

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

Impact of Ash on the Properties of Fluidized Bed Materials

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CHALMERS UNIVERSITY OF TECHNOLOGY

Gothenburg, Sweden 2022

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ISBN 978-91-7905-693-3

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Doktorsavhandlingar vid Chalmers tekniska högskola
Ny serie nr 5159
ISSN 0346-718X

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Cover:

The cover shows a scanning electron microscopy cross-section of a bed material particle after three days exposure time to woody biomass ash. The characteristics of the bed material that are discussed in this work are represented schematically.

Printed by Chalmers Digitaltryck
Gothenburg, Sweden 2022

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Abstract

The utilization of the fluidized bed technology offers the possibility of thermally converting a large variety of biogenic feedstocks. The characteristics of the bed material which is used in the process play a major role regarding the overall process performance. These characteristics are influenced by interactions between the bed material and the fuel ash. The materials investigated within this work were quartz, ilmenite, olivine, and two different feldspars. This work investigates several different properties of the bed material which can be influenced by interactions with the fuel ash. Depending on the combinations of fuel and bed material, as well as the choice of thermal conversion process, these interactions can be beneficial or detrimental.

It was found that quartz and ilmenite have a strong tendency to react with alkali and can thereby mitigate to a certain degree alkali-induced corrosion of metallic components in the reactor. In the case of quartz, this bed material-alkali interaction leads to the formation of alkali-silicates which exhibit a low melting temperature and can therefore cause agglomeration of the bed material.

Olivine and feldspar are more resistant towards agglomeration. Interactions with biomass ash leads to the formation of an ash layer which has catalytic properties towards tar removal, which is necessary to avoid problems associated with tar condensation during gasification. After longer residence times, the particles acquire an oxygen carrying ability due to the formation of a surface layer containing Fe and Mn. This decreases the calorific value of the product gas and requires bed material replacement. If fuel containing high amounts of phosphorus is converted, this waste stream can further be utilized for nutrient recovery.

Ilmenite is used in a process which exploits its oxygen carrying ability. Dilution of ilmenite by fuel ash diminishes this property but the necessary replacement of material can be decreased by magnetically separating active ilmenite from inactive ash.

Keywords: fluidized bed, bed material, ash interaction, layer formation, catalytic tar removal, oxygen carrying, agglomeration

Acknowledgements

This work would not have been possible without all the help that I received by my colleagues. During my time as a PhD student, I had the luxury of meeting and working with a lot of brilliant people who played a major role in my scientific journey. For this, I am deeply grateful.

First and foremost, I would like to thank my supervisor, Pavleta Knutsson for her guidance and support. I always looked forwards to our meetings and left them full of inspiration and motivation to do science. I would also like to thank my co-supervisors Martin Seemann and Fredrik Lind for providing a different perspective on the material in our discussions.

Thanks to my colleagues from Chalmers, Teresa Berdugo Vilches, Jelena Maric, Sébastien Pissot, Henrik Thunman, and Britt-Marie Steenari for making it possible for me to investigate so many different interesting samples.

Special thanks to my colleagues from Luleå, Umeå, and Vienna, Tomas Karl Hannl, Ali Valizadeh, Nils Skoglund, Marcus Öhman, Matthias Kuba, and Katharina Fürsatz for all our interesting discussions and the fruitful collaborations.

I would also like to thank Per Malmberg, Mohammad Sattari, Ren Qiu, Mats Halvarsson, and Andreas Schaefer for making it possible to implement novel analysis techniques for this work.

Thanks also for all the help I received during the laboratory work by Alyona Tormachen, Panida Aonsamang, Marcus Sandberg, and Ignacio Lamarca.

Furthermore, I would like to thank the people here at OOMK who made this an excellent working environment. Special thanks go to my fellow Cinder group members, Mariane Vigoureux and Tomas Leffler, and my office mates, Vedad Babic and Julien Phother as well as all of the wonderful people I had the pleasure to meet during lunch and fika.

Lastly, thanks to all of my friends and my family for making these five years the best time of my life, so far.

List of Publications

This thesis is based on the following papers:

Paper I

Comparison of Ash Layer Formation Mechanisms on Si-containing Bed Material during Dual Fluidized Bed Gasification of Woody Biomass

Robin Faust, Teresa Berdugo Vilches, Per Malmberg, Martin Seemann, Pavleta Knutsson

Energy Fuels (2020), 34, 7, 8340–8352

Paper II

Microscopic investigation of layer growth during olivine bed material aging during indirect gasification of biomass

Robin Faust, Mohammad Sattari, Jelena Maric, Martin Seemann, Pavleta Knutsson

Fuel (2020), 266, 117076

Paper III

Ash Layer Formation in Dual Fluidized Bed Gasification of Wood – Impact of Surface Morphology

Robin Faust, Ali Valizadeh, Ren Qiu, Alyona Tormachen, Jelena Maric, Teresa Berdugo Vilches, Nils Skoglund, Martin Seemann, Mats Halvarsson, Marcus Öhman, Pavleta Knutsson

Manuscript

Paper IV

Role of K and Ca for catalytic activation of bed material during biomass gasification

Robin Faust, Jelena Maric, Teresa Berdugo Vilches, Britt-Marie Steenari, Martin Seemann, Pavleta Knutsson

23rd International Conference on Fluidized Bed Conversion (2018), Seoul

Paper V

Layer Formation on Feldspar Bed Particles during Indirect Gasification of Wood – Part 1 K-feldspar

Robin Faust, Thomas Karl Hannl, Teresa Berdugo Vilches, Matthias Kuba, Marcus Öhman, Martin Seemann, Pavleta Knutsson

Energy & Fuels (2019), 33, 7321-7332

Paper VI

Layer Formation on Feldspar Bed Particles during Indirect Gasification of Wood – Part 2 Na-feldspar

*Thomas Karl Hannl, **Robin Faust**, Matthias Kuba, Pavleta Knutsson, Teresa Berdugo Vilches, Martin Seemann, Marcus Öhman*

Energy & Fuels (2019), 33, 7333-7346

Paper VII

Laboratory study of interactions between biomass ash and alkali-feldspar bed material

***Robin Faust**, Pavleta Knutsson*

CFB 2021 - Proceedings of the 13th International Conference on Fluidized Bed Technology

Paper VIII

Early Layer Formation on K-Feldspar during Fluidized Bed Combustion with phosphorus rich fuel

***Robin Faust**, Katharina Fürsatz, Panida Aonsamang, Marcus Sandberg, Matthias Kuba, Nils Skoglund, Pavleta Knutsson*

Submitted to Fuel

Paper IX

Interactions between Automotive Shredder Residue and Olivine Bed Material during Indirect Fluidized Bed Gasification

***Robin Faust**, Panida Aonsamang, Jelena Maric, Alyona Tormachen, Martin Seemann, and Pavleta Knutsson*

Energy Fuels (2021), 35, 19, 15935–15949

Paper X

Development of Oxygen Transport Properties by Olivine and Feldspar in Industrial-Scale Dual Fluidized Bed Gasification of Woody Biomass

*Sébastien Pissot, **Robin Faust**, Panida Aonsamang, Teresa Berdugo Vilches, Jelena Maric, Henrik Thunman, Pavleta Knutsson, and Martin Seemann*

Energy Fuels (2021), 35, 11, 9424–9436

Paper XI

Magnetic Properties of Ilmenite used for Oxygen Carrier Aided Combustion

***Robin Faust**, Ignacio Lamarca, Andreas Schaefer, Fredrik Lind, Pavleta Knutsson*

24th International Conference on Fluidized Bed Conversion (2022), Gothenburg

Contribution

Paper I: Principal author, SEM and XRD analysis, thermodynamic modelling, evaluation of ToF-SIMS results

Paper II: Principal author, AAS, SEM, and XRD analysis, thermodynamic modelling

Paper III: Principal author, SEM analysis, evaluation of TEM data

Paper IV: Principal author, conduction of laboratory exposures, BET, SEM, and XRD analysis

Paper V: Principal author, SEM and XRD analysis, thermodynamic modelling

Paper VI: Supporting author, participation in discussions

Paper VII: Principal author, supervision of laboratory exposures and SEM analysis

Paper VIII: Principal author, SEM analysis, thermodynamic modelling

Paper IX: Principal author, SEM and XRD analysis, thermodynamic modelling

Paper X: Supporting author, IC analysis, participation in discussions

Paper XI: Principal author, evaluation of XRD and XRF, thermodynamic modelling

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1. Introduction

The world total primary energy supply 2019 was around 600 EJ.¹ The sources to feed this energy demand were to more than 80% fossil fuels (oil, coal and natural gas).¹ Anthropogenic greenhouse gas (GHG) emissions have continuously increased from 1970 to 2019² and CO₂ emitted by fossil fuel combustion represents almost 80% of the total emissions.³ The figure for total emissions has increased to 36 GtCO₂/year until 2019.⁴ According to the Intergovernmental Panel on Climate Change (IPCC), these emissions are expected to further increase if no counter measures are realized.² GHG emissions are the main reason for global warming and compared to pre-industrial levels, this would lead to an increase in mean surface temperature of between 3.7 °C and 4.8 °C by the end of the 21st century.³

Several counter measures, also referred to as mitigation options, are listed in the IPCC report, one of which is the implementation of bioenergy.³ The utilization of biomass as feedstock for energy generation presents a renewable alternative towards fossil fuels.⁵⁻⁷ Biomass includes organic matter which is derived from plants or animals.⁸ During its growth, plant-based biomass consumes CO₂ from the atmosphere which is subsequently released back during combustion. Thus, in biomass combustion the net emissions of CO₂ is zero, which is why biomass can be considered a CO₂ neutral feedstock.⁶⁻⁸ Conversion of biomass instead of coal presents therefore a sustainable alternative to fossil fuels. The overall technical energy potential of biomass was calculated to be in the range of 160 – 270 EJ by 2050, representing between 27 – 45 % of the total global energy demand.⁹

Even though it is considered that the CO₂ released by biomass combustion is taken up by the growing biomass, the time interval between release of CO₂ and the re-absorption heavily depends on the type of biomass utilized.^{10,11} When assessing the CO₂ emissions resulting from biomass conversion, it is therefore not sufficient to assume all biomass as CO₂ neutral. Furthermore, the applicability of biomass must also be considered regarding socio-economic factors such as food supply, and environmental issues such as the loss of biodiversity caused by industrial biomass plantations.¹² Accounting for the latter two arguments, the utilization of agricultural residues or woody biomass acquired from afforestation of degraded land, has the greatest benefit on atmospheric CO₂ levels.^{3,11} Forest residues from logging and processing alone were estimated to be 28 EJ/year.¹³ Additionally, plantations of fast-growing plant species such as miscanthus or sugar cane present opportunities of shorter carbon emission and sequestration cycles.³ The total potential of utilizing marginal and degraded land for dedicated biomass plantations was estimated to be about 100 EJ.^{14,15} This number could be further increased, if growing genetically modified plants is considered possible, where the plants' ability to perform photosynthesis is improved.^{16,17} Thus, the utilization of different sources of biomass offers the potential to satisfy a significant share of the global primary energy demand by renewable sources.

Besides biomass, carbonaceous feedstock from waste streams can be utilized for energy generation, such as municipal solid waste,¹⁸ sewage sludge,¹⁹ animal manure,²⁰ or plastic.²¹ Burning waste has the added advantage of decreasing its volume and the content of toxic organic compounds. However, compared to traditional feedstocks, such as coal, biomass and especially waste require dedicated technologies for their thermal conversion. A major challenge with biomass and waste streams is their non-homogeneous composition, regarding both organic and inorganic compounds. This requires flexibility of operational parameters to reach the optimal conditions for thermal conversion of each particular type of feedstock. This

problem is schematically illustrated in Figure 1. While waste combustion decreases the costs associated with disposal, the complexity of the fuel requires a dedicated combustion technology.

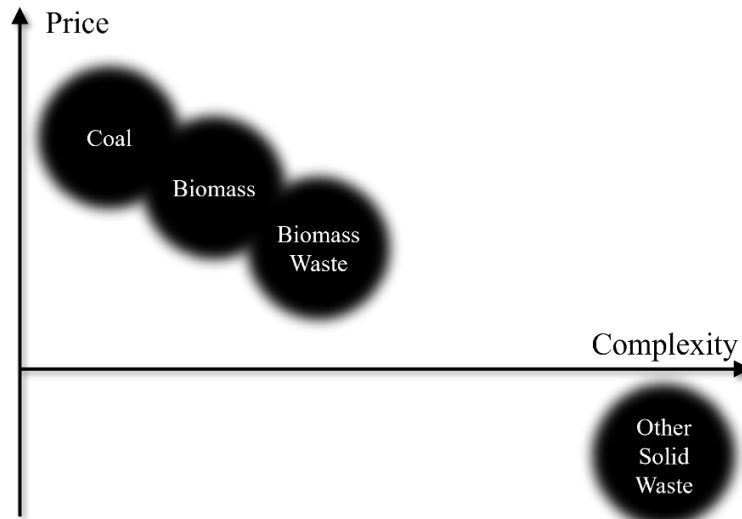


Figure 1: Schematic illustration of the correlation of price and complexity of some selected possible feedstocks.

For biomass and waste, the commonly utilized boiler types are grate-fired boilers and fluidized bed combustion boilers. Grate-fired boilers have the advantage of not requiring preparation of the fuel and no problems associated with the bed material occur. Fluidized bed boilers utilize a high gas velocity to fluidize the used bed material. Thereby, improved combustion compared to grate-fired boilers can be achieved. This makes fluidized beds an efficient and flexible technology for thermal conversion of heterogeneous fuels.²²

2. Processes of Fluidized Bed Conversion

The technology of fluidized bed conversion is based on the application of a bed material which consists of small particles (about 100-300 μm in diameter) through which a gas stream is led. At sufficiently high gas velocity, the particles are fluidized, i.e., they behave like a fluid. This evens out the heat distribution throughout the reactor and enhances the contact between the fuel and the surrounding gas which enables high fuel flexibility. Different conditions can be realized depending on the gas stream and the utilized bed material.

2.1. Oxygen Carrier Aided Combustion

During fluidized bed combustion, an inert bed material, such as quartz sand, is conventionally utilized and fluidized by air. The efficiency of this process is limited by the distribution of oxygen, as oxygen-rich regions (near the gas inlet) and oxygen-poor regions (near the fuel inlet) can occur, which hampers fuel combustion.

To alleviate this problem, the bed material can be changed to a material which exhibits oxygen carrying abilities. These materials usually contain a transition metal (denoted 'M' in the reactions below) which can be oxidized at the gas inlet (Reaction 1) and reduced at the fuel inlet (Reaction 2), thereby transporting oxygen from oxygen-rich to oxygen-poor regions in the reactor. The fuel is simplified as carbon (C) in Reaction 2. The process is schematically shown in Figure 2.

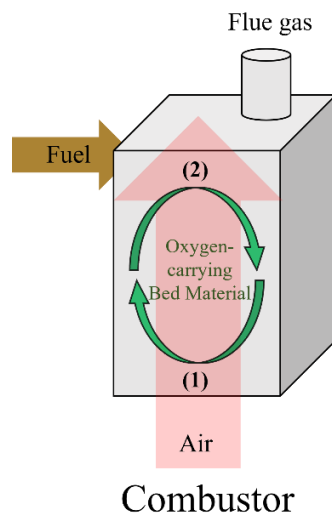
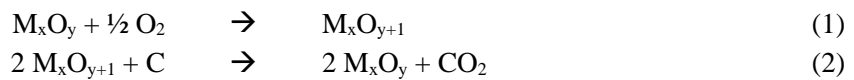


Figure 2: Simplified illustration of the working principle of the oxygen carrier aided combustion (OCAC) concept. Near the air inlet the oxygen-carrying bed material is oxidized according to Reaction 1. Near the fuel inlet the bed material is reduced according to Reaction 2, which enhances fuel conversion.

2.2. Dual Fluidized Bed Gasification

Furthermore, utilizing a fluidized bed offers the possibility to conduct dual fluidized bed gasification (DFB). The technology of DFB gasification is based on two fluidized bed reactors (see Figure 3).^{23,24} In the combustor, fuel is converted in an exothermic reaction to heat and flue gas. This is exemplified in Reaction 3, where the fuel is simplified as carbon (C). The bed material is fluidized by a gas stream and the heat emitted by the oxidation of the fuel is taken up by the bed material and is transported to the gasifier by the circulating fluidized bed material. In the gasifier, H₂O or CO₂ is utilized as fluidization gas and the endothermic gasification reaction takes place which converts fuel to raw gas (Reactions 4a and 4b).

