

THESIS FOR THE DOKTORAL DEGREE

Choice of bed material: a critical parameter in the
optimization of dual fluidized bed systems

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Abstract

Dual Fluidized Bed (DFB) gasification is a promising alternative method for the production of biofuels. In the DFB gasification process, the bed material, which is a crucial component of the process, has two possible roles: 1) to provide the heat needed for the gasification reaction; and 2) if it has catalytic properties, to improve the quality of the produced gas. Ash-forming elements that are introduced together with the biomass into the system can interact with the bed material, and therefore have catalytic potential. As they alternate between the different environments, and depending on the nature of the bonds formed between the bed material and ash elements, some of the inorganic compounds may be released in the gas phase, thereby influencing the final composition of the produced gas. The present work advances current understanding of how biomass ash-induced changes alter the impact of the bed material on the performance of a DFB gasifier. Thus, understanding the bed material-biomass ash interactions can be used to improve the performance of the system. By improving the gasification step, which is the main step in the biomass conversion, the costs associated with the downstream processes, and consequently, the overall cost of the biomass to biofuel pathway can be reduced. In addition, utilizing naturally occurring materials as catalytic bed materials is advantageous given their relatively low price and low environmental impact which in terms of disposal of the material post-process.

The work for this thesis was conducted at the Chalmers facility. The possibilities for process improvement were investigated by the use of different bed materials in the gasifier, as well as in a secondary upgrading step. When applied to the gasification step, the interactions between inorganics and bed material alter the chemical properties of the bed, thereby influencing the gasification process. Within the investigations presented in this thesis, six naturally occurring materials were tested in the beds. Tests with silica sand, olivine sand, and bauxite were performed in the Chalmers 2–4-MW_{th} gasifier. For each tested material, the process was evaluated with respect to: 1) the composition of the produced gas; 2) the tar content; and 3) the physicochemical properties of the bed material. The key finding is that the transport of alkalis from the boiler to the gasifier, where they are released, is the major factor influencing the gas composition. An improved

understanding the importance of potassium transport was crucial in salvaging the commissioning and start-up of the GoBiGas gasification system, which had suffered from the problem of insufficient gas quality. Even though a positive effect of alkali on the gasification is known, high levels of alkali entail a risk for agglomeration. In this regard, a natural ore of iron, ilmenite, was used in the Chalmers 12–MW_{th} boiler as a material for fluidized bed combustion. It was found that ilmenite has the capability to store potassium in a non-releasable form, thereby decreasing the risk of bed agglomeration in fluidized bed boilers. To enable further upgrading of the gas produced by biomass gasification, two naturally occurring materials were tested in a Chemical Looping Reforming system: a manganese ore; and feldspar. Both materials were able to reform tars and persisted throughout the process with negligible decrease in activity.

Keywords: Dual Fluidized Bed; Chemical Looping Reforming; bed material; alkali salts; biomass ash; GoBiGas; ilmenite; feldspar; biofuel

Publications Included in this Thesis

1. Jelena Marinkovic, Nicolas Berguerand, Fredrik Lind, Martin Seemann, Henrik Thunman. Using a manganese ore as catalyst for upgrading biomass derived gas. *Biomass Conversion and Biorefinery*, 2014, pp 1-9.
2. Jelena Marinkovic, Henrik Thunman, Pavleta Knutsson, Martin Seemann. Characteristic of olivine as a bed material in an indirect biomass gasifier. *Chemical Engineering Journal*, 2015, 279(0): p. 555-566.
3. Angelica Corcoran, Jelena Marinkovic, Fredrik Lind, Henrik Thunman, Pavleta Knutsson, and Martin Seemann. Ash properties of ilmenite used as bed material for combustion of biomass in a CFB boiler. *Energy & Fuels*, 2014, 28 (12), pp 7672-7679
4. Jelena Marinkovic, Luís Tarelho, Britt-Marie Steenari, Martin Seemann. Influence of wood ash on the gasification process in the Chalmers indirect BFB gasifier. *In the process of internal review before resubmission*, 2015
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Jelena Marinkovic is the principal author of Papers 1, 2, 4 and 5. Angelica Corcoran is the principal author of Paper 3, which is the result of work towards a Master's degree thesis supervised by Jelena Marinkovic. Nicolas Berguerand and Fredrik Lind contributed with experimental work and editing for Paper 1, and Nicolas Berguerand is principal author of Paper 6. Theresa Berdugo Vilches is the principal author of Paper 7, which summarizes and compares all the investigations undertaken within the scope of this thesis and is the result of mutual discussions and extensive experimental work with Jelena Marinkovic. Martin Seemann, who is the assistant academic supervisor, contributed to the discussion and participated in the experimental work and editing of all the papers. Henrik Thunman, who is the principal academic supervisor, contributed with ideas and discussions, as well as comments on all the papers.

