While increasing sulfation time resulted in a gradual increase in the adhesion strength of the deposits, varying SO₂ concentrations and sintering temperature did not significantly influence the deposit adhesion strength at the investigated conditions. A low degree of sulfation was observed in the experiments (<1 wt % S), suggesting that further investigation is required to understand the effect of heterogeneous sulfation on the adhesion strength.

The practical implications of the conducted studies can be shortly summarized as:

- The most important parameters leading to increased ash deposit formation were an increased fuel ash content, a larger fraction of alkali salts in the ash and an increased flue gas temperature: Generally very volatile alkali species as KOH increases deposit formation rate, while species as CaO with high melting temperature only induced low deposit formation rates.
- Key parameters leading to a deposit more strongly bound to boiler tubes were found to be the metal surface temperature and the deposit composition. A sharp increase in adherence strength was observed near the ash deformation / melting point temperature. At a fixed surface temperature increased concentration of compounds which increase the melt fraction of the deposit, such as alkali salt species, increased the adhesion strength of the deposit. By use of additives that transfer alkali to species with a high melting temperature the deposits boiler tube adherence strength will decrease.
- Colling of the deposit often lead to a detachment of deposit from the tube material because of different expansion coefficients. This indicates that large load changes on a boiler could assist deposit removal processes.

Some areas need further studies to obtain a full understanding of the deposit formation and removal:

- The deposit prediction model needs further development to accurately predict the influence of probe surface temperature, gas velocity and probe residence time. Furthermore, a model that can simulate both the deposit formation and shedding process is still not available today.

- The sulfation of deposits seems to be an important process for the increase in attachment to tube surfaces. However, this seems to be a relatively slow process that was difficult to simulate in the laboratory. Further work is needed to obtain a full understanding of the deposit sulfation influence on deposit adherence strength increase.

3.0 Potassium capture by kaolin and coal fly ash

During the combustion of biomass, significant amount of K-species are released to gas phase in the boiler chamber, as KOH, KCl and K₂SO₄, and this may consequently lead to deposit formation, corrosion of boiler tubes and de-activation of SCR (Selective Catalytic Reduction) catalysts. One option to tackle these ash-related problems is to use additives to capture gaseous alkali species in flue gas. Kaolin and coal fly ash are two possibly effective Al-Si based additives to capture alkali species. By a reaction between the additive and the alkali species the alkali metal is fixed in species, which have a high melting point and therefore are relatively benign with respect to deposit formation, corrosion and SCR de-activation.

The mechanisms and kinetics of alkali capture by kaolin and coal fly ash have previously been investigated in several studies. However, most of these studies were conducted in fixed bed reactors, where kaolin or coal fly ash appearing as relatively large pellets or flakes were utilized. In suspension fired boilers, kaolin and coal fly ash particles are well dispersed in flue gas, with a total residence time of a few seconds and the controlling mechanisms could be considerably different from that in fixed bed reactors. Therefore as part of this project, the reaction between gaseous potassium species (KOH, K₂CO₃, KCl and K₂SO₄) and different condensed phase Al-Si based additives (kaolin, mullite and coal fly ash) was investigated under well-controlled suspension-fired conditions by performing experiments in the DTU entrained flow reactor (EFR).

A long range of experiments was conducted on the EFR reactor where additive and different alkali species were feed to the reactor in a water liquid solution. Fly ash was collected in a cyclone and a filter and the product was analyzed for total and water-soluble alkali content, and thereby the degree of conversion of the alkali salts into Si-Al-K species could be quantified. The EFR tests simulated the reactions between additives and alkali species released from biomass fuel during combustion in power plant PF biomass boilers. Based on analysis of the fly ash the K-capture level of additives C_k (g K/(g additive)) and conversion of the inlet K X_k (%) could then be determined. (C_k is the mass of potassium captured by 1 g of additive; X_k is the percentage of fed potassium captured by the additive). The impact of different parameters, such as K-concentration in flue gas (50-1000 ppmv), molar ratio of K/(Al+Si) in reactants (0.048-0.961), reaction temperature (800-1450 °C), gas residence time (0.6-1.9 s), additive particle size as well as the type of coal fly ashes and kaolin on the K-capture reaction was studied. Corresponding equilibrium calculations were carried out using the equilibrium module of FactSage 7.0, to shed light upon how far the EFR reaction system is from the equilibrium, and thereby provide more in debt information for understanding the EFR experimental results.