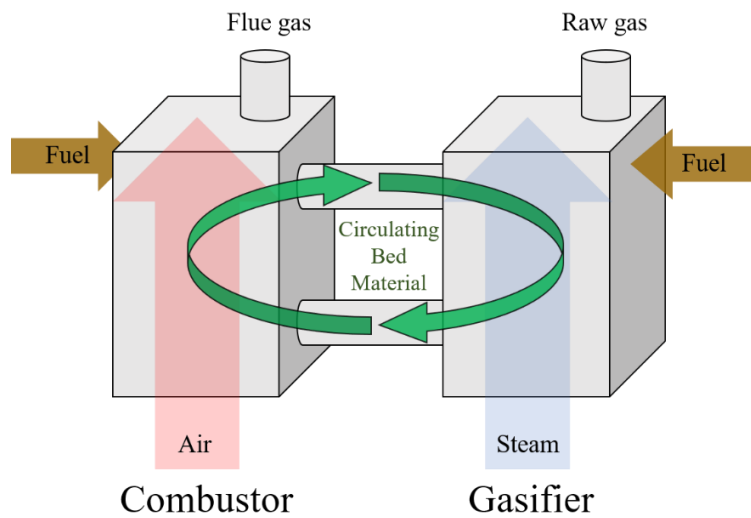
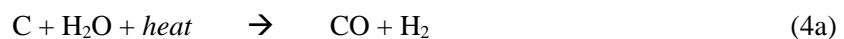


Figure 3: Simplified illustration of the working principle of a dual fluidized bed (DFB) gasifier. In the combustor, fuel is converted in an exothermic reaction. The heat is transported by fluidized bed material to the gasifier, where the endothermic gasification reaction converts the fuel to raw gas.



The produced raw gas contains mainly CO, CO₂, H₂, H₂O, CH₄ but also other hydrocarbons. This gas can be further purified for H₂ production or processed into a precursor for biofuel or other chemicals.^{6,25} An important parameter for the gas quality is the concentration and composition of the hydrocarbons (heavier than CH₄) in the produced gas. Especially the generation of tar, which is the group of larger polyaromatic hydrocarbons, (such as benzene, toluene and naphthalene) poses a problem to the gasification process.^{26,27} The tar released during the gasification process tends to condensate on downstream equipment, where it causes problems such as clogging which often requires unplanned shut-downs of the process.^{28,29} Furthermore, as chemical energy is stored in the bonds, tar represents a loss of energy in the raw gas. The formation of tar has therefore been identified as the most critical problem during biomass gasification.^{25,28-}

³¹ While a number of different materials can be used as fluidized bed materials, major research efforts have been made to minimize the formation of tar, where the application of catalytically active bed material has proven to be an effective strategy.^{27,32-35} Several naturally occurring minerals have been tested as bed material, such as quartz, olivine, dolomite, feldspar, bauxite, ilmenite, as well as mixtures of them.^{19,33-38}

3. Materials and Material Interactions

While the majority of the interactions within the fluidized system happen between gas streams and solid materials, most of the gases eventually leave the reactors and are processed by downstream equipment. The material that remains is the solid fraction which consists of the bed material and the fuel ash. As a result of the high temperatures applied during thermal conversion, bed material and fuel ash interact with each other, which impacts the behavior of the bed material in various ways. These interactions are also possible to be influenced by the use of additives.

3.1. Bed Materials

In order for the bed material to sustain the process, it needs to withstand thermal and mechanical stresses which are associated with the application. During the process, loss of material due to attrition (mechanical stress) cannot be completely avoided. This is why economic factors such as availability and low disposal costs which are connected to the environmental impact of the bed material, need also to be taken into account when selecting bed material.³⁹ Lastly, interactions with the fuel ash can alter the characteristics of the bed material and need to be taken into consideration when selecting a material. Over the course of this work, material interactions were investigated on several different naturally occurring minerals which were applied as bed materials – quartz, olivine, feldspar, and ilmenite.

The majority of the mineral matter found in the earth's crust are silicate-based minerals. As these minerals are abundant and cheap and at the same time attrition resistant, they present suitable candidates for application as bed material.

Quartz (SiO_2) is commonly employed as bed material, due to its mechanical stability and low cost. One important property of quartz is its resistance to chemical weathering which facilitates its application as bed material. However, interactions of quartz sand with ash-derived potassium cause agglomeration which leads to defluidization of the material.

Olivine [$(\text{Mg}, \text{Fe})_2\text{SiO}_4$] can be used as an alternative bed material which is resistant towards agglomeration. Olivine has even shown to be catalytically active towards tar removal when calcined prior to its application as bed material.^{40,41} However, the content of environmentally harmful metals, i.e., Ni and Cr(VI), complicates the disposal of spent material.

Lately, alkali-feldspar [$(\text{K}, \text{Na})\text{AlSi}_3\text{O}_8$] has been tested as a bed material and shown promising behavior.^{38,42} Feldspar is one of the most abundant minerals in earth's crust and therefore cheap and readily available. Feldspar is more vulnerable to chemical weathering and therefore seldom available as sand. Instead, the mineral is mined and separated from rocks consisting of several different minerals. Besides K, Na, Al, and Si, a common cation found in feldspar is Ca.

For oxygen carrier aided combustion, the commonly employed mineral is ilmenite (FeTiO_3) where Fe functions as the transition metal alternating between Fe^{2+} and Fe^{3+} to transport oxygen. As ilmenite is a naturally occurring mineral, it is cheaper than synthetically produced oxygen carriers. Ilmenite is usually utilized as a raw material for pigment production. It is available as both sand ilmenite, and as rock ilmenite, which is crushed to the desired particle size.

3.2. Fuel Ash

Ash is the inorganic fraction of the fuel which remains in the reactor after thermal conversion. Ash usually consists of oxides of mainly Si, Ca, K, P, Al, Mg, Fe, S, Na, Mn, and Ti. However, this list is not complete. Elements found in the ash can be both resulting from a biological compound of the plant-derived biomass and thereby incorporated into the plant/biomass structure (for example phytoliths which consist of amorphous silica,⁴³ or calcium oxalate⁴⁴), and/or mineral matter which is included as contaminants within the fuel.

For woody biomass, the most abundant ash elements are calcium, silicon and potassium, whereas herbaceous biomass (grasses and straws) contain more silicon and potassium than woody biomass.⁴⁵

Bark usually has a higher ash concentration than stem wood and consists mostly of calcium and silicon.⁴⁵ The high concentration of Ca in the ash can be explained by the presence of Ca-oxalate crystals which are commonly found in bark.^{46,47}

The ash fraction of animal manures differs from plant-derived biomass most notably in their high concentration of phosphorus.⁴⁵ The inclusion of bedding material (e.g., straw) in manure causes high concentrations of potassium and silicon. Manures commonly contain high moisture contents which decreases their calorific value when utilized as fuel.

Generally, the ash compositions of the fuels depend heavily on the applied handling and preparation methods which can be especially impactful during the utilization of waste streams. For example, during the acquisition of biomass, contamination can be introduced by the soil. The ash composition of waste streams is furthermore dependent on changes in the recycling or separation techniques which are applied prior to thermal conversion. Thus, fuels even of the same type can vary substantially in their content. The fuel compositions are provided in detail in Chapter 4.2 for the specific fuels which were used during this work.

3.3. Interactions

Interactions occur between the fuel ash elements and bed material during fluidized bed conversion, which influence the properties of the bed material. The interactions can evoke changes in the bed material which can be both detrimental and beneficial. Depending on the ash content and composition, regular or unplanned shutdowns of the reactors might be required to remove the accumulated ash. Alternatively, accumulation of ash can improve some of the properties of the utilized bed material. Some of the possible results of the interactions are described in the following sections.

3.3.1. Alkali Capture

Plant-derived biomass usually contains significant amounts of alkali metals, especially potassium. Material degradation caused by alkali metals released during combustion is a known phenomenon in the field of high-temperature corrosion. This problem can be alleviated if the bed material can form stable compounds with alkali metals which reduces their potential to contribute to corrosion. An example of a bed material which can participate in alkali capture is ilmenite (FeTiO_3). Investigations on ilmenite used as bed material for biomass combustion have shown the formation of $\text{KTi}_8\text{O}_{16}$.⁴⁸ Furthermore, chemical analysis revealed the presence of potassium inside the core of the ilmenite particles, where its interaction with the metallic

surfaces of the reactors is unlikely. Similar observations are commonly made with quartz (SiO_2). The interaction of quartz bed material with a fuel containing potassium leads to the formation of a layer containing potassium and silicon. Compared to, for example, olivine, quartz can thereby effectively remove potassium from the environment and mitigate corrosion.⁴⁹ However, the alkali capture capacity of quartz is limited and more importantly, the formed K-silicates exhibit a low melting temperature and exist in a molten state at the temperatures usually applied for thermal conversion. These molten K-silicates are sticky and ultimately lead to agglomeration of the bed material. Unlike quartz, silicate and low-melting compounds have not been detected in the case of ilmenite.

3.3.2. Agglomeration

Agglomeration describes the process of bed material particles sticking together to larger clusters. Agglomerate formation hampers bed pressure and can in the worst case lead to defluidization of the bed material. The severity of agglomeration related problems depends on the choice of bed material, the composition of biomass ash and the interactions between the bed material and the formed ash. In the literature, three different mechanisms are described causing agglomeration of bed material, which are schematically shown in Figure 4.⁵⁰⁻⁵³

- Agglomeration caused by melt deposition (Figure 4a). Agglomeration caused by melt deposition is typical for biomass which is inherently rich in potassium and silicon. Biomass rich in potassium and silicon can therefore lead to agglomeration almost regardless of the bed material applied.
- Agglomeration caused by coating formation (Figure 4b). If on the other hand, the concentration of silicon in the biomass is low, but the potassium concentration is high, the interaction with the bed material has to be taken into consideration. Potassium can be released from the biomass as gaseous KOH which can interact with the bed material, following the mechanism shown in Figure 4b. The interaction of $\text{KOH}_{(g)}$ with the bed material can lead to the formation of low melting K-silicates that results in a coating around the particles.
- Agglomeration caused by ash that is deposited as a coating layer around the bed particles (Figure 4c). Similar to the interaction with the gas phase, interactions of the coating layer with the bed particle can lead to a layer of low melting phases. The difference of the previous mechanism is the formation of a molten phase due to interactions in the solid state.

Collision between two particles with a formed molten surface layer can cause the particles to stick together which ultimately leads to the formation of larger particle agglomerates that cannot be further fluidized by the gas stream.⁵⁰⁻⁵²

Alkali-silicates which exhibit low melting temperatures have generally been identified as the decisive species to cause agglomeration.^{54,55} This can be explained from a thermodynamic point of view as shown in Figure 5. While pure quartz exhibits a melting point of close to 2000 K, any addition of K_2O (or Na_2O) leads to lowering of the melting point. Thus, especially the combination of quartz sand and biomass yielding ash rich in alkali metals, has been reported to cause defluidization of the bed material.^{50,54-59} Therefore, alternative bed materials have been successfully applied, which are significantly less vulnerable to agglomeration than quartz, such as olivine, feldspar and dolomite.^{38,54,56,59} Generally, the knowledge of the

interaction between biomass ash and bed material can aid to choose suitable combinations of bed material, fuel, and additives to prevent or delay agglomeration related problems.

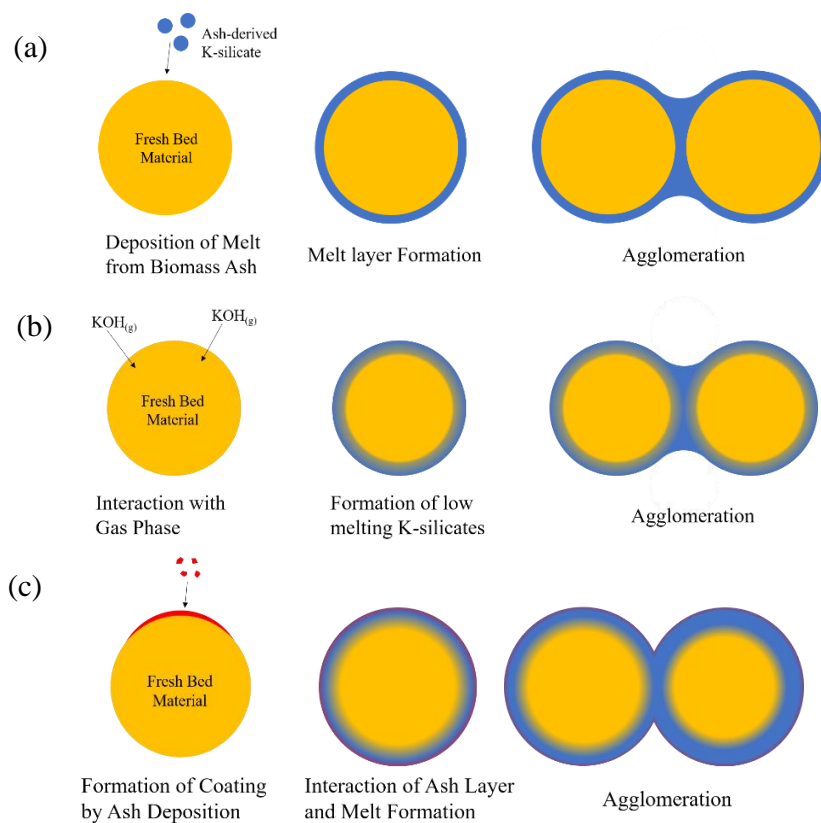


Figure 4: Schematic depiction of the main agglomeration mechanisms observed as a result of bed material-ash interactions. (a) agglomeration caused by melt deposition, (b) agglomeration caused by melt formation due to interaction with gaseous KOH, (c) agglomeration caused by the interaction of the coating layer with the bed particle.

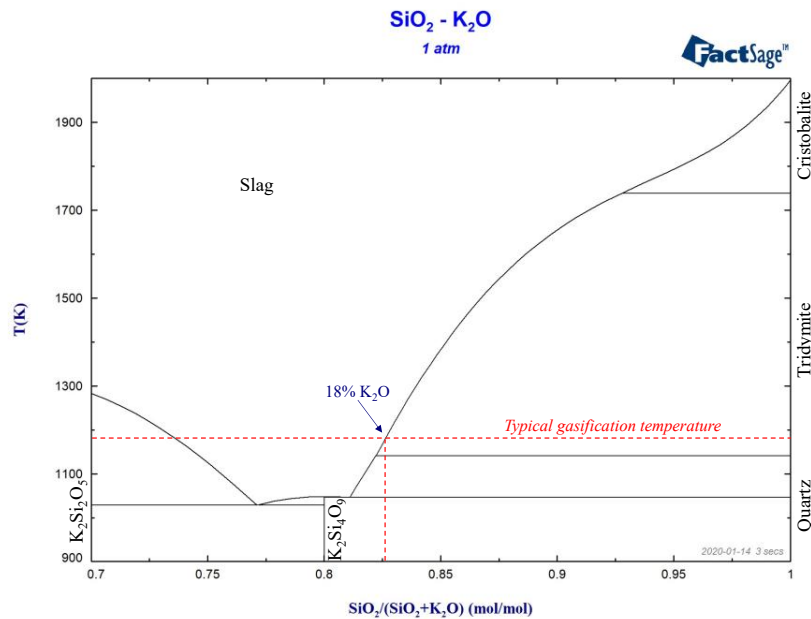


Figure 5: Phase diagram of SiO_2 and K_2O of the SiO_2 -rich side at 1 atm. For low concentrations of K_2O , the region corresponds to tridymite and slag (melt). The share of melt increases with increasing K_2O concentration until pure melt is expected at around 18 % K_2O .⁶⁰

3.3.3. Catalytic Activity

Formation of tar is a common problem associated with biomass gasification. This problem can be alleviated by ash-derived species accumulated on the surface of the bed material particles. The formed layer containing ash-derived species, has been shown to decrease the concentration of tar in the product gas.³⁵ Ash elements commonly associated with catalytic activity towards tar removal, are iron, potassium and calcium. During combustion of biomass, these elements are released (among others) and form a coating layer around the bed material. The thickness of the layer increases at longer retention times of the bed material in the reactors, which is accompanied by an increase in activity towards tar removal of the bed material. However, for quartz, the accumulation of potassium causes agglomeration which necessitates frequent bed material replacement. Due to the increased risk for agglomerate formation with time, prolonged retention time of the quartz particles in the gasification system, which would be necessary for the activation, is therefore not practical.