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Jelena Marinkovic, Göteborg 2016

*To my father,
who always believed in me
and taught me that persistence and hard work always pay off.*

*Za mog oca,
koji je uvek verovao u mene
i koji me je naučio da se upornost i rad uvek isplate.*

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1. Introduction

1.1. Dual Fluidized Bed

Energy production from biomass has attracted strong interest as it represents a means for decreasing CO₂ emissions. Furthermore, increased production of energy from biomass may lead to an end to the dependence on fossil fuels [1-5]. However, this route of energy production is reliant on the availability of a biomass source. Sweden, being a biomass-rich country, aims towards energy independence and has set the goal of having a vehicle fleet that is fossil fuel-free by Year 2030 and with zero net emissions of greenhouse gases by Year 2050 [6].

Biomass gasification is a sustainable way to meet the increasing demands for energy in modern society. The gas that is produced through biomass gasification contains CO, CO₂, CH₄, H₂, H₂O, and N₂, together with some light hydrocarbons. In addition, impurities, such as tars and inorganic compounds, are present. The final composition of the produced gas depends on the gasification method and fuel used. Tars, which are present in the product gas, represent a loss of chemically stored energy and are deleterious for cold regions within the system. Condensation of tar species in the system results in clogging and leads to severe operational problems [2, 7-10]. Inorganics that originate from the fuel, such as potassium, chlorine, and sulfur, cause corrosion and slagging problems and are detrimental to the catalysts acting downstream of the gasification process.

A schematic of the biofuel production process, starting from the biomass, is shown in Figure 1, where each box represents several operational units. After appropriate pretreatment of the biomass, the main step of the ‘solid to gas’ conversion takes place. In order for the gas that is produced in the gasification step to be used further along the process chain (product synthesis), it needs to fulfill specific requirements regarding purity, H₂/CO ratio, and CO₂ content. To meet these requirements, several operational steps are needed, which drastically influence the overall cost of the process. Optimization of the gasification part of the process is the first step towards decreasing the cost of the overall process, which entails improving process efficiency and simplifying the gas-conditioning process.

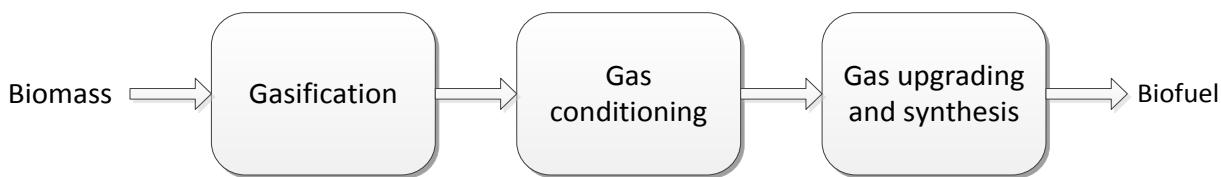


Figure 1. Schematic of the biomass to biofuel production process *via* gasification.

One gasification technique that can be used is Dual Fluidized Bed (DFB) gasification (Fig. 2). The underlying principle of the process is the circulation of the bed material, which is used as a source of heat for the endothermic gasification reaction. The bed material is heated in the combustion section by burning a portion of the fuel and is then circulated to the gasification section where it releases the heat and enables the gasification reaction. The combustion section is fluidized with air, while the gasification section can be fluidized with steam. As the gasifier in this set-up is separate from the combustion chamber, the raw gas product is not diluted with nitrogen, underlining the advantage of this gasification technique over direct gasification (where air is used as the gasification medium). DFB gasification has been successfully implemented in several demonstration CHP-plants, including Güssing, Oberwart in Austria and Senden in Germany, and in one plant for the production of SNG, GoBiGas in Göteborg, Sweden. However, to achieve economic profitability, improvement of the process is still needed. The aim is to increase the efficiency of the process to >85%.

The same principle of DFB can be applied downstream of the gasifier for secondary step-gas cleaning, in which the employed bed material is catalytically active. Chemical Looping Reforming (CLR) is similar to the Fluid Catalytic Cracking (FCC) process commonly used in the oil industry. The CLR unit employs two reactors in which the catalyst reforms the raw gas in one reactor (reformer) and is then reactivated with diluted air in the other reactor (regenerator). In the regenerator, circulated catalytic material that is deactivated by the carbon deposits in the reformer regain activity after deposits are burnt off. Since it is applied downstream of the gasification process, this system facilitates optimization of biomass conversion to raw gas.

