THE INFLUENCE OF VOLATILE ALKALI SPECIES ON COATING FORMATION IN BIOMASS FIRED FLUIDIZED BEDS

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ABSTRACT: The research in this paper focuses on the mechanisms leading to bed agglomeration in biomass fired fluidized bed combustion. This phenomenon is caused by low melting ash components and is responsible for the bed particles to stick together and the eventual disruption of the fluidization. An alkali containing ash layer is formed around the particles, which in turn acts as an adhesive for the agglomeration. This paper investigates one of the suggested effects leading to the creation of such layers, the influence of heterogeneous (gas/solid) chemical reactions. In chemical literature, this concept is described as chemical vapor transport (CVT) and has been thoroughly studied. A short summary of these studies is presented here, along with thermodynamical simulations of the proposed reactions under biomass combustion conditions. To validate the simulation results the L.A.P.I.S. (Labscale reactor for Agglomeration Prediction and In-situ detection of Sintering) setup was modified to reproduce CVT reactions between ash components and bed material. The considerations leading to this modification, as well as the results of first test runs are described in this paper. These experiments revealed no measurable deposition based on chemical transport, but some variation of the setup and process parameters is necessary in order to draw profound conclusions.

Keywords: Fluidised Bed Combustion; Ash Agglomeration; High Ash Biomass Fuels

1 INTRODUCTION

The phenomenon of bed agglomeration is a major obstacle to a widespread use of biogenic fuels in fluidized beds. Caused by low ash melting points, these fuels create sticky coatings around the bed material particles that are responsible for an increase in inter-particle forces. When these forces reach the same magnitude as the other forces that keep the particle afloat within the fluidized bed – drag and gravity – an agglomerate is formed. These agglomerates grow over time and cause the defluidisation of the bed, if not counteracted. The problem was described in detail by Gluckman et at. [1]. Further investigations by Seville [2] and Skrifvars [3] focused on the mechanisms and influencing factors of agglomeration. Based on these studies, boiler operators have developed strategies to avoid the occurrence of this problem. Current countermeasures include the lowering of the bed temperatures, frequent exchange of bed materials and the use of additives, all of which have a certain economical impact. Bartels [4] has deducted an extensive review on the topic, concluding that the use of additives and optimized ash compositions – by the use of fuel mixtures – are most promising. Additionally he describes several applications for the online detection of agglomeration, that allow for a more efficient use of the aforementioned countermeasures. Lin [5] concluded the lowering of bed temperatures to be the most effective process parameter variation concerning agglomeration prevention. Finally, Davidsson [6] investigated various additives, with Kaolin and metal-sulfates showing the highest potential. He also describes the economical impact of additives with additional costs below 1€MWh. In order to decrease these cost factors this work tries to cover the mechanisms leading to coating formation and by doing so, possibly to find new ways of agglomeration inhibition. The most probable coating formation mechanisms, as described in literature [7], can be summarized as the physical impact of ash particles on the bed material, its contact with molten ash, the condensation of volatile alkali species on bed particles and heterogeneous chemical reactions between the gas phase and the particles. Visser [8] adds the influence of burning char particles to the list of mechanisms, but Winter [9] found no evidence of elevated temperatures in burning particles, so this point is still open for discussion. The investigations conducted in the current work focus on the influence of heterogeneous reactions. To clarify the impact of this mechanism the chemical backgrounds are explained, their applicability for combustion processes is evaluated by the use of thermodynamic simulations and finally a suitable experimental setup is developed to isolate this effect from the other aforementioned mechanisms.

## 2 HETEROGENEOUS CHEMICAL REACTIONS

This chapter describes the chemical backgrounds of the suggested reactions, as well as their quantitative analysis. In a next step, the concepts are fed into a thermodynamical simulation software to determine the composition of the products and possible process parameters for the experiments.

2.1 Theory

The reactions that occur during coating formation are constraint to gas – solid interactions. These types of reactions have long been studied and are referenced as chemical vapour transport (CVT). First research dates back to as early as mid 19th century, when Bunsen described the transport of ferrous oxide by the HCl content of volcanic gases (Eq. 1. Also the formation of crystals in geodes can be described using CVT [10]. A first technical application was the halogen bulb, which counteracts the evaporation of its tungsten filament by CVT from condensed tungsten on the bulb glass [11]. The production of pure Nickel using Nickeltetracarbonyl [Ni(CO)$_4$] as transport medium would be another industrial application ("Mond" process).