Alternative bed materials, such as olivine can obtain catalytic activity towards tar reduction without the tendency to participate in agglomeration.^{28,33,61} It was observed that the activity of olivine could be improved by calcination of the particles prior to application, an effect that was explained by accumulation of iron oxide on the particles' surface.³⁶ The interaction of biomass ash with olivine was shown to further enhance the activity of the material. By prolonged retention time (aging) of the particles in the gasification system, the tar concentration in the product gas could be gradually decreased.⁶² The increased activity with time spent in the gasifier of the olivine particles could be explained by the formation of a layer rich in ash derived elements, such as potassium and calcium. The mechanism of layer formation and its effect on the

tar concentration has been the topic of extensive research.^{32,63–68} It was found that the interaction of ash elements with olivine does not lead to agglomeration associated problems (as was previously observed in the case of quartz sand), as the uptake of potassium into the olivine structure is minor compared to that in quartz.⁶⁸ Instead of the formation of low-temperature melting potassium silicates, the formation of calcium silicate by a replacement of magnesium and iron from the olivine lattice was reported.⁶⁸ Furthermore, the location of potassium was found to be decisive for the activity of the material. When located close to the surface, potassium could enhance the activity, but after migration towards the particles' cores, it was no longer available at the surface and the material became deactivated.⁶⁷

Similarly to olivine, alkali-feldspar has been successfully applied as bed material for biomass gasification.^{38,42,69} It has been shown that the interaction of feldspar with biomass ash does not cause major problems with agglomeration – instead, activation (as found for olivine) was reported.^{42,69} Again, this was associated with the formation of layers rich in ash elements.^{42,70} In a study on K-feldspar used for combustion of woody biomass, the mechanism for the layer formation was described as a substitution of K^+ by ash-derived Ca^{2+} -ions. The accumulation of calcium (apart from activating the bed material) can also become problematic in the case of feldspar, as the formation of cracks was observed after prolonged retention time of the particles. The reaction with alkaline species on the other hand, was found to be low.⁷⁰

3.3.4. Oxygen Carrying

Besides an increase in catalytic activity towards tar, prolonged interaction of the bed material with biomass ash can be accompanied by the development of an oxygen carrying capacity.

As a result of the different oxygen partial pressures inside the gasifier compared to the combustor, there are several chemical elements present in the reactors that are capable of changing their oxidation state between the two reactors. This allows transport of oxygen from the combustor to the gasifier, which results in a decrease in calorific value of the product gas, as it enables the conversion of H_2 and CO to H_2O and CO_2 respectively. Hence, for dual fluidized bed gasification, the development of an oxygen carrying capacity is usually an unwanted side-effect of the interactions between bed material and ash. Ash elements commonly suggested to contribute to the oxygen carrying capacity are transition metals (mainly iron and manganese) and sulfur.^{42,71}

Conversely, in oxygen carrier aided combustion (OCAC), the oxygen carrying effect of the bed material is utilized to enhance the process performance. In an OCAC reactor, different oxygen partial pressures are present within one reactor and the bed material is used as an oxygen carrier, to improve the oxygen distribution. In this thesis, the Fe-based mineral ilmenite was investigated as an oxygen carrier, in which Fe can alternate between the two oxidation states Fe^{2+}/Fe^{3+} and thereby transport oxygen throughout the reactor. Processes utilizing ilmenite have shown that an activation of ilmenite occurs during prolonged residence time which was explained by a migration of Fe towards the surface of the particles.^{72–76} However, interactions with the fuel ash can result in ash layer build-up that can cover the Fe-rich layer and thereby decrease the oxygen carrying ability.^{77,78} Alternatively, a dilution of the active ilmenite particles with inorganic material introduced by the fuel could occur, which decreases the overall oxygen carrying capacity of the bed material. Therefore, a possible separation of the two fractions is seen as beneficial to reduce the requirement of fresh material addition.

3.4. Material Handling

Accumulation of ash elements changes the composition of the bed material which can deteriorate its properties. Addition of fresh bed material is therefore required to compensate for deactivation, fragmentation and subsequent entrainment, as well as defluidization. This addition of fresh material is associated with costs, which can be a significant operational cost when comparably expensive bed materials are utilized (i.e., ilmenite). Furthermore, disposal of used bed material represents a waste stream that requires handling. Thus, to increase the sustainability and circularity of the process and to avoid landfilling of large volumes of used material, separation and reuse of still active material as well as possible uses of the inactive material need to be investigated.

3.4.1. Magnetic Properties

One property that can be utilized for separating the material with remaining activity is the magnetic susceptibility of the material. Minerals containing elements with magnetic moments exhibit magnetic susceptibility and can therefore be attracted and separated by an external magnetic field. A magnetic moment is caused by unpaired electrons, which is a commonly encountered property of transition metals. Among the minerals commonly utilized as bed materials, only ilmenite exhibits a positive magnetic susceptibility (see Table 1), caused by the Fe^{2+} cations. The magnetic susceptibility of ilmenite is therefore higher than ash-derived phases (alkali and alkaline earth metal oxides and silicates) and common fuel contaminants (such as quartz and feldspar). Ilmenite particles are therefore attracted stronger by an external magnetic field and can be separated from ash phases or other contaminants. This enables the possibility to recycle the magnetic fraction of used ilmenite, which contains a higher concentration of iron and accordingly can exhibit higher oxygen carrying capacity than the non-magnetic fraction or mixed fraction.⁷⁷

Table 1: Mass specific magnetic susceptibilities of minerals which were commonly found with X-ray diffraction of aged ilmenite.⁷⁹

Mineral	Chemical Formula	Mass specific magnetic susceptibility ($10^{-8} \text{ m}^3/\text{kg}$)
Quartz	SiO_2	-0.5 – -0.6
Orthoclase (K-feldspar)	KAlSi_3O_8	-0.49 – -0.67
Forsterite	Mg_2SiO_4	-0.39
Fayalite	Fe_2SiO_4	130
Ilmenite	FeTiO_3	46 – 80000
Hematite	Fe_2O_3	10 – 760
Magnetite	Fe_3O_4	20000 – 110000

3.4.2. Ash Recovery

Separation and reuse of used material offers one option of ash recovery, which decreases the required input of fresh bed material and the costs associated with disposal. However, after the bed material has been used for a long time, significant amounts of ash accumulate within the solid inventory and the mechanical properties of the bed deteriorate. Ash elements building a layer on the surface of oxygen carriers can also

diminish their oxygen carrying capacity. Furthermore, material loss due to entrainment with the gas flow causes the deposition of fines inside downstream filters. These cases represent a solid waste stream that requires handling which can be complicated depending on the composition of both bed material and fuel ash. On the other hand, biomass ash usually contains high concentrations of calcium and potassium which are important plant nutrients. This offers the possibility of used bed material to be applied as fertilizers. Especially ash obtained from thermal conversion of animal manure can be interesting for nutrient recovery, due to its high content of phosphorus. Thermal conversion can therefore even function as a method to preconcentrate nutrients in the ash fraction.

Olivine is a mineral which commonly contains low concentrations of heavy metals (nickel and chromium). As these are toxic species, used olivine requires special attention during landfilling and its possible application as a fertilizer is limited. As opposed to this, feldspar is free of heavy metals and its applicability for nutrient recovery is only dependent on the fuel ash composition. Thus, utilizing feldspar as a bed material for thermal conversion of animal manure offers the possibility to obtain material which can function as a fertilizer, or a precursor for fertilizer production.

3.5. Additives

Besides the fuel ash that is added to the bed inventory, different additives can be utilized in order to manage properties of the bed during the use of various fuel. For example, for fuel and bed combinations which are prone to experience agglomeration, the objective of the addition of additives is to capture the species which lead to agglomeration. As described previously, agglomeration is usually encountered during the interaction of alkali-metals with quartz bed material and additives can be utilized which react with potassium to form phases which exhibit a higher melting temperature than K-silicates. This was successfully demonstrated with the addition of kaolin [$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$] or Al_2O_3 as a substance to bind alkali-metals released from the ash. Kaolin additions managed to avoid the formation of low-melting alkali-silicates, and alkali-aluminosilicates formed instead which exhibit a higher melting point.^{58,80-82} Alternatively, addition of calcite (CaCO_3) could reduce the formation of K-silicates and thereby lower the tendency for agglomeration.⁸³

Furthermore, additives can be added to achieve an increase in the catalytic activity of the bed material. As the activity is influenced by the presence of the ash elements potassium and calcium, recirculation of ash can be implemented to increase the concentration of potassium and calcium in the reactor. Furthermore, the additions of CaCO_3 or K_2CO_3 have successfully achieved increased activation of the bed material and decreased the levels of tar in the product gas.^{63,67,84,85}

3.6. Goal

The interplay of ash elements and bed materials changes the characteristics of the bed material, which can be advantageous or disadvantageous for the process. Investigating the results of different combinations of bed materials, fuels, and additives can therefore illustrate the *challenges* (e.g., agglomeration or development of an oxygen carrying ability) and *opportunities* (e.g., alkali capture or catalytic activity) which exist for the selected combinations. Lastly, handling of bed material which has been used for prolonged time, requires knowledge about its properties and composition. This knowledge can aid to

decrease disposal of used material, increase the lifetime of the bed material in the reactor, and increase the circularity of the process.

The goal of this work was thus to investigate the behavior of a selection of promising bed materials which were utilized in several experimental campaigns. Thereby, insight is gained about the interactions between bed material and ash, which elucidates the challenges and opportunities which exist for each combination of bed material and fuel.

4. Experimental Campaigns

To enable the investigation of the interaction between different bed materials and ash, bed material samples were acquired from fluidized bed processes with varying conditions (see Table 2). The bed materials utilized were quartz, olivine, alkali-feldspar, K-feldspar, and ilmenite. Experiments were conducted with woody biomass and waste streams, which are fundamentally different regarding ash composition. The results from the semi-industrial unit were complemented by samples obtained from exposures conducted in laboratory conditions.

Table 2: Overview of the bed material/fuel combinations investigated in the present thesis and the respective processes.

Publication	Bed Material	Fuels / Salts	Process	Exposure Time
1	Quartz Alkali-feldspar Olivine	Wood Chips Wood Pellets	DFB Gasification	3 Days
2	Olivine	Wood Chips Wood Pellets	DFB Gasification	1, 2, 4 Days
3	Olivine Alkali-feldspar	Wood Chips Wood Pellets	DFB Gasification	3 Days
4	Olivine	Wood Chips Wood Pellets	DFB Gasification	1, 2, 4 Days
	Olivine Stones	CaCO ₃ , CaCl ₂ K ₂ SO ₄ , K ₂ CO ₃	Laboratory Exposure	1 Day
5	Alkali-feldspar	Wood Chips Wood Pellets	DFB Gasification	1-6 Days
6	Alkali-feldspar	Wood Chips Wood Pellets	DFB Gasification	1-6 Days
7	Alkali-feldspar	CaCl ₂ K ₂ CO ₃ , KOH	Laboratory Exposure	1 Day
8	K-feldspar	Bark Chicken Manure Mixture	BFB Combustion	4 h, 8 h
	K-feldspar	CaHPO ₄ , Mg ₃ (PO ₄) ₂ K ₃ PO ₄ , Na ₃ PO ₄	Laboratory Exposure	1 Day
9	Olivine	Wood Chips ASR	Chemical-Looping Gasification	2 weeks
10	Olivine Alkali-feldspar	Wood Chips Wood Pellets	DFB Gasification	3 Days
11	Ilmenite	Recycled waste wood	Oxygen Carrier Aided Combustion	2 weeks

4.1. Bed Materials

The composition of the bed materials utilized for the different processes is shown in Table 3. The quartz sand that is utilized in the Chalmers DFB gasifier is a high-grade sand which means it exhibits a low content of Fe. To avoid the problems associated with agglomeration of quartz, experiments were conducted with Norwegian olivine. The olivine utilized is a mixture of ~90% forsterite (Mg_2SiO_4) and ~10 % fayalite (Fe_2SiO_4) and is mined as a rock. Due to the content of Ni and Cr in olivine, special deposition of the waste material is required, which is why the utilization of alkali-feldspar was investigated. The used alkali-feldspar originates from Finland and is obtained from pegmatite rock. It consists of 48% K-feldspar, 40% Na-feldspar, and minor amounts of Ca-feldspar and quartz (6% each). The K-feldspar utilized for bubbling fluidized bed (BFB) combustion was obtained from a kaolin deposit and contains 87% K-feldspar, 7% Na-feldspar, 4% quartz, and 2% clay. The oxygen carrier ilmenite which was used for oxygen carrier aided combustion (OCAC) was mined from rock in Norway and crushed to the desired particle size. It should be mentioned that common contaminant in the fresh ilmenite is feldspar, which is to the largest extent removed prior to utilization. As can be seen in Table 3, minor contents of K, Na, Al, and Si remain, representing roughly 2% feldspar in the fresh material.

Table 3: Elemental composition (mol %) of the bed materials studied in the present thesis, as provided by the material suppliers on an oxygen-free basis.

Material	Quartz	Olivine	Alkali-Feldspar	K-feldspar	Ilmenite
Application	Chalmers DFB Gasifier	Chalmers DFB Gasifier	Chalmers DFB Gasifier	BFB Combustion	OCAC
Na			7.6	1.9	0.3
Mg		60.5	0.1		6.1
Al	0.2	0.4	20.1	24.9	1.0
Si	99.8	34.1	61.3	50.6	2.7
P			0.1	0.1	
K			9.7	22.2	0.1
Ca			1.2		0.5
Ti					40.5
Cr		0.2			
Fe		4.6	0.1		48.5
Ni		0.2			
Ba				0.2	
Mn					0.2

4.2. Fuels

The fuels used during the course of this work were woody biomass (chips, pellets, and bark), chicken manure and automotive shredder residue (ASR). The ash fractions and compositions of the different fuels are shown in Table 4 and Figure 6.

Table 4: Ash fraction of the fuels used for this study in weight percent (dry fuel basis). ASR = Automotive Shredder Residue.

Fuel	Wood Chips	Wood Pellets	Bark	Chicken Manure	ASR
Ash % dry basis	0.5	0.4	8.1	25.4	47

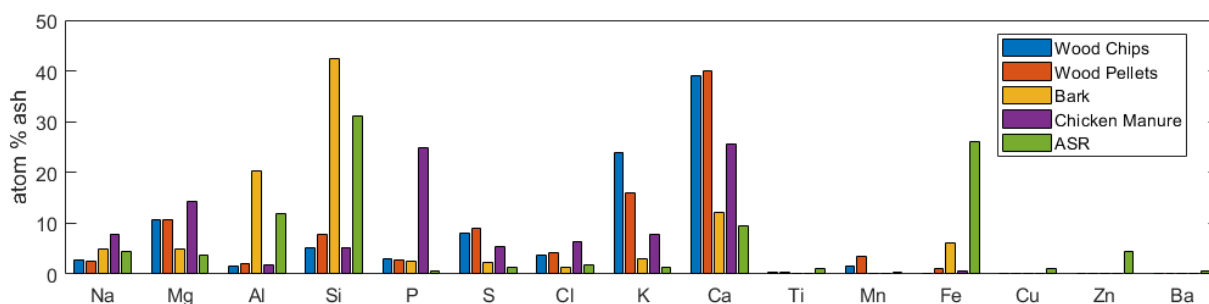


Figure 6: Elemental ash composition of the fuels investigated in the present thesis (in atom % on an O-free basis.). ASR = Automotive Shredder Residue.

Wood chips and wood pellets derived from softwood (spruce) were utilized as fuel in the Chalmers DFB gasifier. The ash fractions of the two fuels resembled each other and both were relatively ash-lean [around 0.5 weight percent (wt. %)]. The most abundant ash elements were calcium and potassium. Due to the low ash content in the fuel, they represent relatively ‘clean’ fuels.