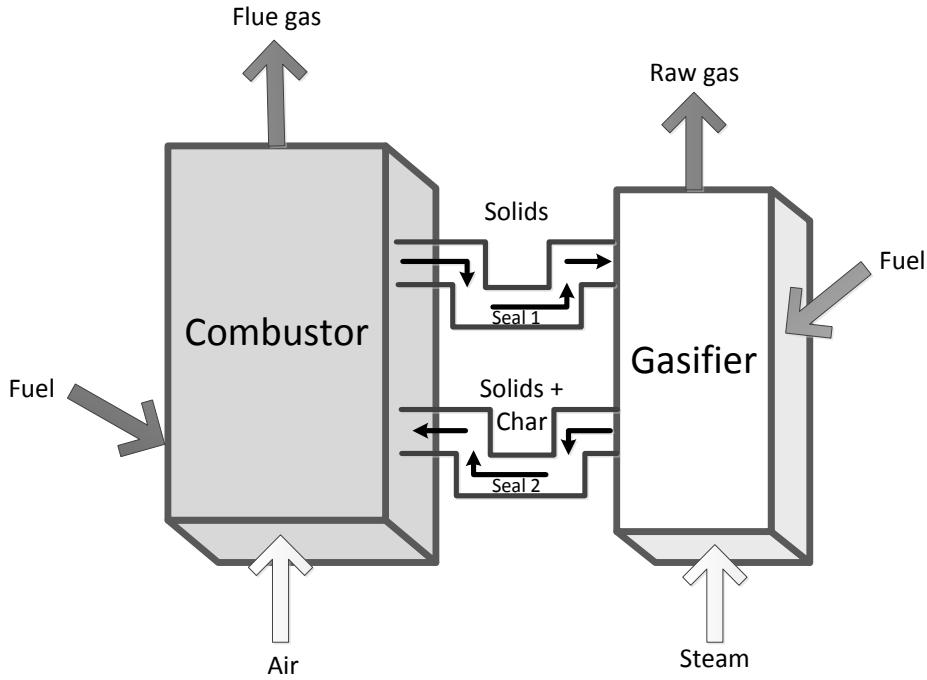


Figure 2. Schematic of the Chalmers Dual Fluidized Bed Unit.

1.2. Biomass and ash

For the utilization of gasification to become CO₂-neutral, biomass is the fuel of choice. Biomass comprises all organic materials originating from plants, such as trees, crops, and algae, with C, H, and O being the principal elements. In thermochemical conversion of the biomass particle, ash is generated as a residual product. The ash content of the biomass and its composition are highly dependent upon: the origin of the biomass; growth conditions; the part fraction and the time of harvesting. The ash content can range from less than 1%wt. for wood, up to a few percentage points for herbaceous biomass [11, 12]. The main ash-forming elements are Ca, Si, K, Na, S, Cl, Al, Fe, P, Mg, and Mn. These elements, their levels, and their associations exert significant influences on the performance of the process and may even raise environmental issues [13, 14]. Depending of the distribution of aforementioned elements, biomass ash entails problems for the operation of the system. The critical and the most reactive elements are K, Ca, Si, S and Cl; their distribution pattern in a DFB system is schematically presented in Figure 3.

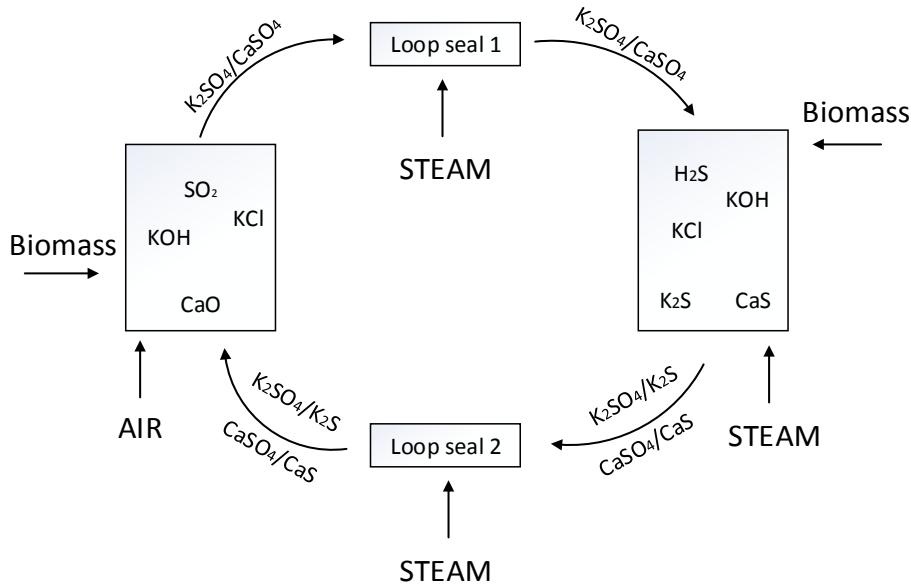
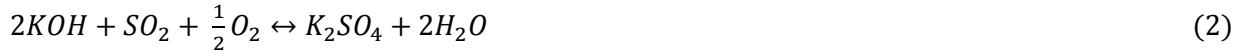


Figure 3. Schematic of the flow of ash elements in the DFB gasifier.