The results of the K-capture experiments using kaolin at 1100 °C or 1300 °C showed that for all the four K-species, KOH, K₂CO₃, KCl and K₂SO₄, the K-capture level (C_k) increased considerably when the K-concentration in the flue gas changed from 50 ppmv to 500 ppmv (molar ratio of K/(Al+Si) in reactants varied from 0.048 to 0.481). However, no obvious increase of C_k was observed when the K-concentration increased further to 750 ppmv and 1000 ppmv (molar ratio of K/(Al+Si) in reactants was 0.721 and 0.961). This is probably because at a high relative K concentration all kaolin Si has been consumed forming K-aluminosilicates at 500 ppmv.

Results of K-capture experiments using kaolin at different temperatures show that, for KOH, KCl and K_2CO_3 , the K-capture level (C_K) and K-conversion (X_K) by kaolin generally followed the equilibrium predictions at 1100 °C and above, when using a kaolin particle size of $D_{50} = 5.47 \mu\text{m}$ and a gas residence time of 1.2 s. This reveals that a nearly full conversion of kaolin to K-aluminosilicates was achieved without kinetic or diffusion limitations under the applied conditions. At 800 °C and 900 °C, the measured conversions were lower than the equilibrium predictions, indicating that either of the reactions were kinetically or diffusion controlled. For K_2SO_4 , the measured C_K was obviously lower than the equilibrium predictions. Kaliophilite ($KAlSiO_4$) was predicted by the equilibrium calculations; however, the XRD analysis results revealed that leucite ($KAlSi_2O_6$) was actually formed.

Results of K-capture experiments by kaolin using different K-species show that, for KOH and K_2CO_3 , leucite ($KAlSi_2O_6$) was formed at low K-concentration of 250 ppmv, while at higher K-concentration (500-1000 ppmv), kaliophilite ($KAlSiO_4$) was detected in the products. But in the experiments with KCl and K_2SO_4 , only leucite ($KAlSi_2O_6$) was detected by XRD analysis. Another difference was that the C_K of K_2CO_3 was comparable to that of KOH, while C_K of KCl and K_2SO_4 by kaolin were both relatively lower.

The results of K-capture experiments using coal fly ash showed that the behaviors of the studied four K-species were similar to what was observed when using kaolin. As seen on Figure 4 a higher capture level (C_K) was observed for KOH and K_2CO_3 than for KCl and K_2SO_4 . Furthermore, it is observed that for increased temperature an increased K capture level is obtained.

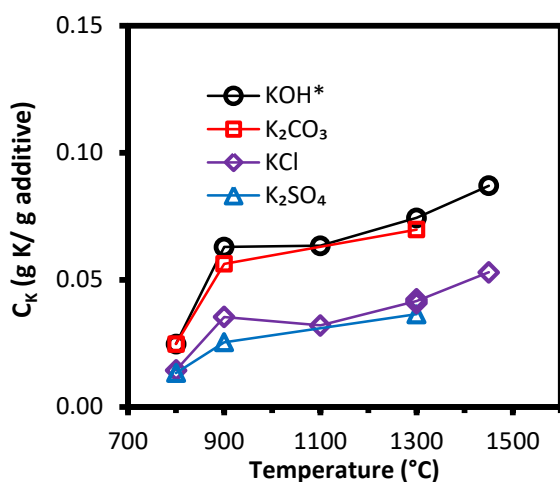


Figure 4. Comparison of C_K of K-capture by ASV2CFA0-32 (coal fly ash) using different K-species (KOH, K_2CO_3 , KCl and K_2SO_4). The K-concentration was 500 ppmv; molar K/(Al+Si) ratio in reactants was 0.481. The gas residence time was 1.2 s.

The results of K-capture experiments using coal fly ash with different potassium concentrations also showed that the behaviors of the studied four K-species were similar to what was observed when using kaolin. C_K and X_K increased when K-concentration increased from 50 ppmv to 500 ppmv (molar ratio of K/(Al+Si) in reactants varied from 0.048 to 0.481), and they did not increase further at K-concentration of 750 ppmv and 1000 ppmv (molar ratio of K/(Al+Si) in reactants was 0.721 and 0.961). One difference observed was that at 250 ppmv K and above, the measured C_K and X_K of coal fly ash was lower than the equilibrium predictions. In addition, compared with kaolin, although the types of formed K-aluminosilicates agreed with that of kaolin,

coal fly ash captured the K-species less effectively at a K-concentration higher than 250 ppmv (molar ratio of $K/(Al+Si)$ in reactants changed from 0.240 to 0.961).