Compared to wood chips and pellets, bark, while also being derived woody biomass, differs in both ash content (around 8 wt. %) and ash composition. The most abundant elements in bark are silicon, aluminum, and a lower fraction of calcium. Bark is a residual biogenic fuel, and its application has the potential to increase the economic feasibility of the utilization of biomass. Due to the higher fraction of ash, bark could be more problematic to handle, as frequent bed material replacement or ash removal might be necessary.

Another residual fuel tested in the present work is chicken manure which contains a large fraction of ash (25 wt. %). The main elements in chicken manure ash are calcium and phosphorus. The phosphorus contained in chicken manure ash is of special interest during its application as fuel, as phosphorus concentration in the ash could potentially be relevant for ash recycling. However, the high ash content of chicken manure and its difference in chemical composition, significantly alters the mechanism of interaction compared to the relatively ash lean woody biomass. This could be potentially associated with operating problems.

Lastly, automotive shredded residue (ASR) describes the material that is obtained during the recycling of end-of-life vehicles (ELV) at the end of the recycling process. ASR consists of various materials, such as plastic, metal, rubber, foam, and glass. Its exact composition depends on ELV model as well as the techniques applied for shredding and separation. Thus, ASR is a highly heterogeneous fuel, which makes the use of fluidized bed for its thermal conversion attractive. The ash content of ASR is almost 50 wt. %

and contains a high concentration of iron. The oxygen-carrying effect of iron can be exploited by utilizing ASR as a fuel for chemical-looping gasification.

4.3. DFB Gasification

Gasification experiments were conducted on a semi-industrial scale in the Chalmers dual fluidized bed (DFB) gasifier. The system consists of a 12 MW_{th} circulating fluidized bed (CFB) furnace and a 2-4 MW_{th} bubbling fluidized bed (BFB) gasifier. A schematic representation of the plant is shown in Figure 7. The bed material is heated up in the furnace (1) where wood chips are combusted with air used as fluidization gas. The heated bed material particles from the combustor are separated from the fine fraction in the gas by the cyclone (4) and transported by the particle distributor (9) to the gasifier (11). The gasifier has a separate fuel feeding system, where wood pellets are used as feedstock. From the gasifier, bed material and remaining unconverted char are transported back to the furnace. To avoid gas leakage, loop seals, which are fluidized with steam, are placed in between the cyclone and the gasifier, and between the gasifier and the furnace. A detailed description of the system can be found elsewhere.²²

The bed temperature is typically between 800 and 850 °C. Quartz, olivine, and alkali-feldspar were utilized as bed materials, and their catalytic activity was investigated by monitoring the tar concentration in the syngas sampled from the gasifier. Around 4 tons of bed material are circulating in the whole system. The fuel feeding rates were 2000 kg/h to the combustor (wood chips) and 300 kg/h (wood pellets) to the gasifier.

A set of samples were investigated which were obtained from different experimental campaigns conducted in the Chalmers DFB gasifier (see Table 2). In paper I, a comparison is conducted of quartz, olivine, and alkali-feldspar which were utilized as bed material for the same exposure time of three days. At the point of extraction, the bed material is in an ‘active’ state, meaning the tar concentration in the syngas is significantly lower than at the start of the process. Except for additions of ammonium sulfate to the campaign conducted with olivine, no further significant additions or replacements were done, in order to ensure the specified age of the particles. Paper III investigates the same materials (except for quartz) and provides further detail on the surface layer of the particles, which is most likely the origin of the observed catalytic activity.

Papers II and IV investigate an aging experiment of olivine bed material, where particles were extracted after one, two, and four days exposure time in the system. The time-resolved formation of the ash layer is investigated in these studies. Similarly, papers V and VI investigate aging experiment where the difference is the applied bed material, which is alkali-feldspar. Here, samples were extracted at five different points of time within six days.

Lastly, paper X investigates oxygen transport, tar yield, and catalytic activity towards the water-gas-shift reaction from several different experimental campaigns utilizing olivine and feldspar as bed material.

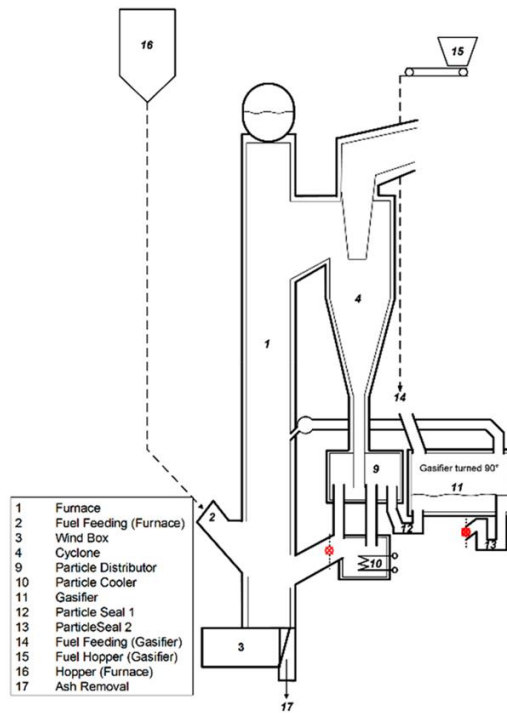


Figure 7: Schematic representation of the Chalmers Dual Fluidized Bed (DFB) gasifier with numbers indicating the different parts of the system. The samples discussed within this thesis were extracted from the particle seals (shown as 12 and 13 in the figure).²²

4.4. Chemical-Looping Gasification

Chemical looping gasification was investigated in the Chalmers DFB gasifier by changing the fuel that was fed to the gasifier to automotive shredder residue (ASR), while maintaining the same fuel feeding rate as previously (300 kg/h). The temperature was between 830 °C in the gasifier and 900 °C in the combustor. The bed material applied in this study was olivine, which had previously interacted with woody biomass for one week (see Figure 8). The high amount of ash which exhibits significant oxygen carrying enabled the utilization of the system as a chemical-looping gasification process. The samples obtained from this campaign are analyzed in paper IX. At the start of the campaign, the particles had acquired an ash layer composed of woody biomass ash-derived elements. It should be noted that the fuel feeding of ASR to the gasifier was interrupted during weekends. Samples for investigation were extracted after one, four, seven and 13 days, according to the schematic shown in Figure 8.

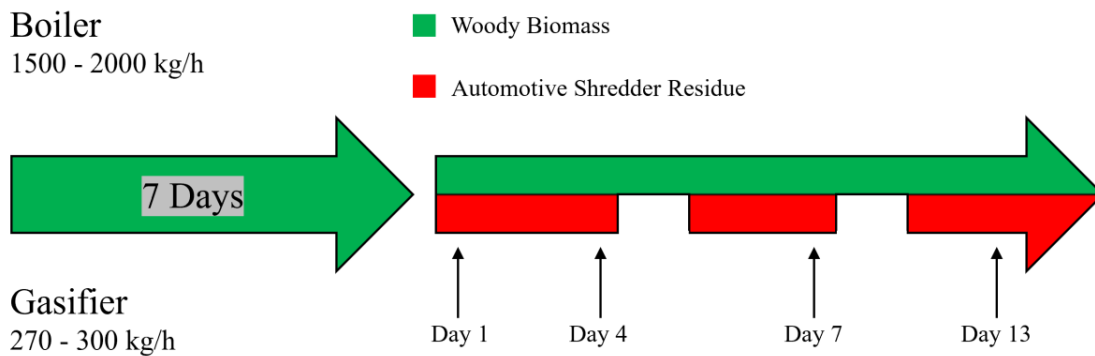


Figure 8: Overview of the exposure history of the samples from the chemical looping gasification study using automotive shredder residues (ASR) as fuel and olivine as bed material. Before the start of the addition of ASR to the gasifier, the particles were exposed to woody biomass for 7 days. The gasifier was fed with ASR for about 6 hours during the days of operation, which was interrupted during weekends. The boiler was fed with woody biomass throughout the entire exposure period.

4.5. Bubbling Fluidized Bed Combustion

Bubbling fluidized bed combustion of biogenic wastes was investigated in a bench-scale 5 kW fluidized bed reactor, schematically represented in Figure 9. 540 g K-feldspar was utilized as bed material which was fluidized with primary air. Secondary air was introduced above the bed. The furnace was electrically heated to ensure a bed temperature between 790 and 810 °C. In this campaign, the influence of residual biogenic fuels was investigated, for which bark, chicken manure, and their mixture was used as fuel. The fuel feeding rate was 0.7 kg/h. The goal was to conduct combustion continuously for 40 h. However, due to the high ash content of chicken manure, the experiment had to be interrupted after 11 h. Hence, the early layer formation is investigated in paper VIII, i.e., samples were analyzed which had been exposed for four and eight hours accordingly.

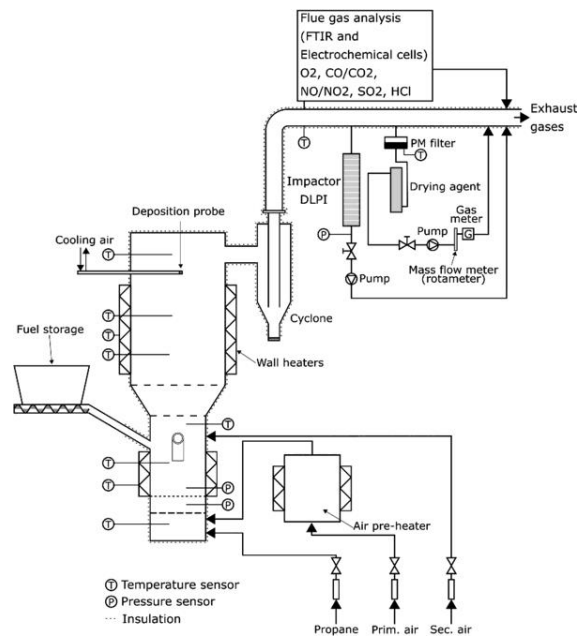


Figure 9: Schematic representation of the 5 kW bubbling fluidized bed used for the combustion experiments with indicated temperature and pressure measurement points.⁸⁶

4.6. Oxygen Carrier Aided Combustion

Norwegian rock ilmenite was used as an oxygen carrier in an industrial oxygen carrier aided combustion (OCAC) process with a nominal capacity of 115 MW_{th}, with wood chips and recycled waste wood as fuel. Around 60 tons of bed material were utilized in the system and the average temperature in the bed was 850 °C. The reactor was operated with quartz bed material which was replaced stepwise by ilmenite (2-15 t/day) in order to investigate the impact of an oxygen carrier on the efficiency of the process.

Due to the significant added cost of ilmenite in comparison to conventionally used quartz, an attempt was made to decrease the amount of fresh material that needs to be added. This was done by separating the used bed material in fractions of inert ash and active oxygen carriers by a magnet and investigating the possibility to recycle the magnetic fraction. To investigate this possibility, samples were extracted after one and two weeks exposure and the obtained material was separated by a magnetic drum into two fractions (see Figure 10). Paper XI evaluates the efficiency of the magnetic separation by investigating the material prior to the separation as well as both the material from magnetic and the non-magnetic fractions.

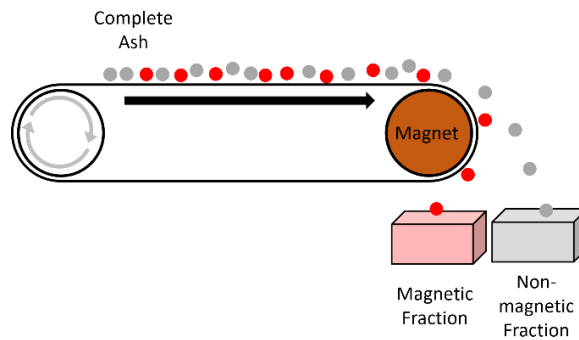


Figure 10: Schematic representation of the magnetic separation process conducted for the bed material acquired from the OCAC campaign using ilmenite as bed material and recycled waste wood as fuel.

4.7. Salt Exposures

Exposures were conducted under fixed bed conditions to investigate the interactions of chosen salts that mimic separate ash compounds with the bed materials. The purpose was to compare the interactions with salt exposures to those occurring between the bed material and biomass ash. Therefore, the selected salts were chosen based on the main ash compounds found in the biomass-derived ash, namely Ca, K, Mg and Na. The exposures were conducted in three different ways: 1) by placing the salt as a slurry onto olivine stones (as visualized in Figure 11a); 2) by placing the salt and the samples in separate crucibles to investigate interactions of gaseous ash compounds (Figure 11b); or 3) by placing the salt and samples in the same crucible in a box furnace (Figure 11c). The exposures and the respective salts utilized are summarized in Table 5. The different experimental setups were designed to investigate the interactions of bed material and salt in solid and gaseous state, in order to compare them with the interactions found on samples acquired from larger fluidized bed reactors.

Olivine stones were exposed together with a slurry of different Ca and K salts to mimic ash layer formation in controlled single ash compound fixed bed conditions. Furthermore, the reactivity of the utilized salts was assessed. Alkali-feldspar particles were exposed to salts by mixing the feldspar particles and the chosen salt in solid condition in a crucible. Salts which had shown sufficient reactivity in the experiment with olivine stones were utilized. The impact of KOH vapor was investigated as well by placing KOH adjacent to alkali-feldspar in a tubular furnace and transporting the KOH by an air flow. The influence of different alkali and alkaline earth metal phosphates was tested using the same fresh K-feldspar which had been used for the exposures with P-rich chicken manure.

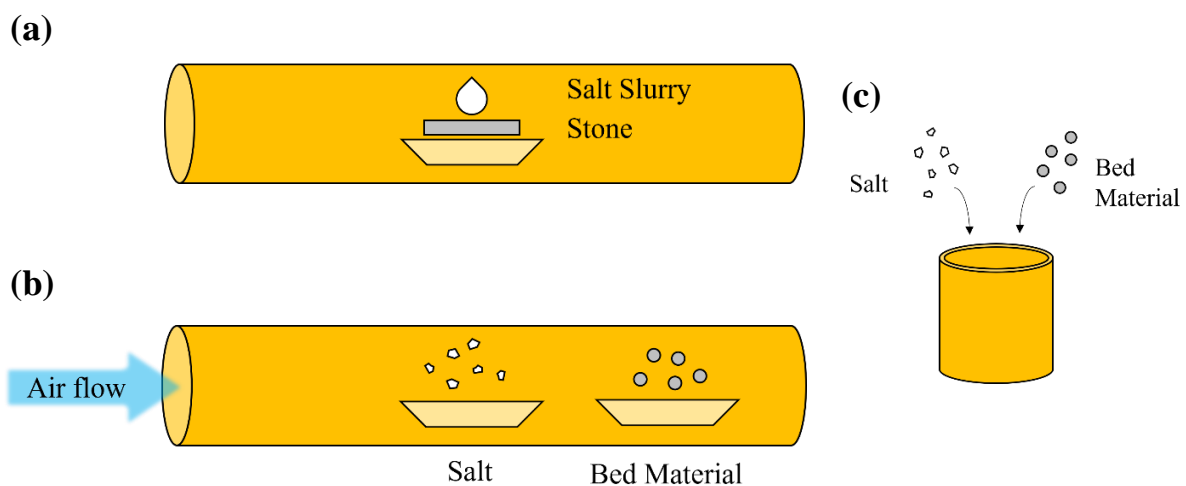


Figure 11: Schematic depiction of the exposures conducted at fixed bed conditions in the laboratory. (a) experiments where different salts were placed as a slurry onto olivine stones and exposed at 850 °C. (b) set-up of the tubular furnace where salt was placed in a separate crucible at 820 °C and the salt vapor was transported onto the bed material by air flow. (c) exposures conducted in box furnace, where the interactions of bed material particles with salt in direct contact at 820 or 830 °C were investigated.

Table 5: Summary of the exposures conducted in fixed bed conditions in laboratory to simulate the bed material-ash interactions using most abundant ash compounds. The used temperature interval for the experiments was based on the typical temperatures used in the semi-industrial exposures: 850 °C represents the approximate temperature in the combustor side of the Chalmers DFB gasifier, and 820 °C the temperature in the gasifier side. 830 °C is the temperature in the BFB combustion reactor used for the experiments with K-feldspar.