Potassium is one of the most important ash elements. It is released from the biomass already during devolatilization to the gas phase where it is involved in reactions, chemical and physical, with not only other ash-forming elements, but also with the bed material. When bound to chlorine, potassium in the form of KCl represents a high risk for corrosion, while potassium released in the form of a sulfate creates deposits on heat transfer surfaces [15]. The presence of high levels of potassium and silicon in the biomass creates problems of slagging and agglomeration, as the reaction of volatile potassium with silicon form a non-volatile mixture that has a low melting point [16, 17]. Agglomeration due to ash melting can cause bed defluidization in a DFB system and lead to shut-down of the process, with consequent increased maintenance costs [18]. Whether potassium will form chloride, sulfate, or silicate compounds in the system depends on the ratios between these elements in the system. Moreover, the presence of calcium can affect the reactions and prevent the formation of potassium silicate [19]. During the combustion of biomasses of different origins (willow, forest residue, and waste wood), Valmari et al. [20] observed that potassium, rather than forming the chloride or sulfate species tended to react with silicon in the fuel, in the case of a silicon-rich fuel. Thus, the fraction of the potassium that forms K_2SO_4 is highly dependent upon the Si/K ratio. A high silicon concentration in the fuel or the bed material leads to the formation of potassium silicates rather than potassium sulfate [21, 22].

Sulfur is released from the biomass during devolatilization and char conversion. Depending on the prevailing gas atmosphere and ash composition, the sulfur ends up in the produced gas in the form of H_2S , COS, SO_2 or organic sulfur components (thiophene, dibenzothiophene etc.) [23]. These components further react with alkali and alkali earth metals to create sulfides and sulfates, depending on the environment in the reactor. Thus, the presence of alkali and alkali earth metals in the biomass promotes the retention of sulfur in the ash [24]. The formation of sulfates of potassium and calcium in an oxidizing environment follows reactions (1), (2), and (3) [20]:



A study of biomass combustion performed by Nordin et al. [24] showed that ash has the ability to bond levels of sulfur in the bed similar to those bound by $CaCO_3$, which was used as the additive material. Considering the aforementioned interactions between Ca, K and Si and those between S, K and Ca, Knudsen et al. [25] concluded that sulfur retention in the ash is a function of the Si/(Ca+K) ratio. This means that the combustion of a silicon-lean fuel results in greater retention of sulfur in the ash, as compared with the combustion of a silicon-rich fuel due to the creation of K- and Ca-silicates, which prevent sulfate formation.

The sulfation reaction (1) presented above is highly sensitive to the sulfur concentration in the flue gas. Thus, an increased SO_2 content in the flue gas can redirect the chemistry from chloride formation towards the sulfation reaction. Increasing the sulfur concentration in the reactor above the fuel feed is recognized as a measure for controlling the $KCl_{(g)}$ concentration in the flue gases [26].

With regard to the aforementioned problems caused by the presence of ash, additives, such as kaolin, calcite, and bauxite, have been investigated as sorbents that could prevent the undesirable release of potassium- and sulfur-containing compounds to the gas phase [27, 28]. With this approach, the chemical reactions in the system can be controlled to some extent.

1.3. Bed materials

The concept of a DFB gasifier is reliant on the circulating bed material, the main role of which is to supply the heat needed for the gasification reaction. However, through careful selection of catalytically active materials, the bed material can be used for optimization of the gasification process. In this way, it is possible to increase the quality of the produced gas by facilitating a high level of fuel conversion and ensuring low levels of tar, sulfur, and alkali in the gas.

The bed materials used in DFB gasification systems need to be durable, considering the temperature and environmental fluctuations to which they are subjected during circulation. Figure 4 shows a simplified schematic of the pathway taken by the bed material during one cycle in the system. In the boiler, the bed material is exposed to an oxidative environment in the upper part of the reactor (freeboard), while in the region close to the fuel feed, the material encounters a locally reducing environment. Within the gasifier, the bed material is exposed to a very reducive environment in the region where the fuel is being devolatilized, while at the same time it

experiences a mildly oxidative environment at the bottom of the bed, where the steam is fed into the reactor. Furthermore, as it circulates between the two reactors, the bed material is exposed to the mildly oxidative environment in the two loop seals. In the Chalmers unit, in which all the investigations of the present work were conducted, the fuel is fed in at the top of the gasifier and consequently, in the gasifier itself the two aforementioned zones (steam-rich zone and volatile-rich zone) are clearly distinguishable.