$$Fe_2O_{3(s)} + 6HCl_{(g)} \leftrightarrow 2FeCl_{3(g)} + 3H_2O_{(g)} \qquad (Eq.\ 1)$$
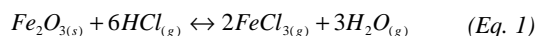
CVT reactions can be performed in three setups, by the use of fluid flow in open systems, or in closed systems by diffusion or convective transport of the gaseous medium. As the fluidised bed reactor is an open system, the further considerations are limited to the first case. The overall reaction equation is given in (Eq. 2) [10].

$$iA_{(s)} + kB_{(g)} \leftrightarrow jC_{(g)} \qquad (Eq.\ 2)$$
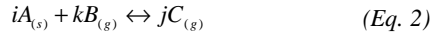
A is defined as the precipitate, B the transport medium and C is the reaction product. The process is reversible and dependent on temperature and pressure, so the precipitate can be "soluted" in the gas phase and deposited at another location – with other thermodynamic conditions. Endothermic reactions cause a transport from high to low temperatures as opposed to exothermic types [11]. The quantitative analysis of such processes is described in (Eq. 3) and (Eq. 4) according to Schäfer [10]. The main influencing factors are the initial amounts (n_i) of the components and their partial pressures (p_i), which can be determined using thermodynamic simulations (s. Chap.2.2).

$$\frac{n_A}{n_{B(init)}} = \frac{i}{j} \cdot \frac{\left(n_{C,2} - n_{C,1}\right)}{n_{B(init)}} \qquad (Eq.\ 3)$$

$$\frac{n_{C,x}}{n_{B(init)}} = \frac{p_C}{p_{B(init)}} \cdot \left[\frac{1}{1 - \frac{p_C}{p_{B(init)}} \cdot \frac{(j-k)}{j}} \right] \qquad (Eq.\ 4)$$

Another concept to describe the process quantitatively is the gas phase solubility λ [11]. In analogy to solid-liquid reactions, λ defines the amount of substrate that can be sustained in the gas phase. It is calculated according to (Eq. 5) and symbolizes the fraction of the volatilized substrate to the sum of gaseous components, expressed in partial pressures.

$$\lambda = \frac{\sum p_{i(substrate)}}{\sum p_{j(g)}} \qquad (Eq.\ 5)$$

This concept allows the calculation of more complex reaction mechanisms and can be combined with (Eq. 4) to determine the amount of transported material. The gas phase solubility replaces the term $p_C/p_{B(init)}$. A plot of λ versus temperature shows what direction a reaction will take. A rising solubility will deposit material at lower temperatures and vice versa.
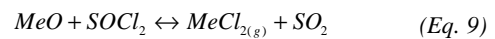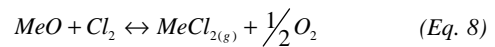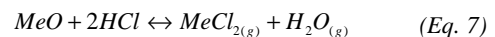
The original application of CVT processes was the creation of pure materials, much like the crystallization in liquid solutions. Within the last decades, another utilization was developed, that much closer resembles the processes leading to bed agglomeration. It is referred to as chemical vapour deposition (CVD) and is used for the creation of ultra thin coatings of various source materials. Examples would be Titanium coatings of ball bearings [12], AlSi protective coatings for high temperature steels [13], or nanostructured surfaces [14]. In comparison to CVT, only the backward reaction is used here. This means that the substrate is already added in its soluted form, as a compound with the transport medium. In the reactor suitable conditions for a deposition are realized. There are many variants for this process, differentiated by

the type of substrate introduction, the supply of activation energy and the handling of the coated material [14][15]. If a controlled growth of the coatings is desired, i.e. for nanostructures, the precursor material is kept in a fixed position within the reactor. For a more unified coating, however the concept of fluidized bed CVD has many advantages. Here, the precursors (glass beads, bearing balls etc.) are suspended in an FBC reactor and the substrate is added to the fluidisation gas stream. The result is a very homogenous coating on each particle [16]. This again is a parallel to ash induced coating formation in biomass combustion, where a homogenous layer of Potassium Silicates is formed around the bed material particles [17].

2.2 Thermodynamic calculations

In order to determine the effect of CVT reactions in the agglomeration process, thermodynamical simulations were conducted, using the software package "FACTsage" (Bale [18]). The aim was to calculate reaction enthalpies and the amount of liquid species formed at common boiler temperatures. The calculations are based on a large database of material properties that includes single components as well as binary or ternary solutions of several elements. For the calculation of the reaction products the principal of minimized Gibb's Energy is applied, based on a quasichemical model of the components.