Comparison of KOH-capture by kaolin, mullite and coal fly ashes at 500 ppmv KOH are shown on Figure 5. It is seen that kaolin is the most effective additive for alkali capture followed by mullite and coal fly ashes. For the coal fly ashes are seen a moderate increase in capture level with temperature. However, using a lower KOH concentration, as shown in Figure 5B, no obvious difference was observed between the three additives at 50 ppmv KOH ($K/(Al+Si) = 0.048$). In addition, when the reaction temperature was varied from 800 to 1450 °C (at 500 ppmv KOH), C_k of kaolin firstly increased then decreased, reaching a peak at 1300 °C. C_k of mullite and coal fly generally increased with increasing temperatures from 800 to 1450 °C.

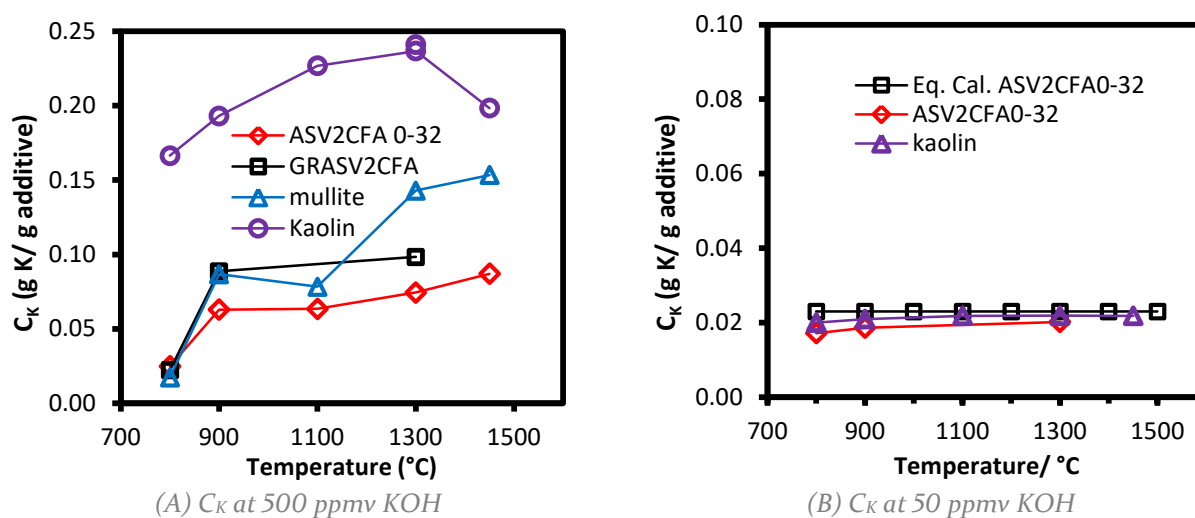


Figure 5. K-capture level of kaolin, mullite, and coal fly ash. (A) 500 ppmv KOH, molar $K/(Al+Si)$ ratio of 0.481 (B) 50 ppmv KOH, molar $K/(Al+Si)$ ratio of 0.048. Gas residence time was 1.2 s.

Kaolin and coal fly ash can be applied as K-capture additives in PF-boilers (pulverized fuel fired boilers). Kaolin is the most effective additive for alkali capture, while coal fly ash is the only additive, which has been commercially, utilized in full-scale biomass fired PF-boilers. Based on the results from this study and the open literature, some recommendations and guidelines for optimal utilization of kaolin and coal fly ash to capture alkali species in PF-boilers can be provided.