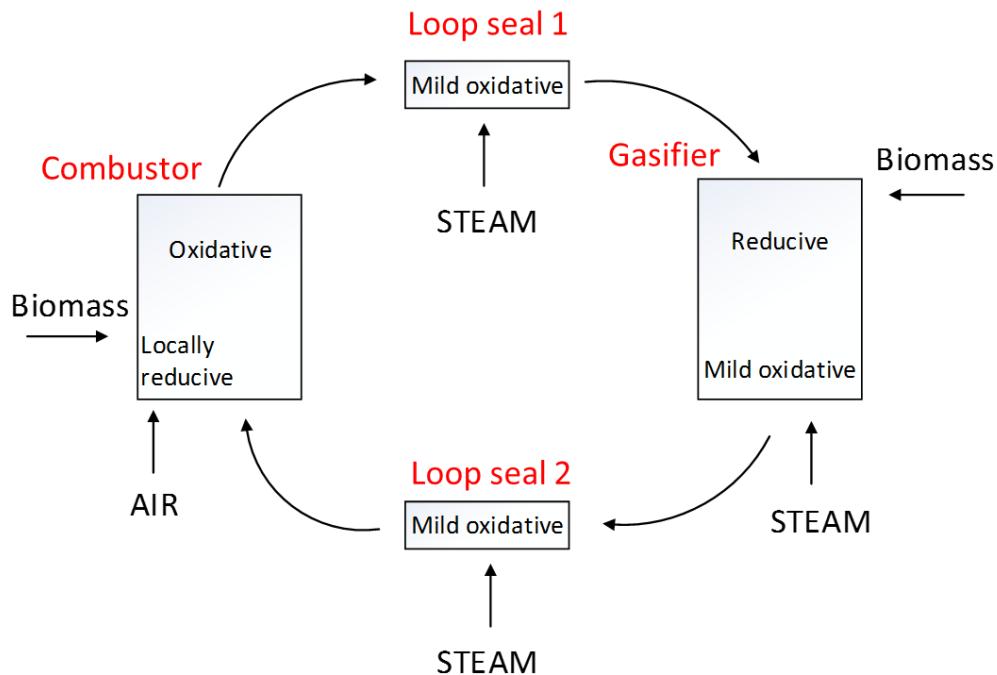


Figure 4. Schematic of the pathway taken by the bed material during one cycle in the Chalmers DFB system.

Reflecting on the complexity of the system and the chemical interactions that occur therein, the selection of bed material to be used in the process has to be done carefully. The properties of the material that need to be considered (Fig. 5) are as follows:

- Mechanical properties (resistance to thermal and mechanical degradation);
- Chemical properties (catalytic activity, low oxygen-carrying capacity, resistance to chemical degradation, and desirable interactions with ash-forming elements);
- Economic aspects (good availability and low costs for disposal).

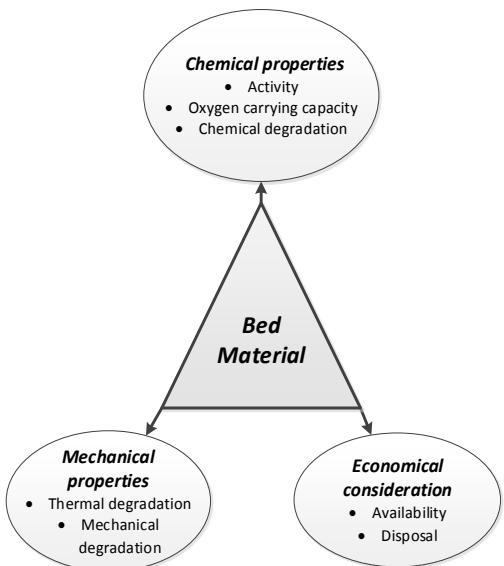


Figure 5. The primary criteria for selecting a bed material for use in a DFB gasifier.

MECHANICAL PROPERTIES OF BED MATERIALS

As mentioned above, the bed material in the DFB gasification system undergoes environmental changes, temperature swings, and fluidization. These conditions have impacts on the structure of the bed material, with consequent mechanical and temperature-related degradation.

In general, mechanical damage results in a loss of mass or function of the bed material. As fluidized beds are in the topic of this work, the loss of mass caused by attrition is a particularly common phenomena and resistance to attrition is one of the most important properties of the bed material. Considering the temperature used in DFB process, sintering of the catalytic material can occur. Sintering is influenced by temperature, the atmosphere, and the type of metal. A higher temperature is beneficial for the sintering process, while the presence of steam and alkali in the atmosphere accelerates sintering for some metal oxides, such as alumina, by forming new phases and mobile surface hydroxyl groups, which volatilize at high temperatures [29]. The presence of high levels of carbon species in the system can also affect the performance of the bed material. This effect is known as fouling, which involves mechanical degradation of bed material due to physical deposits on the surfaces of the particles, which in an advanced stage result in pore blockage and disintegration of the catalyst particles.