Paper	Material	Temperature	Furnace	Time	Salt
4	Olivine Stones	850 °C	Tube	24 hours	CaCO ₃ K ₂ CO ₃ CaCl ₂ K ₂ SO ₄
				48 hours	CaCO ₃ and K ₂ CO ₃ CaCl ₂ and K ₂ SO ₄
7	Alkali-feldspar	820 °C	Box	24 hours	CaCl ₂ K ₂ CO ₃
			Tube	24 hours	KOH
			Box and Tube	48 hours	CaCl ₂ and KOH
8	K-feldspar	830 °C	Box	24 hours	CaHPO ₄ Mg ₃ (PO ₄) ₂ K ₃ PO ₄ Na ₃ PO ₄

4.8. Batch Reactors

The oxygen carrying capacity of the bed material was investigated in a batch fluidized bed reactor. The fluidization gas was alternated between an oxidizing gas and a reducing gas. If the material exhibits oxygen carrying properties, it can pick up oxygen during the oxidizing step and release it in the reducing one. The reactor used for these experiments is shown schematically in Figure 12. It consists of a quartz glass tube with an inner diameter of 22 mm, and it is electrically heated to 850 °C. Around 15 grams of bed material was used for the tests which was placed on a porous plate in the reactor. For the experiments conducted during this work, the material was exposed to several cycles of oxidizing and reducing atmosphere. The oxygen carrying ability of the material was measured by the partial pressure of CO₂ which was released during the reduction step, and the difference in inlet and outlet O₂ during the oxidation step. The cycles consisted of several stages:

- Inert stage: N₂ for 300 s
- Oxidation stage: with 5% O₂ in N₂ for 600 s
- Inert stage: N₂ for 300 s
- Reduction stage: 50% CO in N₂ for 40 s, or 50% CO and 50% H₂ for 20 s

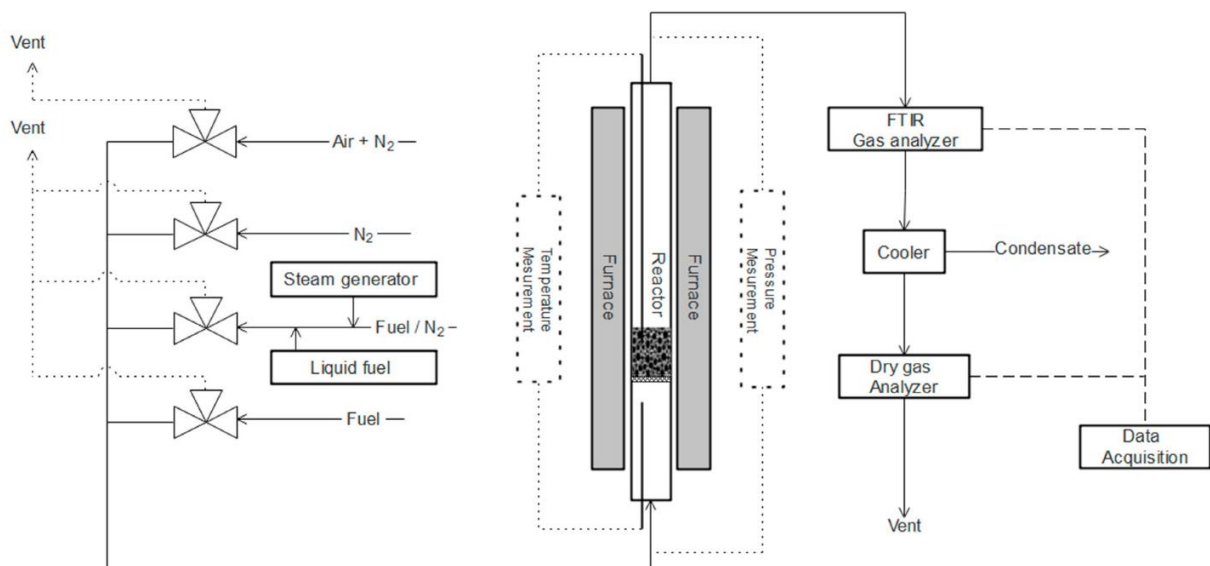


Figure 12: Schematic representation of the fluidized bed batch reactor system which was utilized for measuring the oxygen carrying ability of the bed materials. Adapted from Leion et al.⁷⁵

5. Analysis

Bed material samples were extracted from the previously listed campaigns and the obtained particles were characterized by a multitude of different techniques. It should be noted that several tons of bed material are typically used in the different industrial and semi-industrial processes which requires special considerations about the conclusions which can be drawn from a sample. The amount of material that is usually analyzed represents just a fraction of the entire bed inventory. Ensuring that a sample is representative is therefore crucial to draw conclusions applicable for the whole bed inventory. As both fresh bed material, as well as the used fuel are natural materials, they vary in composition and can therefore cause fluctuations in the samples. Since the information acquired by the techniques differs, they can be employed complementary to each other.

5.1. Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy

To analyze the influence of fuel ash and additives on the bed material, particles were investigated with a scanning electron microscope (SEM). The particles were mounted on a conductive carbon tape onto a SEM-stub and information about the morphology was acquired by recording micrographs. Furthermore, cross-sections of the particles were prepared which necessitated the immobilization of the bed material particles. This was achieved by two different methods.

In the first method, a mixture of epoxy resin and hardener was used for embedding the bed material particles. After curing, the samples could be ground and polished with SiC paper (until P2400). To avoid dissolution of the alkali salts during preparation, this was done without cooling agent. By this method, a great number of particles (several hundreds) could be prepared for analysis simultaneously which was useful for preliminary material analysis as well as for statistical analysis. This method is widely used within the field and gives a good understanding of the materials. However, when grinding material with different mechanical properties (i.e., particles and their layers), the mechanically weaker part gets ground quicker which can cause damage in the ash layer and thus hamper the analysis. Furthermore, by mechanical grinding one is limited in the final surface quality that can be achieved.

In order to overcome the enumerated limitations, a second sample preparation method was developed. Small amounts of sample particles were embedded between two silicon wafers with cyanoacrylate glue. After curing, the 'sandwich' was mounted in a broad ion beam (BIB) system. The process is schematically shown in Figure 13. The lower part of the sandwich was protected from the beam with a mask and only the topmost few millimeters were removed by the beam. Thereby, cross-sections of a small number of particles were created at the same time and a surface finish with a high quality was obtained. A direct comparison of the two sample preparation methods can be seen in Figure 14. The figure shows two olivine particles from the same sample which has been exposed to biomass ash for 24 hours in the Chalmers gasifier. From the image it is visible, that only by the second method (BIB milling), sufficient surface quality can be achieved that can be used for further analysis of the ash layer. This surface quality is especially important for the early layer formation, where the ash layer is too thin to be analyzed otherwise.

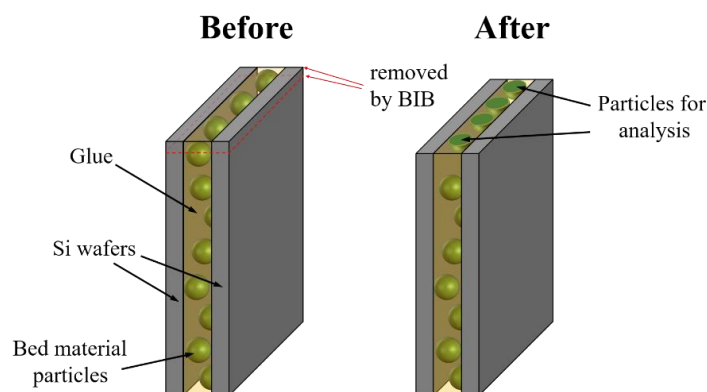


Figure 13: Schematic representation of the cross-section sample preparation method with broad ion beam (BIB) milling. The particles were embedded between two silicon wafers with cyanoacrylate glue and subsequently the topmost part was removed by BIB-milling. Thereby, cross-sections of a few particles were created.

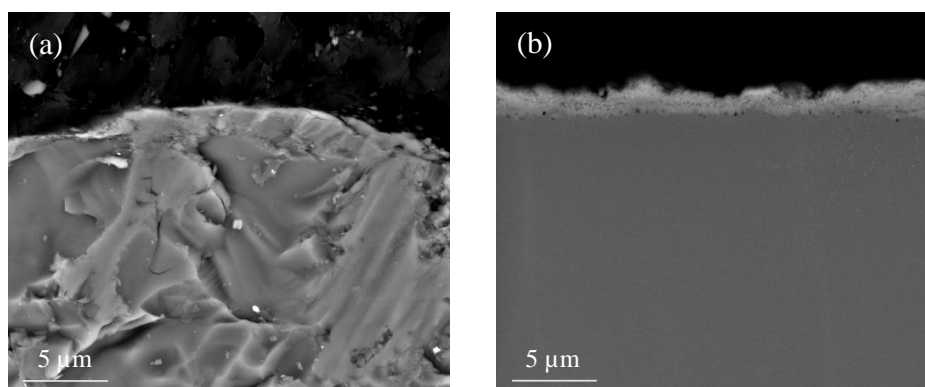


Figure 14: Scanning Electron Micrograph (SEM) micrographs of an olivine sample, which was exposed to biomass ash for 24 hours, illustrating the two different sample preparation methods. (a): grinding with SiC paper; (b): Broad ion beam (BIB) milling.

Furthermore, by utilizing energy dispersive X-ray spectroscopy (EDS), information about the elemental composition was acquired. Thereby, the distribution of ash-derived elements throughout the surface layer of the particles can be followed. By studying the composition throughout the ash-layers, conclusions can be made on elemental distribution and whether agglomeration is likely to occur or if tar-reduction can be attributed to the elemental composition on the particles' surface. While measuring the composition is useful to derive which elements are involved in activation of the bed material, no crystallographic information can be acquired by SEM-EDS, which is why this technique is commonly complemented by X-ray diffraction.

5.2. X-ray Diffraction

Crystallographic information can be acquired with X-ray diffraction (XRD). The samples were ground to a fine powder prior to analysis to improve the statistical distribution of the crystallites. The recorded spectra were compared qualitatively to the X-ray diffraction patterns from existing databases (PDF 4+). Together with compositional data from SEM-EDS, information on the phases present on the samples could therewith be acquired.

Ash interactions occur to the largest extent on the surface of the particles whereas the signal of XRD is acquired from the entire particle, i.e., mostly the bulk phase. Comparing the patterns obtained from fresh material with used material enables drawing conclusions about phases which had formed due to ash interaction. However, the signal stemming from these phases is weak, compared to the rest of the bed material and the detection limit of the technique is usually a few volume percent (1 – 3%), below which a phase cannot be detected with XRD. It can therefore become challenging to precisely identify minor phases formed during the interaction.

5.3. Transmission Electron Microscopy

For the purpose of higher resolution analysis, lift-out lamellas (about 6 μm x 10 μm) of samples were created by focused ion beam (FIB) milling using gallium ions. The samples were polished down to a thickness of about 100 nm (until they were sufficiently thin for electrons to pass through), to be analyzed by transmission electron microscopy (TEM). This process requires multiple sample preparation steps making it time-consuming and expensive. Furthermore, only a small part of the surface of one particle can be analyzed which could make it questionable whether the sample is representative for the whole bed material in the gasifier. It is therefore crucial to conduct the previously described analysis (SEM-EDS and XRD) beforehand and to carefully select a representative location of the particle. Once the representativity of the sample was ensured, TEM could be used for high-resolution imaging, elemental analysis (TEM-EDS) and to obtain crystallographic information by TEM-diffraction.

5.4. X-ray Fluorescence Spectrometry

Compositional information from a comparably large number of particles at the same time, was acquired by X-ray fluorescence spectrometry (XRF) where around 5 grams of sample was investigated. This technique was used for the oxygen carrier aided combustion experiment with ilmenite, to analyze the correlation of elemental composition with the magnetic properties. XRF could be utilized to gain insight on preferential distribution of the elements near the surface or in the core of the particles. The attenuation length (which describes the depth from which the signal of an element is collected) is dependent on the element that is investigated, where heavier elements emit higher energy X-rays which can escape from deeper within the sample (i.e., they have a higher attenuation length). With a density of ilmenite of 4.5 g/cm^3 , attenuation lengths between 10 and 20 μm for K_α -lines of the most abundant elements in ilmenite and the fuel ash (i.e., Ca, Si, Fe, Ti) could be assumed. This is sufficient to analyze the ash layer of the particles, by measuring the samples both in their original state, where the compositional information is acquired from the surface, and in their ground state, where the information is acquired from the bulk (see Figure 15).

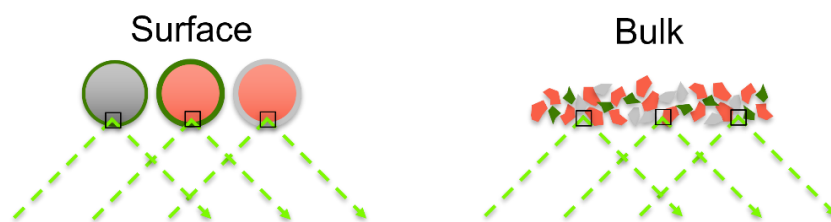


Figure 15: Schematic depiction of the methodology chosen using XRF for obtaining information of preferential distribution of elements. Analyzing whole particles provides information of elements preferentially found on the surface (left). Grinding the particles prior to analysis shows which elements are more concentrated in the bulk (right).

5.5. Magnetic Susceptibility

To analyze the effect of magnetic separation, the magnetic properties of the samples were investigated. This was done by measuring their magnetic susceptibility. For this, around 25 g of the sample was placed into a plastic container which is exposed to an external magnetic field. The response of the material to the external magnetic field provides information about the magnetic susceptibility of the material which determines whether it will be attracted or repelled by a magnet.

5.6. X-ray microtomography

X-Ray Microtomography (XMT) was used to create 2-dimensional cross-sections of a volume of around 0.5 mm^3 , corresponding to 50 – 100 particles. In this technique, image contrast is generated by differences in the optical density of areas in the particles, where denser areas appear brighter in contrast. For the case of ash-covered particles, the ash layer appears brighter, as it contains heavier elements than the fresh bed material. The acquired 2-dimensional scans can be combined by dedicated software to create 3-dimensional images of the particles which provides information about the morphology of the particles. Furthermore, the difference in contrast between the ash layer and the unreacted particle can be used to obtain information about the layer thickness of the whole sample volume.

5.7. Additional Analysis

Complementary to the listed techniques, a number of other analysis techniques were applied. Since the amount of surface area of the bed material available to the gas phase could influence the catalytic tar cracking reactions, Brunauer-Emmett-Teller (BET) analysis were conducted. The elemental distribution of bed material cross-sections was investigated by time of flight secondary ion mass spectroscopy (ToF-SIMS) to investigate whether molecular-ions could be found. This information was used complementary to XRD to derive the nearest neighbors of elements found in the active layers. Leaching studies were conducted to study the effect of potassium in surface vicinity, as well as the content of water-leachable sulfate and phosphate. For this, 1 g of bed material particles was immersed in water to leach out soluble species. The concentration of soluble K^+ was analyzed with atomic absorption spectroscopy (AAS) and sulfates and phosphates were investigated with ion chromatography (IC). An overview of the instruments utilized for each analysis technique is given in Table 6.

Table 6: Analysis techniques and corresponding machine(s) utilized for this work.

Technique	Machine
XRF	Malvern-PANalytical Axios spectrometer
XRD	Siemens D8 Siemens D5000
SEM	FEI Quanta 200 Phenom ProX
BIB	Leica EM TIC 3X
XMT	Xradia 620 Versa
TEM	FEI Titan 80-300
FIB	FEI Versa3D
BET	Micromeritics ASAP2020
ToF-SIMS	TOFSIMS.5
Magnetic Susceptibility	Bartington MS2B magnetic susceptibility sensor
AAS	PerkinElmer PinAAcle500
IC	Dionex ICS90

5.8. Thermodynamic Modelling

Complementary to the experimental results, thermodynamic modelling offers theoretical information on the material's development. Therefore, FactSage was used to calculate the inorganic phases which are stable at the conditions present in the different systems. The calculations are based on minimizing the Gibbs free energy which results in information on the phases which are thermodynamically stable, without accounting for the process kinetics. The elemental compositions found with SEM-EDS were used as input data (as their respective oxides) and the calculations could be used to investigate melting behavior and to support the results found with XRD. Furthermore, by studying possible reactions, the mechanism of the interaction between bed material and biomass ash compounds could be derived.