The laboratory entrained flow reactor studies show that, at 500 ppmv (kaolin can capture more than 0.2 g K/(g additive) at 900-1450 °C, if K exists in the form of KOH. Coal fly ash has also shown to be an efficient additive, however, with a lower capacity than kaolin. ASV2CFA0-32 coal fly ash can capture up to 0.1 g K/(g additive) at 1450 °C. The AMVCFA0-32 coal fly ash with lower melting point and higher Si concentration captures more K (0.15 g K/(g additive)). At 50 ppmv KOH in the flue gas and a relative amount of additive to alkali metal corresponding to a molar ratio of $K/(Al+Si) = 0.048$, which is comparable to the K-concentration in wood-fired full-scale boilers, the K-capture level of kaolin and coal fly ash was similar, about $C_k = 0.02$ g K/(g additive). C_k at this alkali to additive ratio was independent of reaction temperature. The composition of coal fly ash has some influence on its K-capture capability. Bituminous coal ash rich in Al and Si usually can capture K-species more effectively than lignite coal ashes, which are rich in Ca and Mg.⁹³

The use of solid Si and Al rich additives is efficient for low ash content wood species. In case of herbaceous biomass as straw, the potassium content is so high, that the amount of additive needed is very large and therefore the use of solid additives in straw-fired boilers is probably not economically attractive.

The conducted tests have shown, that if one tries to minimize the amount of additives used, and at the same time want to obtain a maximum alkali salt removal, then the temperature that the additives experience has a significant influence on the K-capture capability. To obtain an optimal K-capture behavior, an appropriate injection temperature window should be selected. In the case of utilizing coal fly ash for K-capture, the highest K-capture level was observed at 1300 and 1450 °C, probably due to the melting of the coal ash particles, and a consequent enhanced internal K diffusion at high temperature.

The results indicate that an additive mean size of below 10 µm is advantageous, and that with the short residence times available in PF boilers, coal fly ash with a size above 50 µm shall not be applied.

There have been obtained a very extensive understanding of solid Si and Al rich additive behavior in biomass PF boilers. However to improve our capability to predict additive behavior in PF boilers, a model that account for the detailed reaction processes should be developed in the future.

The obtained understanding of solid additive behavior is used by Ørsted when applying additives on the Danish power plants. It support the practical biomass power plant additive use with respect to additive purchase and optimization of additive dosage when using different biomass mixtures.

4.0 Biomass particle ignition in mill equipment

Use of biomass dusts to replace pulverized coal in power plants has led to several incidents in which fires have appeared in the plants' mills. Transport air passing through the mills is pre-heated, which serves to both dry the fuel and also as a method of internal heat recovery in the power plant. High combustion air temperatures are therefore desirable from the point of view of overall plant efficiency, but poor predictability of critical conditions for mill fires has led operators to adopt cautiously low inlet air temperatures (≤ 423 K, $< 150^\circ\text{C}$). In this project studies was conducted that can lead to an improved understanding of the processes that lead to ignition in power plants mills.

The work on biomass mill ignition included the following activities:

- Collection of experiences from power plants regarding mill fire incidents
- Studies on single particle ignition was conducted to improve our understanding of low temperature ignition
- TGA (Thermal Gravimetric Analysis) measurements to determine the low temperature pyrolysis and oxidation kinetics of different biomasses
- Laboratory measurements on the ignition and propagation of smoldering combustion in beds of biomass
- Development of a model that can predict the low temperature ignition of biomass beds

A dialog with the power plant operators revealed that most mill fires was initiated when mills have been stopped for some time, and then was re-activated. Fire incidents typically appeared shortly after a mill was

started. It was on that basis concluded, that the ignition source probably came from the beds of biomass material left in the mills, the hot biomass (up to 425°K) left over after the mill stopped. Initiation of smoldering combustion in those biomass bed assemblies could during start up initiate a full fire in the suspended biomass material, when the mill starts up. It was therefore concluded that mill fires are likely caused by self-heating and spontaneous ignition of settled dust accumulations. A study on the initiation of smoldering combustion in biomass dust beds at relatively low temperatures was therefore conducted.

Self-ignition experiments were carried out with single wood pellet particles (0.25 g) in an externally heated reactor. Spontaneous ignition of beech and pine wood pellets in air occurred at ambient temperatures around 500 °K and upward. Ignition was characterized by a sudden, sharp increase in temperature of the pellet, and a complete conversion of the organic fraction. During burnout, the pellet could reach temperatures up to 900 °K and emitted a visible glow. A temperature of 900°K is relatively low compared to what is measured in flaming combustion. This behavior was distinct from flaming ignition, which required higher ambient temperatures (>700 °K). Despite exceeding this critical threshold on burnout, no transition between the glowing and flaming modes was observed in the single pellet experiments. It was concluded that heterogeneous oxidation is the main mechanism leading to ignition and burnout of biomass samples at low temperatures.