CHEMICAL PROPERTIES OF THE BED MATERIAL

The chemical activity of the bed material is the property that has the strongest impact on the final gas composition, due to its effect not only on the heat balance, but also on the chemistry of the system. An active bed material can be used as a primary or secondary measure for gas upgrading, depending on whether it is applied within the gasification unit itself or in a process downstream of the gasifier.

Not only that the gas composition is affected by the catalytic activity of the material, but also the rate of fuel conversion. Numerous bed materials have been investigated previously, being either added directly to the gasification process or used as active agents for secondary cleaning of the gas, downstream of the gasification process. The tested bed materials include metal-based, metal-oxide-based, and alkali-salt-based compounds. In many cases, in order to increase the mechanical stability and/or to provide a large surface area, the active component is combined with a support material. Commonly, the support is an inert oxide, such as Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , MgO , CeO_2 or zeolites (microporous solids based on alumino-silicate). In Figure 6, the spectrum of activities, in relation to fuel conversion and both tar and sulfur removal, is shown for different bed materials.

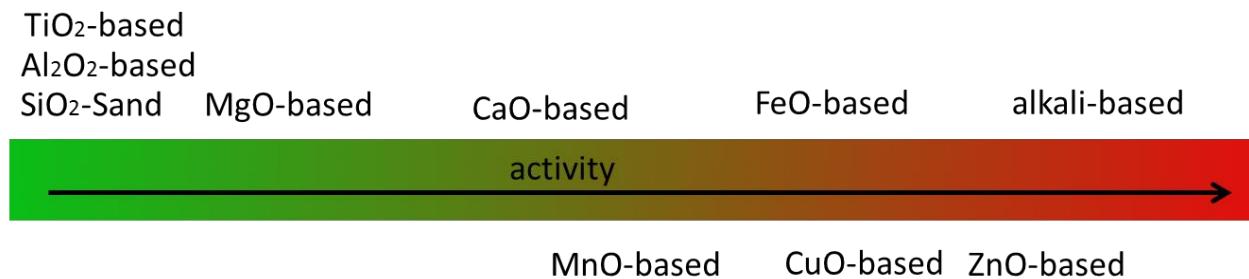


Figure 6. Activity spectrum for a range of oxide-based bed materials.

Silica sand is considered to be inert within the system, as it will not increase the quality of the produced gas, e.g., provide a high hydrogen yield or low tar content. The same is true for oxides that are used as a support. For the purpose of improving the characteristics of the produced gas, numerous naturally occurring materials and synthetically produced materials based on Ca-, Fe-, and alkali-salts have been studied [3, 7, 10, 30-32]. FeO- and CaO-based materials have been studied both as primary and secondary catalysts, while CuO-, ZnO-, MnO-, and NiO-based catalysts have been studied mainly as tar- and sulfur-cleaning materials at high temperatures [10, 33-37]. Alkali salt-based catalysts have been studied in different process set-ups for the purpose of increasing the rate of carbon conversion in the gasification process [3, 38-41]. Figueiredo et al. have presented a scheme (Fig. 7) of reactions for the potassium-catalyzed steam gasification of

coal, starting from the various potassium salts [42]. In addition, some salts, such as K_2CO_3 , have been shown to be active in suppressing the formation of tar species [7, 43]. Even alkali salts that originate from the wood ash have shown a catalytic effect on the reactivity of the fuel [44].

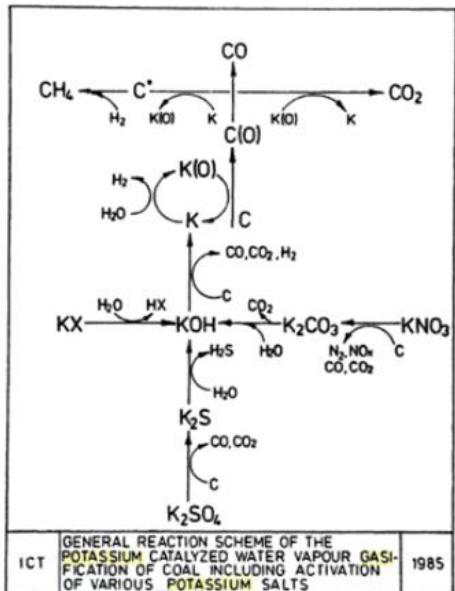


Figure 7. Schematic of potassium-catalyzed carbon gasification starting from three different salts [42]