A first step in the investigation of CVT processes is the determination of possible chemical reactions applicable to the task. Schäfer [10] collected a comprehensive list of possible reactions suitable for CVT processes. Among those the most probable types to occur during biomass combustion are listed in (Eq. 6) to (Eq. 9). *Me* in these cases would be Potassium or Sodium, as those are considered to be responsible for coating formation. The presence of Chlorine in all listed variants hints at its importance as a mediator for agglomeration phenomena.

$$MeO + CO + Cl_2 \leftrightarrow MeCl_{2(g)} + CO_2 \qquad (Eq.\ 6)$$

$$MeO + 2HCl \leftrightarrow MeCl_{2(g)} + H_2O_{(g)} \qquad (Eq.\ 7)$$

$$MeO + Cl_2 \leftrightarrow MeCl_{2(g)} + \frac{1}{2}O_2 \qquad (Eq.\ 8)$$

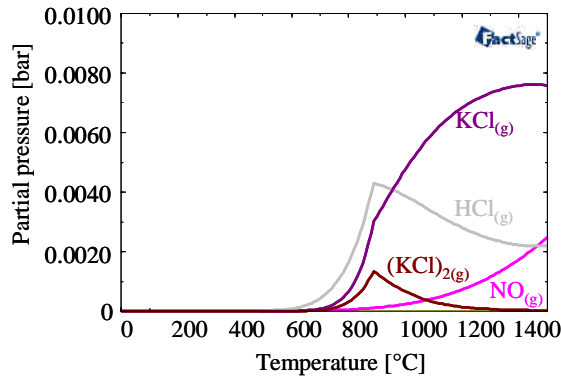$$MeO + SOCl_2 \leftrightarrow MeCl_{2(g)} + SO_2 \qquad (Eq.\ 9)$$

An analysis of the Gibbs energy vs. temperature plot for the given reactions reveals the direction of the equilibrium as well as the probability for the reactions to occur. Figure 1 shows that (Eq. 6) and (Eq. 9) are endothermic, thus transported from high to low temperatures, while the other two are slightly exothermic. The strong bias of the equilibrium for CO_2 and SO_2 also suggests that these reactions are not ideally suited for CVT, as the side of educts is strongly preferred, thus only little material is soluted in the gas phase [10]. (Eq. 7) and (Eq. 8), however are much more balanced, so forward and backwards reactions are equally likely.

The following calculations investigate the vapour compositions from SiO_2 and KCl mixtures with typical flue gas compositions. Eutectics forming from SiO_2 and KCl mixtures are the predominant reasons for agglomeration in fluidized beds during combustion of biomass.
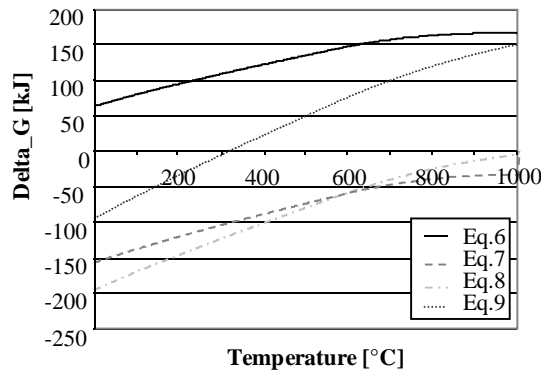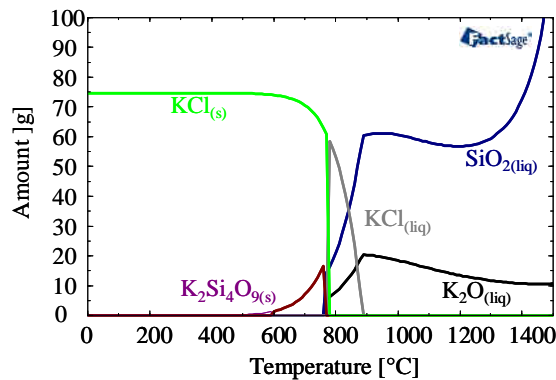
Figure 1: Gibbs energy of the four CVT reactions Eq.6 to Eq.9

Based on the findings of the reaction equilibrium further simulations were performed. The partial pressures of the transport medium (p_B) for the most likely reaction (Eq. 7) indicate that below 700°C no potassium is in gaseous form (Figure 2) for mixtures of SiO_2 with KCl in typical flue gas compositions (i.e. 65% N_2, 15% H_2O, 10% O_2, 10% CO_2). This leads to the conclusion that KCl is formed at higher temperatures and deposited below 700°C. The reaction product is $K_2Si_4O_9$ as seen in Figure 4 and has a melting point of 770°C. Its formation begins at 500°C, so the deposition range can be defined between these two points (500°C – 700°C).