Based on the TGA measurements the kinetic rates for pyrolysis and oxidation was determined for six biomasses types: beech and pinewood, wheat straw, sunflower husk pellets, and two types of commercial wood pellets. The kinetic parameters were determined in the temperature range of 423–523°K (150 - 250°C), using stepwise isothermal thermogravimetric experiments. The measuring data was applied to develop a simple reaction model that describe parallel oxidation and pyrolysis of biomass at low temperatures. The mechanism takes the composition of biomass into account, distinguishing between volatilizable fractions of extractives, hemicellulose, lignin and cellulose, as well as char. Within the range considered, the oxidation reaction could be described with an activation energy of $E_a = 130$ kJ/mol and reaction orders in oxygen between 0.4–0.5 (dependent on the biomass type). It was further found that the reactivity of the different biomasses could to some degree be related to its composition: biomass rich in extractives had increased mass loss rates at low temperatures (<470 K), while biomasses rich in potassium (in the inorganic fraction) had high reaction rates above 500 K.

Lab scale experiments on loosely packed dust beds (10–40 g) were carried out to gain a further understanding of the ignition process in lumps of biomass. The samples were placed in a cylindrical wire mesh basket and gradually heated (1 K/min) to a set final temperature. Oxygen atmospheres were varied from 0 vol% to 20 vol%. Onset of oxidation reactions was detectable by low concentrations of CO and CO₂ from around 373 K, which gradually increased with temperature. Larger bulk densities and higher ambient oxygen concentrations favored thermal runaway of the samples, which could otherwise (i.e., under 'subcritical' conditions) also stabilize and slowly oxidize. Critical conditions for thermal runaway depended on the material tested. Thermal run away for the biomass bed samples were at conditions of constant heating rate 1K/min and in 20% O₂ observed in the temperature region from 480 to 507K. Sunflower and beech showed an early reaction onset, while the reactivity of what and pine increased towards higher temperatures (>500 K).

A one-dimensional numerical model was developed to describe self-heating and ignition in biomass dust beds, including reactions (pyrolysis and oxidation), mass and heat transfer. The reaction model and kinetic data derived from the thermogravimetric experiments were used in the model, while values for material

property parameters could be found in the literature. The central aim of the model is to predict critical temperatures for ignition under different conditions. The lab scale experiments could be simulated with good accuracy, where ignition temperatures were predicted 2–5 % lower than the measured values. No parameters were fitted to get the same results as the fixed bed experiments. Sensitivity to various parameters used in the model was investigated. Onset of thermal runaway appeared to be controlled largely by a balance between the energy release from the oxidation, and the heat loss of the sample to the surroundings. Material properties, in comparison, had a very low influence. Further simulations were carried out to investigate effects of sample size and oxygen availability. Increasing the characteristic length scale or the bulk density of the sample drastically lowered the predicted ignition temperatures. As shown in Figure 6 increasing the bed diameter size decrease the ignition temperature down to 395 to 415 °K Thus, the scaling study demonstrated that self-ignition of settled biomass dust beds could plausibly explain mill fires.

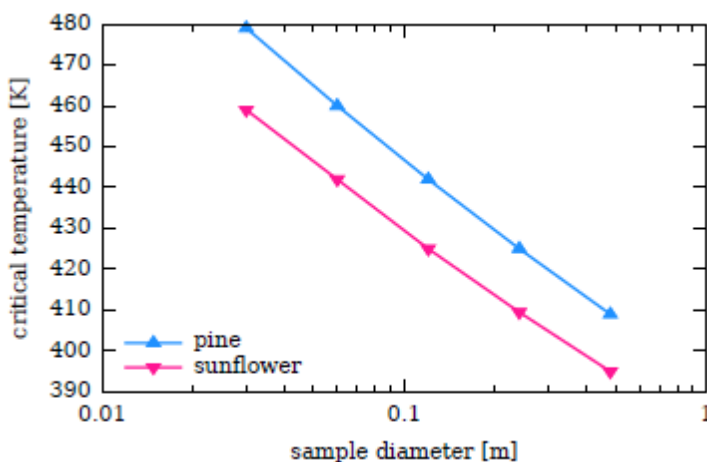


Figure 6. Modeling of critical temperature of bed samples with a diameter from 3 cm up to 50 cm. Reference sample size calculation was done with a diameter of 3 cm corresponding the size of the sample holder used in the fixed bed experiments.