A naturally occurring material, olivine $[(Mg,Fe)_2SiO_4]$, has been extensively studied as a catalytic bed material for *in situ* gas cleaning in gasification processes. Studies have been performed with both the pure form and olivine mixed with an active component, such as Ni or Fe [3, 5, 32, 45], and it has been shown that to achieve the desired catalytic effect for tar species, the olivine needs to be activated. The mechanism of olivine activation has been attributed to the migration of Fe to the surface of the particle, interactions with inorganics in the ash, and the formation of the CaO layer [45-48]. The use of an iron-based natural ore, ilmenite ($FeTiO_3$), has been studied intensively in Chemical Looping Combustion (CLC) systems due to its oxygen-carrying ability [49]. Partially reduced ilmenite also has been shown to have the ability to reform biomass-derived raw gas. Lind et al. [50] demonstrated the reforming capability of partially reduced ilmenite in the Chalmers CLR unit and reported a tar conversion rate of 60% when 100% ilmenite was used. In the same system, synthetically produced NiO- and Mn_3O_4 -based catalysts decreased the total tar level by 95.0% and 44.5%, respectively [36, 50]. In addition to the main bed material, additives can be introduced into fluidized bed systems. Aluminum-based materials, such as bauxite, kaolin, and emathlite are commonly used for alkali adsorption and the prevention of corrosion [27, 28, 51, 52].

When a metal oxide bed material is used in the DFB gasification set-up, the problem of oxygen transport can appear due to the occurrence of oxidation in the combustion section. Circulation of

oxidized bed material to the gasification part of the unit may result in the combustion of valuable gas components and dilution of the gas with CO₂. As a consequence, the heating value of the produced gas is decreased [53].

The presence of impurities in the system, such as sulfur, which end up in the produced gas, may poison the catalytic material. Catalysts are used in several steps of the biofuel production process. Downstream of the gasification unit, in the final synthesis step, noble metal-based catalysts, which are highly sensitive to the presence of impurities, are used. Sulfur derived from the gasification gas acts as a poison for the active sites in the catalytic material, which results in complete deactivation of the catalyst [29]. The levels of sulfur in the produced gas depend on the type of biomass used in the process. In general, compared to gas derived from coal gasification, the sulfur level in the gas obtained by biomass gasification is relatively low. However, in order for it to be processed further without any negative effect on the catalyst used downstream in the process, an acceptable level of H₂S in the gas often has to be set at ≤1 ppm [54].

ECONOMIC CONSIDERATIONS ASSOCIATED WITH THE BED MATERIAL

Even though the chemical activity of the material has a crucial impact on the final product gas, economic factors determine whether or not a specific material is going to be used as the bed material in a large-scale unit. A balance between the activity and the price of the fresh material has to be reached. When discussing the price of a bed material, the costs linked to both procurement and disposal need to be considered. In the process of biomass gasification, the bed material interacts with biomass ash-forming elements, which results in changes to its chemical and mechanical properties. It can even lead to degradation of the bed material over time; if there is no option implemented for the regeneration and re-use of the same material, partial or complete exchange with fresh material needs to be carried out. After use, the degraded bed material from the system needs to be disposed of in line with environmental protection laws, which entails an additional cost. Taking into account both the purchase of the fresh material and the costs for its eventual disposal, the use of natural materials instead of synthetically produced materials is beneficial. In the past, several oxide-based ores, such as olivine, calcite, dolomite, ilmenite, manganese ore, and bauxite, have been investigated in terms of their potential applications to the thermochemical conversion of solid fuels [50, 55-58].

A bed material to be used in the process of biomass gasification will undergo elemental composition changes due to interactions with ash elements. The means of disposal of the material post-process naturally depend on the final composition of the material and its toxicity, e.g., content of hazardous elements (heavy metals). One option for the disposal and use of the biomass ash is as a fertilizer or soil amendment agent. To meet the requirements for landfilling, environmental regulations stipulate that only specified concentrations of these elements can be present in

leachable form. Alternatives uses for ash include the production of ceramics and construction materials [14].

While synthetically produced catalytic materials have advantages regarding chemical activity, depending on the used metal, the costs of manufacturing and disposal can be high. Reflecting on the materials investigated within the scope of this thesis, olivine can be problematic with respect to disposal, as it contains certain levels of chromium and nickel. Despite the fact that it is a mineral rock and has a low price on the market, as compared to the synthetically produced materials, the eventual disposal of olivine entails additional costs.

1.4. Interactions between the bed material and biomass ash

Besides the bed material and its constituents, the ash elements that interact with the bed material and change its physicochemical properties will be one of the important factors for determining the final gas composition. The most interesting ash elements, which are also those that are the most heavily involved in the reactions within the system, are: K, Ca, Si, S, and Cl. These elements interact with bed material, which can result in agglomeration of the bed [16, 17, 59, 60], as a negative consequence, or in the acquisition of enhanced catalytic properties of the bed elements [3, 47, 61-63], as a positive consequence. Considering the different zones within the system, as described in Section 1.3, the accumulated ash elements can have catalytic activity or even be released from the bed material into the gas phase in specific parts of the system.

The nature of the aforementioned interactions depends on the bed material, its composition and content of biomass ash, the temperature, and the reductive potential of the surrounding gases. Partial exchange of the bed material within the system is commonly used as a measure to prevent agglomeration. This process involves the exchange of a certain amount of the bed inventory with fresh material on a daily basis.