When adding the species of (Eq. 9) to the input compounds the results are slightly shifted (Figure 3). Already at low temperatures a high percentage of Chlorine – in the form of HCl and Cl2 – is present in the gas phase. The reaction responsible for this effect is given in (Eq. 10) and is the basis for the introduction of sulfur containing additives ("Chlor Out") for the reduction of corrosion effects on the heating surfaces of boilers [19].

$$2MeCl + SO_2 + \tfrac{1}{2}O_2 \leftrightarrow Me_2SO_4 + 2HCl \qquad (Eq.\ 10)$$
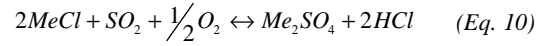
In regard to agglomeration prevention, however the effect looses its impact as the K_2SO_4 forms a eutectic with the KCl resulting in a melting temperature of slightly above 700°C. The results are shown in Figure 5. A variation of the added SO_2, as demonstrated in Figure 6 reveals another effect, as with higher dosage the amount of liquid potassium sulfate is reduced. Here all the KCl is transformed to K_2SO_4, so no eutectic is formed. As a result the melting temperatures rise as high as 950°C, which would be sufficient for the prevention of agglomeration.

Figure 2: Partial pressures of the gaseous species based on (Eq. 7). Input compounds: SiO_2, KCl, H_2O, N_2, O_2, CO_2.
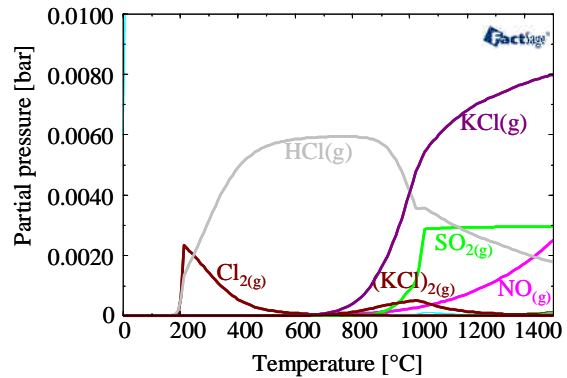
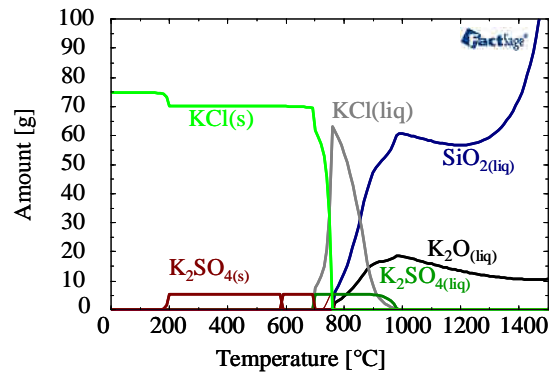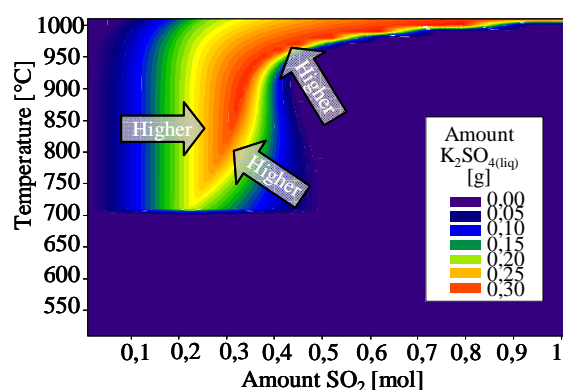**Figure 3: Partial pressures of the gaseous species based on (Eq. 7) and (Eq. 9).** Input compounds: SiO_2, KCl, H_2O, N_2, O_2, CO_2, SO_2.

Figure 4: Amount of solids and liquids (Eq. 7). Input compounds: SiO_2, KCl, H_2O, N_2, O_2, CO_2.

Figure 5: Amount of solids and liquids (Eq. 7) and (Eq. 9). Input compounds: SiO_2, KCl, H_2O, N_2, O_2, CO_2, SO_2.

Figure 6: Amount of K₂SO₄,(liq) with rising SO₂. Input compounds: SiO_2, KCl, H_2O, N_2, O_2, CO_2, SO_2.