6. Results & Discussion

The interactions of fuel ash and bed materials used for different fluidized bed applications lead to various effects in the reactors. The properties of the bed material that are altered by these interactions shall be discussed in the following sections. Briefly, the results of the interactions can be:

- Alkali capture which decreases the propensity of corrosion of parts of the equipment
- Agglomeration which leads to defluidization of the bed material and is therefore detrimental to the process
- Catalytic activation which decreases the tar in the syngas and is beneficial for gasification
- Oxygen carrying ability which is associated with a decrease in tar but also in the calorific value of the product gas
- Changes in the magnetic properties which determine whether magnetic separation of bed particles is an option
- Ash recovery could be an option if the ash is enriched in valuable elements

An overview of the combinations of bed materials and fuels, as well as the enumerated effects which were investigated over the course of this work is summarized in Table 7.

Table 7: Summary of effects that were investigated or discussed during the investigated experimental campaigns (ASR = Automotive Shredder Residue). 1: Alkali capture, 2, Agglomeration; 3: Catalytic activity; 4: Oxygen carrying; 5: Magnetic Properties; 6: Ash recovery

	Quartz	Olivine	Alkali-Feldspar	K-feldspar	Ilmenite
Woody Biomass	1, 2, 3, 4	1, (2), 3, 4	1, 3, 4	3	1, 4, 5
ASR		4, 5, 6			
Chicken Manure				1, 3, 6	
Salts (laboratory)			1, 2	1, 2	

6.1. Alkali Capture

	Quartz	Olivine	Alkali-Feldspar	K-feldspar	Ilmenite
Woody Biomass	X	X	X		X
ASR					
Chicken Manure				X	
Salts (laboratory)			X		

One of the most abundant elements in biomass ash is potassium. Alkali metals in general are commonly associated with corrosion of the metallic surfaces in the used systems. The reactions of additives, ash compounds, or bed material with alkali metals can therefore aid to alleviate corrosion-related problems if they result in the formation of stable phases.

The interaction of sulfur with potassium was observed when sufficient sulfur is available. In the investigations on active olivine, ammonium sulfate was added to the cyclone to control the CO emissions from the boiler. This led to the formation of K_2SO_4 which was found with XRD and confirmed by the coincidence of potassium and sulfur detected by SEM-EDS (see Figure 16). Similar observations were made in the experiment where chicken manure (containing both potassium and sulfur) was combusted with bark using K-feldspar. Again, both XRD and SEM-EDS revealed that both elements were present at the same location (see Figure 17). The interaction of potassium with sulfur can therefore aid alkali capture by forming K_2SO_4 which is stable at the conditions present in the reactors. Thermodynamic calculations conducted for the elemental compositions measured by EDS point analysis in the K- and S- rich locations supported the stability of K_2SO_4 .

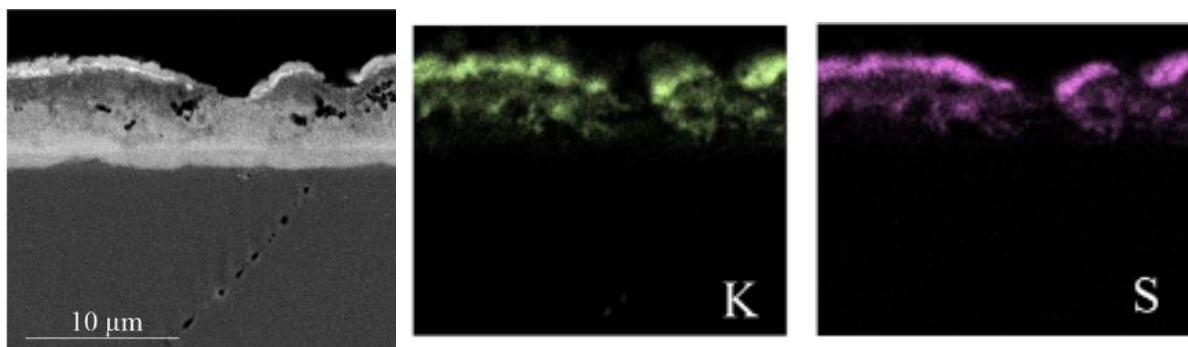


Figure 16: Back-scattered electron micrograph of the cross-section of an olivine particle where ammonium sulfate was added. The sample was extracted after 3 days of residence time in the Chalmers gasifier. The SEM-EDS intensity maps of K and S are depicted as well, showing their presence (colored areas on the respective map) at the same location in the ash layer.

Studying the interactions of two K-salts (solid K_2CO_3 and gaseous KOH) with alkali-feldspar revealed that the result of interaction with woody biomass ash resembles the one of gaseous KOH. This exposure led to the formation of K-feldspar with a migration of sodium to the surface, which was observed as well during the application of the bed material in the Chalmers gasifier. This suggests that the interactions with woody biomass proceed in a similar fashion, i.e., gaseous KOH reacts with Na-feldspar to form K-feldspar.

However, despite its initial resistance towards agglomeration, the influx of alkali metals decreases the degree of polymerization of the underlying silicate structure of feldspar. This proceeds by the forming of non-bridging oxygens and decreases the melting temperature of the product. Melt-formation and subsequent agglomeration was only found during exposures in the laboratory, where the concentration of alkali metals was high, and shall be discussed further in the following chapter.

Similarly, the interaction of potassium and quartz (SiO_2) is even more detrimental than for olivine and feldspar. While quartz has a higher capacity for alkali capture than olivine,⁸⁷ the produced K-silicates exhibit low melting temperatures. At the temperatures usually applied for thermal conversion of biomass in a fluidized bed, these K-silicates are therefore molten and sticky, which can lead to the problem of agglomeration of the bed material.

6.2. Agglomeration

	Quartz	Olivine	Alkali-Feldspar	K-feldspar	Ilmenite
Woody Biomass	X	(X)			
ASR					
Chicken Manure					
Salts (laboratory)			X	X	

Agglomeration is a phenomenon which describes the defluidization of the bed material, caused by sticking together of several bed particles. Of the different mechanisms described in 3.3.2, early symptoms of coating-induced agglomeration were found when quartz was used as bed material for gasification of woody biomass (see Figure 19). As is typical for quartz, gaseous potassium interacted with the SiO_2 and led to the formation of K-silicates which exhibit low melting temperatures. In the present case, this can be followed by the EDS map, where an inner layer consisting of potassium and silicon was found. Characteristically, a bubble is present in the part of the interaction layer which is expected to be molten.

Agglomeration can be prevented or delayed by elements which build a solid layer around the particles. In the present case a surface layer containing calcium and magnesium can be observed which exhibits a composition with a higher melting temperature. Hence, no agglomeration was observed at this stage of the experimental campaign. However, this layer is expected to eventually break down and enable the interaction of the molten layers of several particles and ultimately lead to agglomeration.

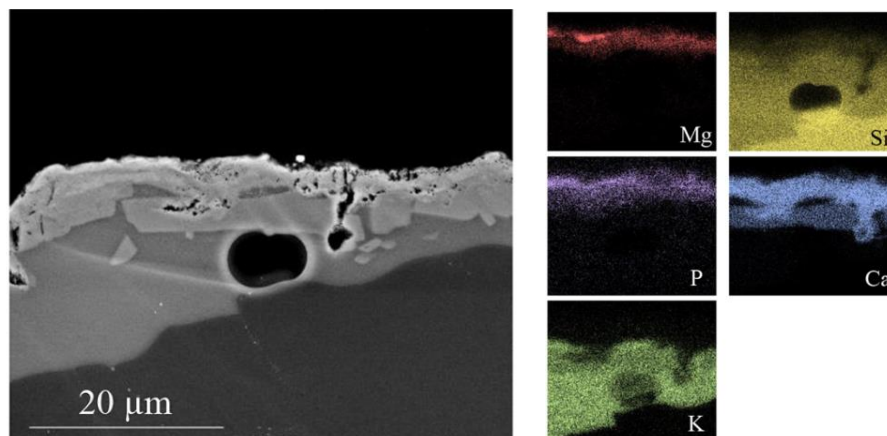


Figure 19: Back-scattered electron micrograph of the cross-section of a quartz particle which was exposed to woody biomass for 3 days. The energy dispersive X-ray spectroscopy intensity mappings show an inner layer consisting of K and Si which is likely to be in a molten state. The outer layer consisting of Mg, P, and Ca is expected to be solid and offer some protection against agglomeration.

The problems associated with agglomeration can be avoided by employing alternative bed materials. Both olivine and feldspar exhibit sufficient resistance towards agglomeration and are therefore suitable alternatives for fluidized bed applications. However, exposures conducted in the laboratory indicated that

at high concentrations of potassium, agglomeration of feldspar could in fact be a problem. Melt formation occurred when alkali-feldspar was exposed to gaseous KOH (see Figure 20). The interaction product which can be found in between the particles consisted of Si, Al, K and Na with a ratio of around 4:3:3:1 (point 1 in Figure 20). Thermodynamic equilibrium calculations conducted with this composition predict melt formation, due to the high concentration of alkali metals and silicon.

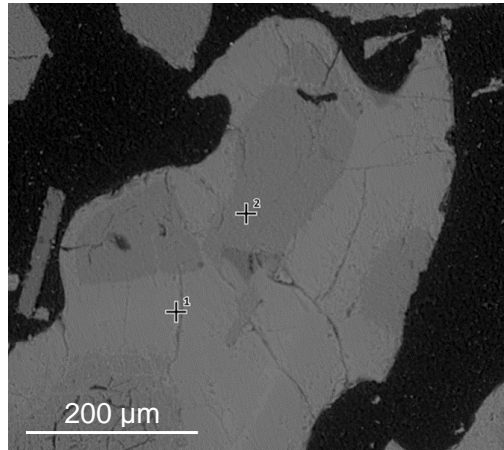


Figure 20: Back-scattered electron micrograph showing alkali-feldspar particle which has interacted with gaseous KOH. The image shows coating-induced agglomeration which can be seen by thick brighter layer around the particles which contains a mixture of elements originally present in the bed material and those introduced with the salt.

Agglomeration was also found when K-feldspar was exposed to K_3PO_4 or Na_3PO_4 . The ratio between potassium and phosphorus was close to the original composition in the salt, with minor amounts of silicon which could have initiated the formation of a melt. The mechanism for agglomeration with alkali-phosphates appears therefore to be melt-induced.

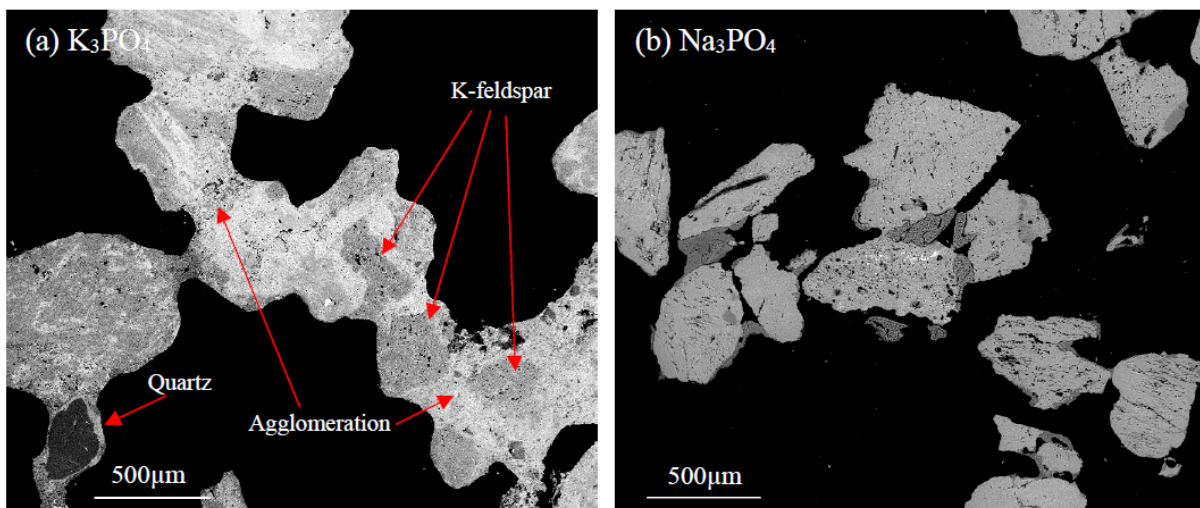


Figure 21: Back-scattered electron micrograph showing the result of the fixed bed laboratory exposures investigating the interaction of K-feldspar with (a) K_3PO_4 , and (b) Na_3PO_4 .

To avoid the problems associated with agglomeration of quartz, alternative bed materials were investigated, for example olivine.⁸⁸ Olivine does not show strong interaction with potassium. Potassium remains in the outer layer of olivine or migrates through cracks and pores.⁸⁹ The inner layer of olivine is rich in magnesium, iron, calcium, and silicon. Still, this layer appears to form melt as well, as found with TEM diffraction (see Figure 23) in the inner layer which corresponds to a location as indicated with the arrow in Figure 22.⁸⁸ However, a common observation of olivine is that its inner layer stays rather constant in thickness (around 1 μm) during longer exposures which could explain why coating-induced agglomeration is usually not observed with olivine.

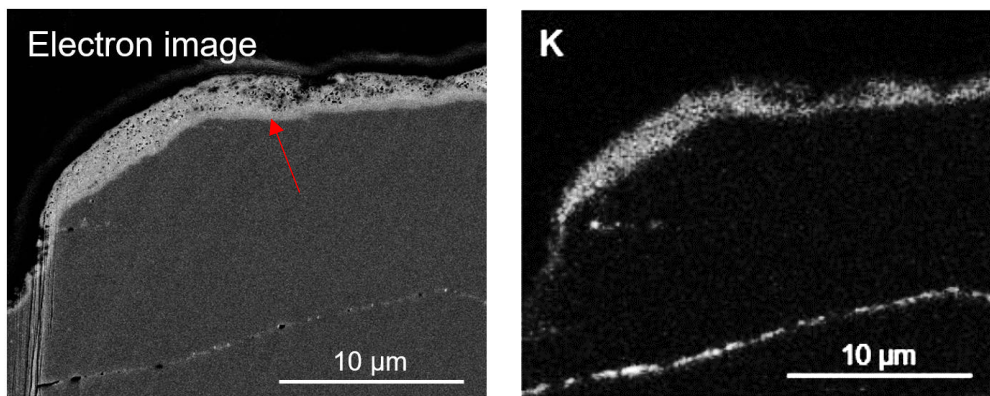
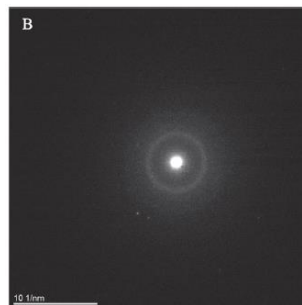


Figure 22: Left: Scanning electron microscopy (SEM) micrograph recorded on olivine which has interacted with biomass ash for 4 days. Right: EDS elemental intensity map of potassium recorded on the same location. The arrow indicates the location of the inner layer.



Mg	Si	Ca	Mn	Fe
19	44	15	6	17

Figure 23: TEM diffraction on the inner layer of olivine (indicated with the red arrow in Figure 22) and the corresponding elemental composition at this location. The diffraction pattern is characteristic such for an amorphous phase.