In summary, self-heating and self-ignition were studied both experimentally and numerically in this work. Results show that critical conditions for self-ignition can be predicted based on the reaction kinetics of heterogeneous oxidation of the biomass. The kinetics of the oxidation reaction can to some degree be tied to the structural composition of biomass. It was observed that parameters as oxygen level, bed temperature level, biomass type, and bed sample size and density have a strong influence the ignition of biomass beds. This study indicates that it is plausible that mill fires is initiated by low temperature oxidation in assemblies of biomass, that slowly initiate smoldering combustion, and then a steep increase in the bed temperature, defined as the actual ignition happens. In power plant mills, the fire may first be recognized when the mill is started and the suspended material also is ignited.

A complete understanding of the fire initiation in power plant biomass mills is not obtained. To be sure, that we understand the full mechanisms it will be needed to also conduct measurements directly on the large-scale power plant mills. This work however indicate that some initiatives possibly could reduce the risk of biomass mill fires:

- When mills are stopped residual biomass could be removed within a short period

- The oxygen level in the mill could be reduced during mill stop periods
- The mill could be cooled down soon after mill stop
- When the mill is re-started flue gas recirculation could be applied for a period to decrease the risk of ignition of the suspended particles.

This study has to some degree been pioneering work, as data on heterogeneous oxidation at low temperatures is very limited in the international literature. To obtain an in debt understanding of ignition in mills, and also to some degree understand ignition in biomass storage facilities, some further studies will be needed in the following areas:

- Determination of heterogeneous oxidation kinetics of biomass at temperatures below 423 °K. At such temperatures TGA cannot be used, but long term fixed bed experiments could provide valuable data.
- Low temperature determination of heterogeneous oxidation kinetics of more biomass types to establish a more accurate relation between biomass composition and low temperature oxidation kinetics
- Measurements on smoldering combustion and ignition in larger bed sizes (in this study modelling of a 50 cm bed have been done, but verification have only been done with a bed diameter of 3 cm)
- Further measurements conducted directly in full scale power plant mills

5.0 Conclusions

In this project, three specific issues were investigated that all are important for the optimal operation of pulverized fired biomass power plant boilers. Laboratory and model studies were conducted to improve the prediction of deposit formation in biomass pulverized fired boilers. Optimization of the use of coal ash and other additives to remove volatile alkali species from the furnace chamber in biomass-fired boilers was investigated. This is done in order to ensure that a minimum amount of additive is used, while still removing harmful volatile alkali from the boiler chamber. Furthermore, inhibition of biomass wood mill fires while using a maximum air preheating temperature to the mills was studied. The main part of the work was performed by conducting three PhD projects.

The project work have resulted in 8 peer reviewed journal research papers (documented in the appendix) and 13 conference contributions with proceedings, and the project has thereby contributed to the very strong Danish international position within research in the use of biomass for production of power and heat. The results also include a model of deposit formation accounting for the influence of local operation conditions, and a model of ignition in biomass beds accounting for biomass type and the influence of bed size and local temperature.

Some practical industrial relevant recommendations regarding biomass ash deposit formation, optimal use of additives and minimization of the risk of biomass mill fires are provided in this report. The deposit formation work has provided new knowledge on how ash chemistry influences deposit adherence strength. The additive studies have provided detailed information on how particle size, fuel ash composition, additive composition, relative additive to alkali salt ratio, temperature and residence time influence the alkali capture reaction. The improved knowledge on solid additives behaviour have helped Ørsted with respect to optimize

the practical use of additives on their power plants. The mill ignition study provided information on how biomass type, temperature and biomass bed size influence the ignition process.

This project has been a continuation of a long lasting collaboration between Ørsted Bioenergy & Thermal power and the CHEC research group at Department of Chemical Engineering at DTU. The project has motivated new novel collaboration projects as; CFD biomass flame modelling, mathematical modelling of the additive reaction with alkali species and measurements of deposit formation with an advanced deposit probe on biomass PF power plant boilers have been initiated.

Besides the research based results the project have contributed to the education of three PhDs and it has supported four master student projects.

In several areas, further research work could still be of high value for the improved operation of PF biomass power plants, and this could include the following subjects: Improved deposit modelling including shedding mechanisms, improved understanding of low temperature smouldering combustion and ignition of especially relevance for biomass storage, and improved understanding of alternative additives other than kaolin and coal fly ash.

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