3   EXPERIMENTAL SETUP

The experimental part of this work was conducted on a lab scale fluidized bed reactor according to the schematics in Figure 7. It features an inner diameter of 60,3mm and a length of 750mm. Fluidizing gas is supplied from pressurized air and regulated by a mass flow controller. The temperature is controlled by an electrical pipe furnace and thermocouples in the bed and the freeboard. The state of fluidization is detected by pressure transmitters, using a method according to Chirone [20].
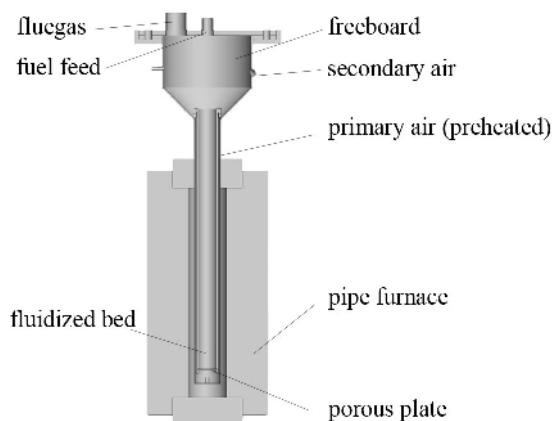

Figure 7: Schematic of the "L.A.P.I.S." fluidized bed reactor. (Labscale reactor for Agglomeration Prediction and In-situ detection of Sintering)

In order to restrict the interaction of the biomass ashes with the bed material to heterogeneous chemical reaction, some modifications to the reactor are necessary. Carlsson [15] lists four different methods to supply the gaseous components into a CVD reactor:

- Gas bottles for compounds that are in gaseous form at room temperature
- Sublimators for solids
- Evaporators or atomizers for liquid precursors or aqueous solutions
- Generators where the specific compound is created in-situ.

The first two variants are to be neglected for the current application, as KCl – the precursor gas used in the experiments – does not fulfill the specified requirements. It is not gaseous at ambient temperature and the

conditions for sublimation are not within practical limits for this reactor. Since KCl is a salt, its solubility in water is very good. For this reason the atomizer seems well suited for the task. Even evaporators could be considered to generate small traces of KCl. A solution of KCl in water is filled into a container, the fluidizing air is bubbled through the solution and saturated. This saturation is a function of temperature, so it is possible to control the amount of vapor to be introduced into the reactor. All ducts from the evaporator to the reactor have to be heated in order to avoid condensation. The amount of KCl to be transported by this method can be evaluated using FactSage, the results are displayed in Figure 8. It is obvious that no significant concentrations can be reached, so this method has to be neglected as well.
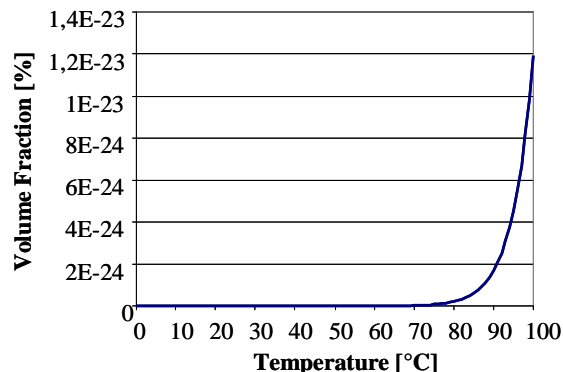

Figure 8: Volume fraction of KCl transported from the evaporator. (Factsage simulation)

The last proposed variant is the use of a generator, Carlsson [15] describes a process where HCl is passed through an Aluminum sponge in order to generate $AlCl_3$. When applied to the formation of ash coatings, a solid form of Potassium would have to be combined with one of the transport media of (Eq. 6) to (Eq. 9). These are all based on Chlorine compounds, so special care should be taken concerning handling and use of constructive materials. Since the L.A.P.I.S. reactor was not designed to be operated with such compounds, a complete redesign would be necessary, which was not within the scope of this work. However as a compromise between close depiction of a CVD process and the simulation of combustion processes, biomass fuels could be used as the provider of gaseous KCl.

Again, two alternatives can be described, firstly, the use of pre-ashed biomass according to DIN 51730 (at 550°C), secondly the actual combustion of the fuel within

the reactor. For the necessary physical separation of the fluidized bed and the source of KCl, a second bed had to be inserted into the reactor (s. Figure 9). In this setup, fuel is added at the top, falls through the fuel pipe and is combusted on the lower porous plate. Gas velocities are configured to ensure a fixed bed combustion.
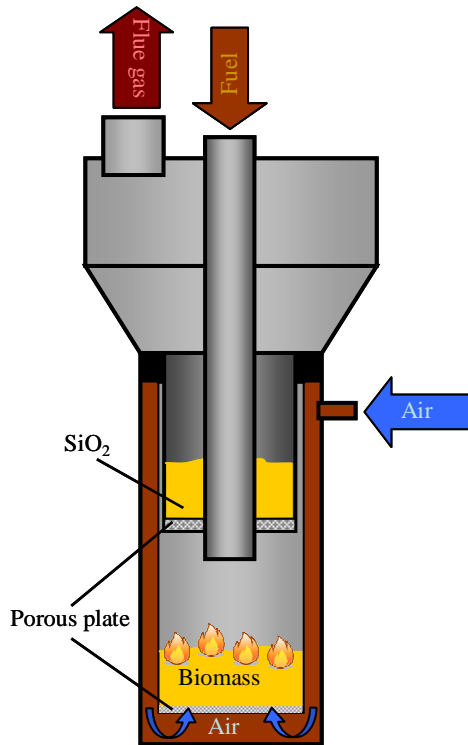
Figure 9: Schematic of the L.A.P.I.S. reactor with the secondary fluidized bed