6.3. Catalytic Activity

	Quartz	Olivine	Alkali-Feldspar	K-feldspar	Ilmenite
Woody Biomass	X	X	X	X	
ASR					
Chicken Manure				X	
Salts (laboratory)		X			

If agglomeration can be avoided, the bed material can be utilized over a longer period of time and thereby interact with ash-derived elements for a longer time. If this is the case, a phenomenon usually observed is the reduction of tar in the syngas during gasification. This form of catalytic activity is highly beneficial and even required for gasification to function, due to the condensation problems associated with tar. Initially, the usually used materials, quartz, uncalcined olivine, and feldspar are seen as inert, but catalytic activity develops in the materials once a layer has formed containing ash-derived elements. The formation of an ash layer is common for all materials. Furthermore, prolonged retention time in the system increased the ash layer thickness, which was associated with the decrease of tar in the syngas. Thus, the possibility to retain ash on the surface of the bed particles appears to have an impact on layer formation. By having cavities in the bed material, this retention of ash could possibly be enhanced. This was tested with a K-feldspar that was obtained from a sedimentary deposit, where the particles have undergone weathering and therefore exhibit cavities. These cavities were found to facilitate ash deposition onto the particles, even when chicken manure was used as fuel where the ash contains very stable Ca-phosphate (see Figure 24 a). Providing bark to the fuel which contains silicon and calcium appeared to improve the deposition of ash and led to the formation of thicker layers (Figure 24 b).⁹⁰

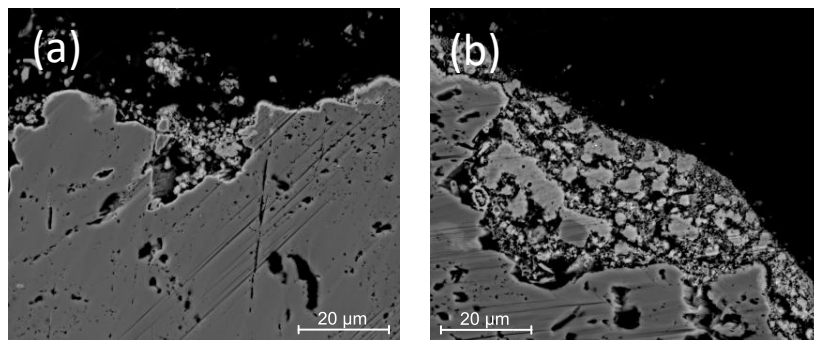


Figure 24: Back-scattered electron micrograph of K-feldspar which was used for 8 h in fluidized bed combustion of (a) chicken manure and (b) a mixture of chicken manure and bark.

The build-up of a catalytic ash layer necessitates chemical stability of the bed material towards agglomeration, which is a requirement that is not fulfilled for quartz. However, the mechanism of layer formation on olivine differs from quartz, due to the difference in interaction with alkali metals. As mentioned previously, while olivine forms an amorphous inner layer this layer stays constant in thickness and does not contribute to the tendency to cause agglomeration. The outer layer, on the other hand, increases

in thickness during longer interaction times. As longer times are associated with an increase in catalytic activity, the thickness of the outer layer specifically appears to positively influence the capability of tar removal of the bed material. The same correlation of layer thickness and catalytic activity was observed for alkali-feldspar. Here, the ash layer formation was accompanied by a replacement of Na-feldspar by K-feldspar⁹¹ which was associated with crack formation.⁹² This might limit the overall stability of Na-feldspar, which is why the application of K-feldspar enables longer residence times and thereby the development of higher catalytic activity.

While a thick ash layer seems to generally decrease the tar yield in the syngas, to participate in catalytic reactions, the elements need to interact with the gas phase. Several different elements that are present in biomass ash are candidate catalysts for the water-gas-shift reaction (WGS). Examples are the alkali metals sodium and potassium, as well as the alkaline earth metals calcium and magnesium and the transition metals iron and nickel. Due to the relative abundance of calcium and potassium in the ash of biomass, their interaction with the bed materials as well as their presence on the surface of the particles is of special interest.

The two bed materials (olivine and feldspar) which were utilized for DFB gasification and investigated in more depth, appear to be similar in their layer formation (see Figure 25 and Figure 26). On the surface (indicated with '1a' or '1b' in Figure 25 and Figure 26), calcium and potassium were found on olivine, and sodium and potassium for feldspar which are known catalysts for the water gas shift (WGS) reaction, making their presence on the surface a possible explanation for the activity of these materials.

Underneath this surface layer consisting of alkali and alkaline earth metals (AAEM), a layer consisting of magnesium, manganese and iron can be found (indicated with '2' in Figure 25 and Figure 26). Among the enumerated metals, iron is also a possible candidate for catalyzing the WGS. Further inside the particle, a layer containing silicon and phosphorus can be found (indicated with '3' in Figure 25 and Figure 26), which possibly is in a molten state and therewith might facilitate ash deposition. The similarity of the ash layers found on olivine and feldspar indicates that the development of activity is less dependent on the bed material and more on the utilized fuel.

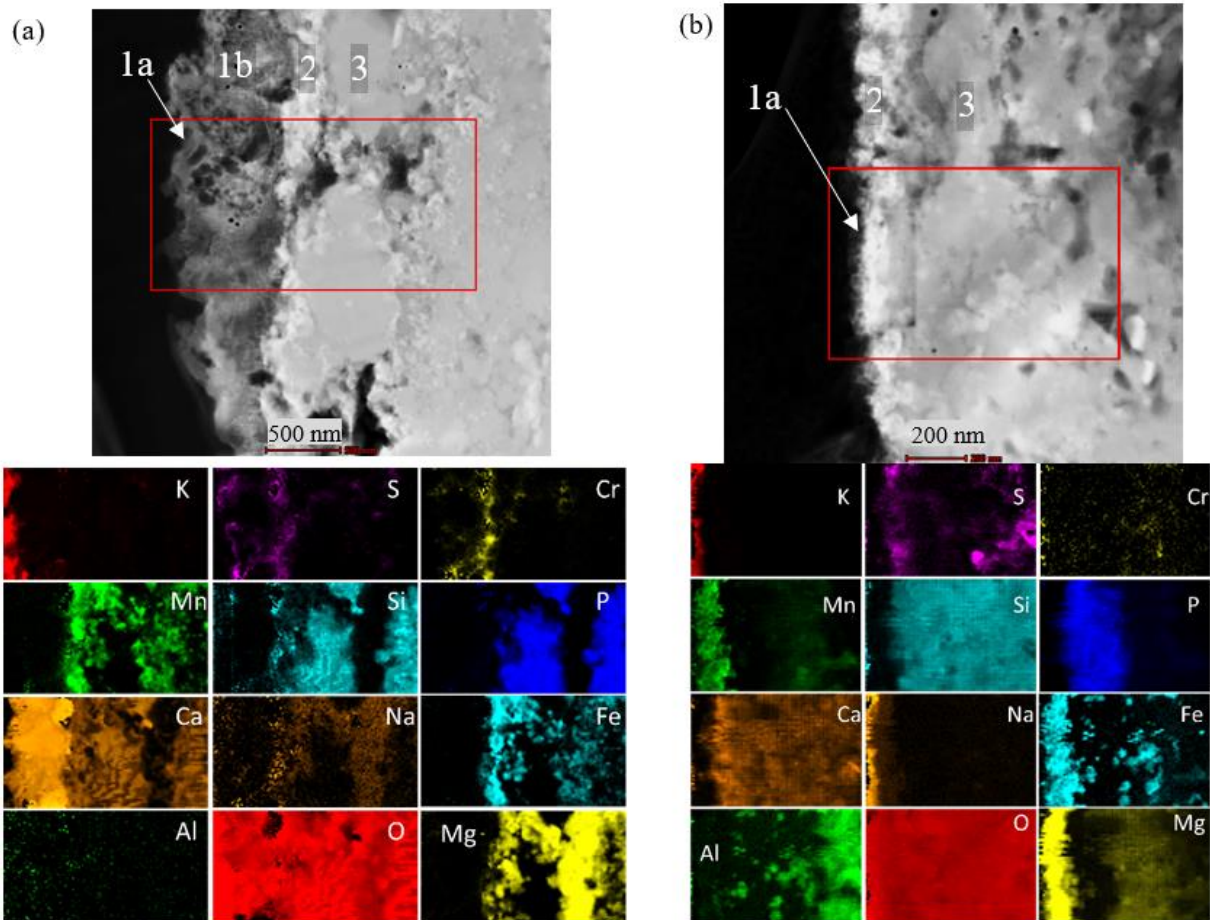


Figure 25: Transmission electron microscopy (TEM) micrograph and energy dispersive X-ray spectroscopy (EDS) elemental intensity map of the surface of (a) olivine and (b) feldspar which have interacted with woody biomass ash for 3 days. The red box in the micrographs indicate the location where the elemental maps were recorded. The similarity between the two materials is indicated with the numbers: **1a** and **1b** denote layers consisting of alkali and alkaline earth metals respectively; **2** denotes a layer consisting of Mn, Fe, and Mg; **3** denotes a layer containing Si and P which is possibly in a molten state.

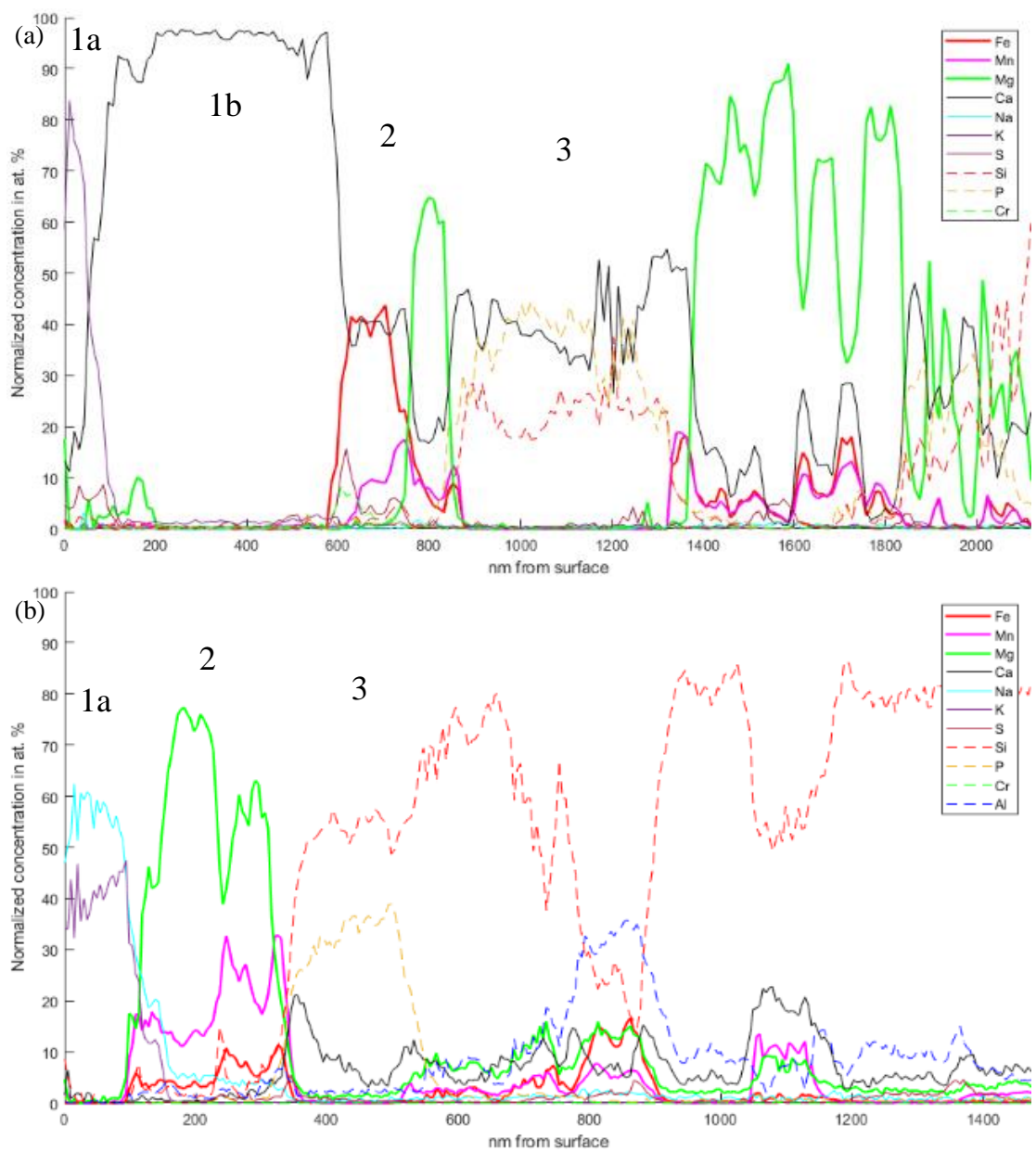


Figure 26: Energy dispersive X-ray spectroscopy (EDS) line-scan recorded with transmission electron microscopy (TEM) on (a) olivine and (b) feldspar which have interacted with woody biomass ash for 3 days. The similarity between the two materials is indicated with numbers: **1a** and **1b** denote layers consisting of alkali and alkaline earth metals respectively; **2** denotes a layer consisting of Mn, Fe, and Mg; **3** denotes a layer containing Si and P which is possibly in a molten state.

6.4. Oxygen Carrying

	Quartz	Olivine	Alkali-Feldspar	K-feldspar	Ilmenite
Woody Biomass	X	X	X		X
ASR		X			
Chicken Manure					
Salts (laboratory)					

Another observation that is made for bed material that is utilized for prolonged exposure to ash elements and the typical atmosphere in the reactors, is the development of oxygen transport with time. After three days retention time in the gasifier, quartz, olivine, and feldspar were able to transport oxygen from the combustor to the gasifier. This was quantified in batch reactor experiments by alternating the atmosphere from oxidizing (air) to reducing (50% CO and 50% H₂). Measuring the concentration of CO₂ in the gas stream leaving the reactor under the reducing atmosphere, provides a value for the oxygen carrying ability of the bed material. Figure 27 shows the values for fresh and ‘active’ material, which refers to the state after three days retention time. In the fresh state, olivine exhibits minor levels of oxygen carrying, most likely due to the inherently present iron, which can change its oxidation state from Fe²⁺ at the oxygen partial pressure of the reducing atmosphere, to Fe³⁺ under the one at the oxidizing atmosphere. After interaction with the biomass ash, all three materials develop levels of oxygen carrying ability which are higher than those for fresh material. This could be explained by ash-derived elements accumulating on the surface of the particles and thereby contributing to the oxygen carrying. Elements present in the ash which can alternate between two oxidation states at the different oxygen partial pressures are Mn (MnO / Mn₂O₃), Fe (FeO / Fe₂O₃) and S (SO₂ / SO₃). The oxygen carrying ability of olivine could be further increased by the migration of iron from the bulk towards the surface.

In fact, iron and the other candidate element, manganese, were found when conducting the previously discussed more in-depth analysis of the ‘active’ bed material particles. The layer indicated with ‘2’ in Figure 25 and Figure 26, containing magnesium, manganese, and iron could possibly contribute to the oxygen carrying effect of the bed material. The latter two elements (iron and manganese) are able to change their oxidation state depending on the oxidizing or reducing potential of their locations in the reactor. Due to the presence of this layer in surface vicinity, it is likely that the layer interacts with the gas phase and thereby contributes to oxygen carrying.

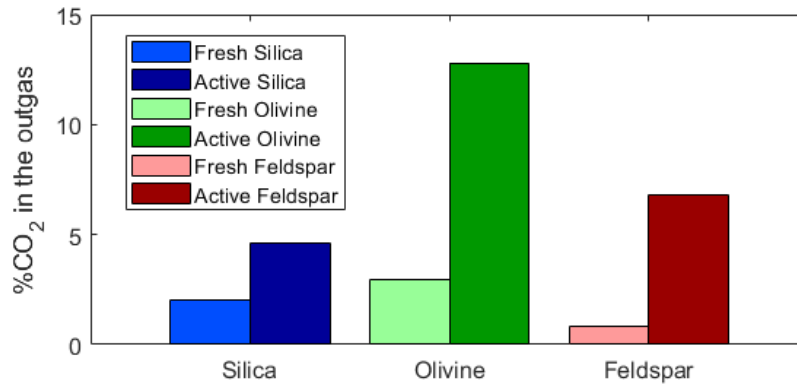


Figure 27: Oxygen carrying ability of quartz, olivine, and feldspar, measured by the concentration of CO₂ in the flue gas leaving the reactor when the tested bed material is exposed to CO/H₂. 'Active' refers to the state of the bed material after three days interaction time with woody biomass ash in the Chalmers gasifier.

The contribution of sulfur specifically to the oxygen carrying ability of active feldspar was investigated with two different reducing gas mixtures (CO/N₂ and CO/H₂). Leaching analysis were done before and after exposure of the particles in the batch reactors. It was found that the amount of leachable SO₄²⁻ decreased after the use of the material in the batch reactors with CO/H₂. However, changing the reducing gas to CO/N₂, did not cause a reduction in leachable SO₄²⁻. Furthermore, the amount of oxygen that is released under reducing conditions is higher when CO/H₂ is applied as reducing gas, compared to CO/N₂ (see Table 8).