The volatile species then pass through a second porous plate, that also acts as a filter element for fly ash and are brought to contact with the SiO_2 sand in the upper bed. Here, due to a smaller cross section, along with the small particle size of the sand, a fluidized bed is realized with a u/u_0 ratio of 2. The temperature of the combustion is controlled by the pipe furnace (set at 950°C) and the bed temperature by the heated wall of the freeboard (at 550°C). This should ensure a large enough volatilization of Alkali species and its subsequent deposition in the upper bed.

The experiments with pre-ashed fuel use the same setup, albeit all the ash is introduced onto the lower plate before the experiment and the fuel pipe is closed. The amount of ash was chosen to generate a volatile ash content equivalent to 10% of the bed material mass.

4   TEST RUNS

The experiments conducted for this paper are separated in two parts. First, the thermodynamic simulations (displayed in Figure 2 to Figure 5) have been evaluated and primary tests with the secondary bed, using pre ashed biomass have been performed.

For the evaluation of the simulations, the same compounds were added into the reactor as in the calculations, with 250g of SiO_2 and 25g of KCl for the base scenario and an addition of 12,5g of $Al_2(SO_4)_3$ for the sulphur case. The fluidization medium was pressurized air. In order to cause agglomeration of the

bed material the bed temperature was raised in steps of 25K per 10min, from a starting point of 550°C. In Figure 10 the data from the first experiment is displayed, revealing an agglomeration temperature of 730°C. The results of the Sulphur case were not equally conclusive, the pressure variance showed no agglomeration up to 1150°C – the upper limit of the reactor – and also a visual inspection of the hot bed confirmed that it was still in fluidized state. However, upon cooling, the bed agglomerated.
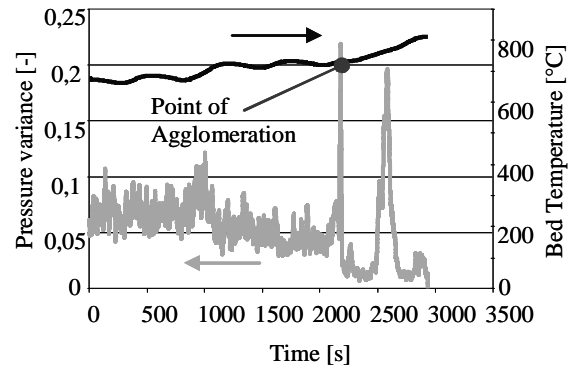

**Figure 10: Agglomeration Temperature of the KCl - SiO_2 test run.**

To further investigate this behaviour, the bed ash of both experiments was analysed using SEM/EDX methods. The results are displayed in Figure 11 through Figure 16. A cross section of the agglomerated particles revealed that no coating formation occurred. Instead, the effect of "melt induced" agglomeration was predominant [7]. The KCl melted at the given conditions and as a consequence it formed liquid bridges between the particles that caused agglomeration (s. Figure 11). Furthermore, there was no reaction between the Potassium and the Silicon, as predicted in the simulations. The most probable explanation for this would be a lack of transport medium, in particular H_2O, which is part of (Eq. 7) and also among the input species of the simulation. To address this topic, future tests will be performed using a humidifier for the fluidization gas.

The Sulphur tests showed the same behaviour, with melt induced agglomeration and no reaction with the Silicon. The binding substance (Figure 12) between the particles is composed of mostly KCl, but some areas of K_2SO_4 could also be found. This is in agreement with the simulation (Figure 5), that predicted a small portion of Potassiumsulphate formation. For the upcoming experiments the amount of added $Al_2(SO_4)_3$ will be increased in order to bind all the Potassium in the Sulphates, thus reaching the high melt temperatures predicted in Figure 6.

There was no trace of Aluminium to be found in the SEM scans, so it is suggested that it left the reactor with the fly ash. As for the agglomeration behaviour, a possible explanation for the described phenomenon would be a lower viscosity of the $KCl-K_2SO_4$ eutectic compared to KCl alone. This leads to lower adhesive forces between the particles, so the drag/gravity forces were able to retain the fluidized state. Upon cooling the viscosity increased up to the point where agglomeration occurred.
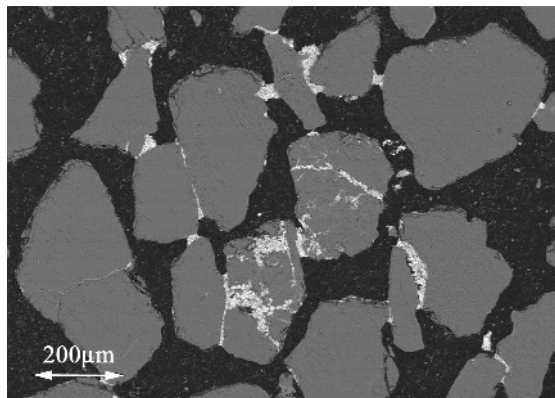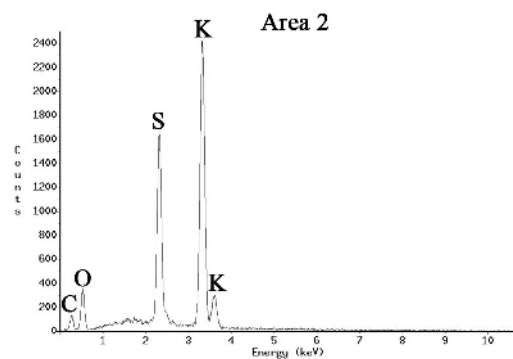
Figure 11: Cross section through an agglomerate. 25g KCl, 250g SiO$_2$, t$_{Agglo}$ = 730°C; Addition of KCl lead to "melt induced" agglomeration
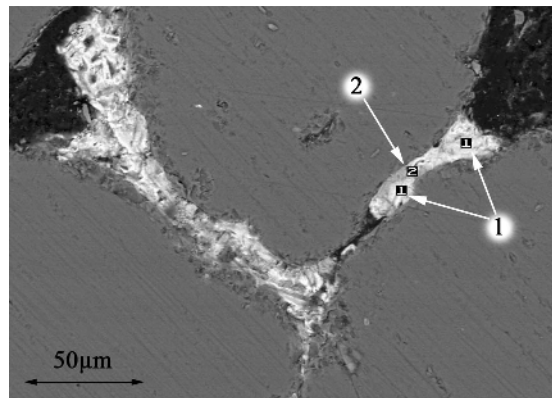
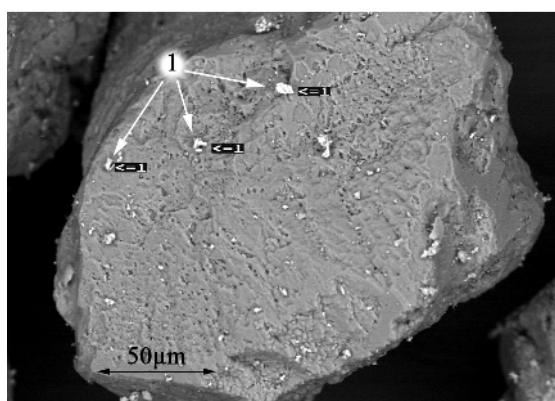**Figure 12: Binding substance.** 25g KCl, 12,5g Al$_2$(SO$_4$)$_4$, 250g SiO$_2$, t$_{Agglo}$ = 1150°C, Sulfur reacted to K$_2$SO$_4$, Aluminium was not found in the bed ash.
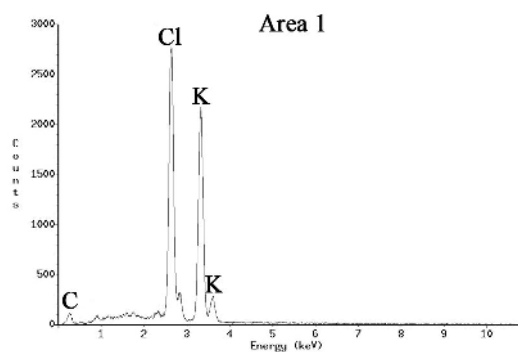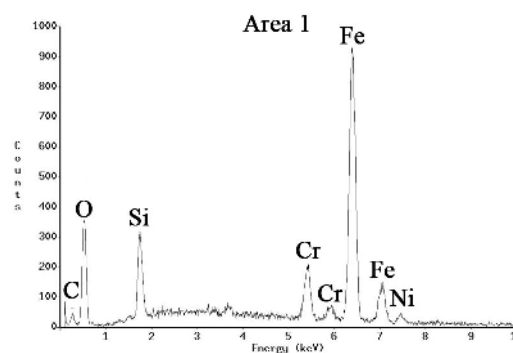