Table 8: Summary of the results from the oxygen carrying tests of active feldspar particles conducted in the laboratory scale batch reactors. Two different atmospheres were investigated, CO/H₂ and CO/N₂. The amount of leachable SO₄²⁻ was measured before and after the exposure to estimate the impact of S on the oxygen carrying effect.

	Start CO/H ₂	End CO/H ₂	Start CO/N ₂	End CO/N ₂
Oxygen Transport [mol O/kg bed]	0.37	0.30	0.09	0.27
Leachable SO ₄ ²⁻ [mg/L]	700	450	700	700

The addition of elemental sulfur to the Chalmers gasifier led to a release of H₂S from the gasifier as well as an increase in oxygen transported from combustor to the gasifier. However, after the addition stopped, the oxygen carrying effect was decreased to the level prior to the sulfur addition. Assuming sulfur is bound as SO₄²⁻ under oxidizing conditions and is released as H₂S under reducing conditions, four oxygen atoms are released per H₂S. Measuring the total oxygen transport and the release of H₂S showed that there is a correlation, but the release of H₂S cannot be responsible for the total oxygen transport exhibited by the bed material.

The increase in oxygen carrying ability of the bed material happens simultaneously to the development of catalytic activity towards the water-gas-shift reaction (WGS) and the decrease in tar yield. This suggests that the two effects are related. However, the application of bed materials that has an inherent high oxygen carrying ability as fresh materials (such as ilmenite or manganese-ore), exhibited neither catalytic activity

towards the WGS, nor the ability to reduce the tar yield. From this it was concluded that the catalytic activity for the WGS is decisive to decrease the tar yield in the syngas.⁹³

The development of an oxygen carrying ability of the bed material during gasification is generally an unwanted side-effect of ash interaction as it decreases the calorific value of the syngas. However, if the bed material has sufficiently high oxygen carrying ability, chemical-looping gasification can be conducted. In this process, the fuel is converted completely in the fuel reactor, with oxygen provided by the bed material. In the air reactor, the bed material is oxidized. The energy required for fuel conversion in the fuel reactor is provided by the heat of the exothermic oxidation and transported by the bed material. To obtain a bed material with sufficiently high oxygen carrying ability, automotive shredder residue (ASR) was used as fuel which contains almost 50% ash, consisting to a large share of transition metals which can contribute to the oxygen carrying ability. In this experimental campaign, olivine was used as bed material and exposed to woody biomass for a week after which the particles exhibited an ash layer typical for woody biomass ash. Afterwards, the fuel on the gasifier side was changed to ASR, whereas the combustor was continuously provided with wood. The analysis of the char conversion during this campaign revealed that the most decisive parameter for the process to function as chemical looping gasification was the oxygen carrying ability of the bed material.⁹⁴

Investigations of the bed material at different time intervals showed that the high concentration of iron on the surface of particles in the bed material was decisive for the oxygen carrying ability. Thermodynamic analysis showed that the oxygen carrying proceeded to the largest extent by $\text{Fe}^{2+}/\text{Fe}^{3+}$ cycles.⁹⁵ Iron accumulated in two different types of particles: either on the surface of the olivine particles which had previously been covered by biomass ash, or ash particles exhibiting a composition similar to the original ASR ash. A schematic representation of the formation of both types of particles is shown in Figure 28. In both cases, a migration of Fe towards the surface was found.

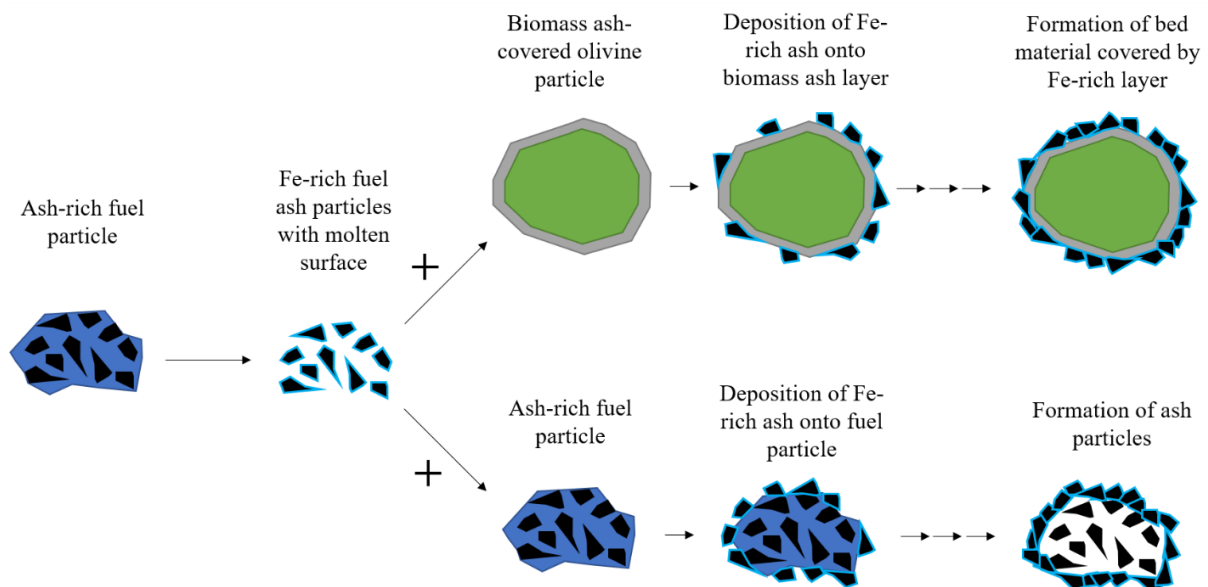


Figure 28: Schematic representation of the mechanism underlying the formation of the two main type of particles exhibiting oxygen carrying ability - ASR ash-covered olivine particles and ASR ash particles.

6.5. Magnetic Properties

	Quartz	Olivine	Alkali-Feldspar	K-feldspar	Ilmenite
Woody Biomass					X
ASR		X			
Chicken Manure					
Salts (laboratory)					

The previous chapters have shown that the interactions of bed material with ash can induce changes in the material which can be both beneficial and detrimental. The problems listed in the previous chapters (agglomeration or changes in oxygen carrying ability) necessitate replacement of material, which decreases the sustainability of the process. If, for example, one fraction of the material consists of contaminants which are less active than the rest of the material, separating this fraction from the active material could minimize waste flows as the active fraction can be reused. For this, the magnetic susceptibility of the material could possibly be exploited by a process called magnetic separation. Characteristic for magnetic susceptibility is the presence of transition metals which can either be inherently present in the bed material or introduced with the fuel and deposited onto the bed particles as ash layers.

Multiple transition metals were observed for the previously discussed experimental campaign utilizing olivine together with automotive shredder residue (ASR), of which iron is most abundant. The thermodynamically stable phase at oxidizing conditions was calculated to be spinel, which is a solid solution including magnetite. As magnetite exhibits a high magnetic susceptibility (Table 1), it could be speculated that magnetically separating the ash obtained from the interaction of olivine and ASR could be an option to concentrate the magnetite-rich and therewith oxygen carrying ash particles in one fraction.

Magnetic separation was done in the case of ilmenite which was used for oxygen carrier aided combustion (OCAC). The goal was to separate the ilmenite particles exhibiting a higher magnetic susceptibility from inactive particles introduced with the ash, in order to reduce the requirement of fresh ilmenite addition. The magnetic susceptibility of the bed material increased throughout the experimental campaign, a suggested reason for which was the increased formation of magnetite. Furthermore, it was found that interactions occurred between ilmenite and fuel ash but also between ilmenite and particles which were added together with the fuel. The feldspar particles that are introduced as contaminants to the ilmenite bed material, form layers consisting of elements originating from ilmenite. These layers appear to render them magnetic as they are found in the magnetic fraction of the material (see Figure 29). The presence of iron on the surface of these particles suggests that they are also oxygen carrying.⁹⁶ Thus, magnetic susceptibility is a property that is useful when doing magnetic separation to concentrate Fe-rich oxygen carrying particles, but this property is changed during interaction with fuel ash.

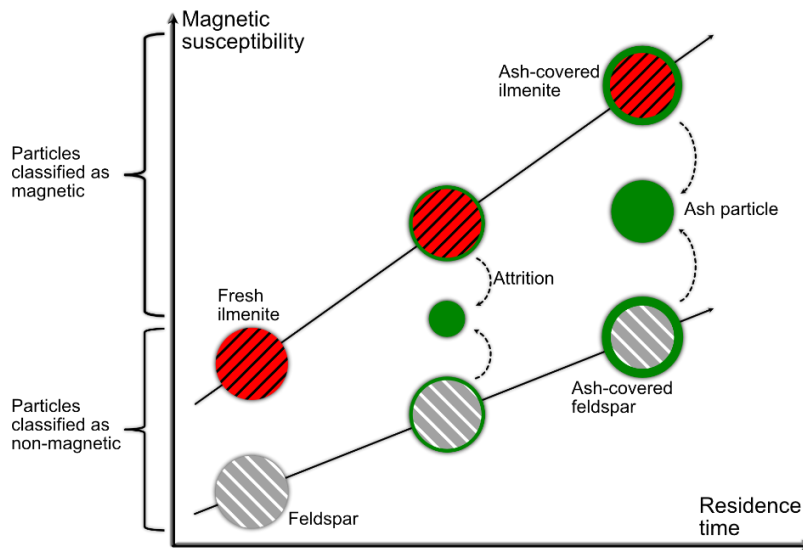


Figure 29: Schematic depiction of the mechanism of development of magnetic properties of bed material particles under oxygen carrier aided combustion (OCAC) conditions with ilmenite used as an oxygen carrier. Three different types of particles which develop magnetic properties throughout exposure can be distinguished during combustion (red: ilmenite, grey: feldspar, green: ash).

6.6. Ash Recovery

	Quartz	Olivine	Alkali-Feldspar	K-feldspar	Ilmenite
Woody Biomass					
ASR		X			
Chicken Manure				X	
Salts (laboratory)					

Depending on the fuel, the generated ash might contain elements which are considered valuable. For the case of (ASR), elements such as copper and zinc could possibly be present in the ash at a concentration that is sufficient for their recovery. Bed material analysis revealed that zinc accumulated mostly in the particles which were identified as ASR ash particles. As they exhibited a high concentration of iron, a comparably high magnetic susceptibility was expected. This property could be utilized to further concentrate the elements present in ASR ash.

Animal manures contain high concentrations of phosphorus, which is why they are commonly applied as fertilizers. The experiment utilizing chicken manure as fuel, yielded a bed material containing a large fraction of phosphorus, bound as calcium phosphate on the surface of the particles. This was further enhanced when the chicken manure was co-combusted with bark. Bed material particles covered with phosphorus could be beneficial for their subsequent utilization as fertilizer. It was also found that the phosphorus is bound as water-insoluble phases which would decrease the risk of uncontrolled run-off from fields, thus limiting the danger of eutrophication of nearby lakes. However, to apply used bed material as fertilizer, it must not contain any heavy metals, which is the case for olivine (namely nickel and chromium). This is why feldspar is an attractive option as a bed material that could accumulate phosphorus and subsequently be used for fertilization purposes.⁹⁰

7. Conclusion

Over the course of this work, a number of bed materials were investigated regarding their interactions with different fuels. The properties of the materials were influenced by the bed material-fuel ash interactions which could lead to beneficial or detrimental effects for the thermal conversion process.

The *challenges* which were identified for interactions of bed material and fuel ash are agglomeration and the development of an oxygen carrying ability during gasification. The following conclusions were drawn regarding these two effects:

- The interaction of quartz with potassium-rich ash leads to the formation of low-melting K-silicates which is the underlying reason for agglomeration.
- By replacing the bed material with olivine or feldspar, agglomeration can be avoided. However, exposures with K-rich salts have shown that there is a limit of the agglomeration resistance of feldspar.
- Bed materials acquire an oxygen carrying ability due to deposition of ash elements (mostly iron and manganese) which are present as an outer layer on the surface of the particles. These elements can alter their state of oxidation between combustor and gasifier and thereby transport oxygen from combustor to gasifier. This can decrease the calorific value of the product gas.

Despite the challenges, a number of *opportunities* exist for the bed material to improve the conversion process. The effects investigated in this work were the possibility of alkali capture to mitigate corrosion and the development of catalytic activity of the bed material towards tar removal. The following conclusions could be drawn:

- The formation of K_2SO_4 on the surface of the bed material was found for all cases where sulfur was present. This phase is less corrosive than KCl and its formation is therefore preferred to decrease the corrosion potential.
- A replacement of Na-feldspar with K-feldspar was found due to interaction with K-rich salts or ash which indicates a capture of potassium by the bed material.
- Ilmenite and quartz can form K-titanate and K-silicate respectively which binds the potassium in a stable form. However, this potential is limited by the available titanium and silicon and also causes agglomeration in the case of quartz.
- The formation of ash layers generally improves the catalytic activity of the bed material for tar removal which is highly beneficial in gasification. The elements which most likely contribute to this effect are calcium and potassium. The mildly oxidative environment provided by the transition metals iron and manganese could also improve this effect. Layers containing these elements were found for all cases investigating thermal conversion of woody biomass.

After utilization of the bed material, replacement will be necessary to counteract the development of detrimental properties. To *handle* the waste stream that is generated in this way, two possibilities were discussed in this work:

- Ilmenite develops magnetic properties when it is utilized as bed material. This offers the possibility to separate the material which has oxygen carrying abilities (which are a

requirement for the OCAC process), from the fuel ash. As the magnetic susceptibility is increased over the course of the process, the separation should not be conducted on fresh material to avoid disposal of active particles.

- During combustion of chicken manure and especially during co-combustion with bark the formation of P-rich layers on K-feldspar particles was found. This could enable utilization of the particles directly as fertilizers or reducing the dependence of import of P-rich rocks.

8. Future Work

The majority of this work investigated the interactions of a relatively clean fuel (woody biomass) with bed materials, especially olivine and feldspar. Feldspar has shown to be a suitable bed material, resisting agglomeration, and achieving catalytic activity towards tar removal. To utilize the fuel flexibility of fluidized bed conversion, interactions of feldspar with alternative fuels should be investigated. Future work should investigate especially the interactions of feldspar with different agricultural residues which would improve the sustainability of fluidized bed gasification. An important issue regarding agricultural residues is the alkali content in the ash. Feldspar has shown to interact with gaseous alkali metals, however, with the experimental setup used during this work it was not possible to quantify its alkali capture potential. Future work could investigate and compare the potentials of different feldspars (K-feldspar and alkali-feldspar), to estimate their applicability as an alkali sink.

The interactions between bed material and ash change the properties of the bed material, which in the case of oxygen carriers often decreases their activity. The results obtained in this work provide insight on the changes of the elemental composition of the oxygen carriers during prolonged interaction time with biomass ash. Further research is needed to draw parallels between composition, age, and activity. This knowledge could aid to select the optimal time when to conduct the magnetic separation of the bed material to obtain the highest fraction of active particles. Apart of OCAC, other fluidized bed technologies utilizing Fe-rich oxygen carriers exist, which can be used to achieve negative CO₂ emissions. The knowledge of the changes in magnetic susceptibility of the oxygen carrier used in this work could be applied for other techniques utilizing Fe-rich oxygen carriers.

Besides the characteristics of the bed material, the generated bottom ash has the potential to be further utilized rather than being disposed of as a waste stream. If valuable elements can be extracted from the ash, fluidized bed conversion can act as a means of preconcentrating valuable elements from the fuel. Thermal conversion of ASR or other waste streams containing valuable ash elements could therefore be a suitable recycling method. Future work could investigate the possibility of extracting elements from the ash that is generated by fluidized bed conversion of these waste streams. Similarly, the phosphorus which is present in manure was found on the surface of the ash particles which is relevant for utilization of the ash as a fertilizer. However, the plant availability of the phosphorus needs to be investigated in order to evaluate the applicability of the ash as a fertilizer. Alternatively, the ash could be used as a raw material for fertilizer production.

9. References

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