Figure 13: EDX Analysis of Figure 12 – Potassium Chloride

Figure 14: EDX Analysis of Figure 12. - Potassium Sulfate

Figure 15: Surface scan of "pre ashed" experiments. No coating formation was detected. Only small spots of metallic compounds originating from the reactor walls were found


Figure 16: EDX Analysis of Figure 15– metallic compounds

The last experiment conducted for this work utilized the aforementioned secondary bed with pre ashed biomass as Alkali source. The type of biomass was sugar beet residues, its ash composition is given in Table 1. A prior experiment revealed an agglomeration temperature of 875°C under standard combustion conditions with well developed coatings (s. Figure 17), so this biomass seems to be a suitable candidate. For the current experiment, the fixed bed temperature was set to 950°C to ensure a sufficient alkali volatilization form the ash resting on the lower porous plate. The upper fluidized bed was kept at a constant 550°C. The test duration was 8h in which an equivalent of 10wt% Alkali content was transported to the upper bed, based on mass balances and thermodynamic calculations.

Table 1: Composition of Sugar beet ash [AE&E Laboratories]

Component	Weight fraction [%]
Ash content	3,66
Na_2O	6,83
K_2O	32,57
CaO	21,3
MgO	10,50
Fe_2O_3	0,99
SiO_2	14,13
Al_2O_3	1,9
P_2O_5	4,20
SO_3	7,04
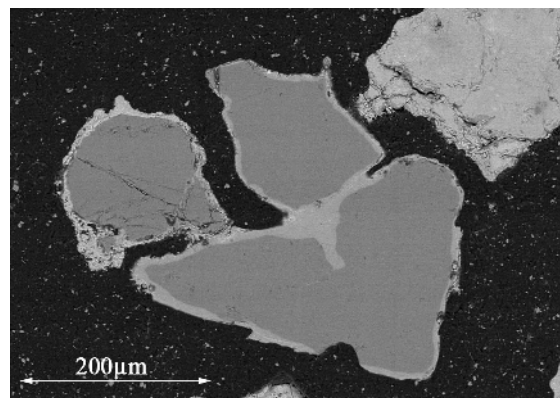
Figure 17: Coating induced agglomeration. Combustion test using sugar beet, t_{Agglo} = 875°C

During the 8h test duration no agglomeration of the bed could be detected and also visual inspection of the bed particles showed no signs of coating formation. This was confirmed by SEM surface scans (s. Figure 15), which showed no coating development. Only small spots of Ferrous containing substance was detected, that most likely originated from the reactor walls – build of a CrNi Alloy. Still, the results are not distinctive and further experiments are necessary. It was shown, however, that the experimental setup is operational, with the inclusion of a fixed and fluidized bed with independently controllable temperatures.

5   CONCLUSION

It is widely agreed that the concept of coating induced agglomeration is responsible for most of the issues occurring in biomass fired FBCs. Among the suggested mechanisms responsible for coating formation – particle impact, molten ash and chemical reactions –

the latter principle was investigated in this work. The concept of heterogeneous chemical reactions, especially that of chemical vapour transport (CVT), has been investigated thoroughly. It is possible to qualitatively and quantitatively predict the reactions occurring in a given system. Using a thermodynamical simulation software (FactSage), it is possible to determine what reactions are most likely – in the case of biomass combustion this would be a reaction of KCl with H_2O – and which compounds are formed depending on the temperature. These simulations also revealed the positive influence of SO_2 on the formation of molten ash components presenting it as a possible additive for agglomeration prevention.

An experimental evaluation of these simulations was attempted and therefore the existing fluidized bed reactor had to be modified. The setup was redesigned to incorporate a primary "generator" stage to create the volatile alkali species and a secondary fluidized bed, in which the gaseous compounds react with the bed material (SiO_2). A first series of test, however, resulted in no measurable deposit of coatings on the quartz particles. To conclude that CVT reactions do not lead to coating formation based on this experiment would be presumptuous, as several other influencing factors could be responsible for this result. These factors include the lack of transport medium, too low ash content or residence time, wrong choice of bed temperatures etc. So the ongoing experiments will address these topics in order to clarify their influence. A humidifier will be applied to the primary air stream, experiments with combustion on the lower bed will be performed and the operating parameters are closely evaluated.

As for the influence of Sulphur containing additives, it was demonstrated that the simulated results – in a low SO_2 case – are well represented in the experiments, so further tests with higher dosage will be performed. These tests will also be extended to real combustion conditions, as opposed to the synthetic ash components used in this work, to evaluate its applicability for biomass fired boilers. Furthermore, the Sulphur containing compound will be varied – $(NH_4)_2SO_4$ or $Fe_2(SO_4)_3$ are possible – to determine the most efficient and economically viable candidate for the additive.

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