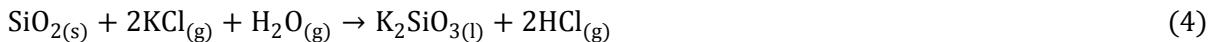
Interactions between the ash components and bed particles can occur on the physical or chemical level, resulting in the formation of layers around the particle. Zevenhoven-Onderwater et al. [64] concluded that these layers are formed *via* three alternative modes of interaction:

- the particle acts simply as a carrier of the ash layer (the layer contains elements that originate exclusively from the fuel);
- a chemical reaction occurs between the particles and ash elements (the layer contains elements that originate from both the fuel and bed material); and
- a combination of the first two interactions.

In a DFB system, the bed material together with the ash is eventually distributed in the following forms: the bottom ash (consisting of ash-coated bed material); coarse ash (consisting of bed

material and ash - a consequence of attrition); and fine fly ash (consisting mainly of ash components) [20]. The nature of the bonds formed between the bed material and ash elements can be chemical or physical or a combination of both types. Considering the presence of numerous elements in the system, as well as the different environmental zones (see Section 1.3), the chemical reactions that involve ash-forming elements are numerous and complex. Chemical equilibrium-based software packages are often used to describe the aforementioned chemistry in the system [26, 60, 65, 66]. However, in reality, the system is not in a steady state, and the use of minerals as the bed material for the process raises certain limitations regarding the selection of all the relevant species that should be included in the calculation. Therefore, this type of software can only be used as an indicative tool and as a supplement to other results.

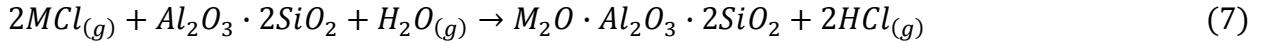
The interaction of ash components with the bed material will differ depending on its main constituents, such as silicon, aluminum, titanium or magnesium. When a *silicon-based* bed material is used, e.g., quartz sand, the alkali elements in the biomass interact chemically with the bed particles. Potassium that is released from the biomass diffuses into the sand particles, creating a eutectic mixture with a relatively low melting point and causing operational problems, such as agglomeration. The problem of agglomeration in relation to the fluidized bed technology has been studied extensively [16, 17, 67]. The reactions responsible for the generation of silicate, the formation of which is considered to be the initiation step of the agglomeration process, are as follows:



The reactions result in a melted layer being formed around the particle. The thickness of the layer increases with increasing ash content of the fuel, as well as increases in the duration of the operation [68, 69]. Potassium that is bound in this form is not active towards the gas, tar or char in the system.

An alkali earth metal, Ca, is expected to react in similar way with quartz-sand, to form Ca-silicate, which has a higher melting point than the K-silicates. He et al. [68] has shown that the composition of the ash layer around the particle is a function of the bed material used and the fuel composition, while it is also dependent upon the reactor set-up. After investigations were carried out on the interactions between biomass ash and a quartz-sand, the formation of melted K-silicate was proposed as the first step in the ash coat build-up. In addition, Ca was shown to react with melted K-silicate, resulting in the release of K and the formation of Ca-silicate. The interactions were tested in two different set-ups, a BFB and a CFB system, and as a result, they showed different elemental distributions within the layers formed around the sand particles. The layer that formed around the particles extracted from the BFB boiler is consisted of a Ca-rich silicate layer, while the particles extracted from the CFB boiler had two layers: an inner layer rich in K; and an outer layer rich in Ca.

Naturally occurring *aluminum-based* materials have been extensively investigated as alkali-adsorbing materials in combustion systems, where the following reaction most probably occurs with alkali-chloride [70]:



With regard to natural aluminum-based materials, Al oxides as an alkali getter have been tested in the form of kaolin, bauxite, and emathlite [27, 28, 51]. All these materials show good adsorption properties for the alkali, although the types of interactions that occur between the alkali and aforementioned materials are highly dependent upon the concentration of impurities, mainly SiO₂. Among the tested materials, kaolin has been shown to be superior to bauxite for this application, mainly because the adsorption of alkalis to kaolinite is irreversible and the saturation levels are higher. Bauxite was found to be the most sensitive to process fluctuations, with consequent partial release of the alkali back into the gas phase [27, 71]. The differences in these behaviors can be explained by the different concentrations of Si in the materials, given that adsorption of the alkali to silicate is chemical in nature, while that to aluminum is physical [72]. Consequently, the reaction that occurs between alumino-silicates and alkali is a combination of both chemical and physical process [73].

Magnesium-based materials, specifically MgO, have been used mainly as support materials for active oxides, such as Fe₂O₃ [74]. The effect of MgO on the pyrolysis of cotton seeds has been tested, and it has been shown that an increase in the MgO content of the bed material increases the gas and char yields; however, interactions with biomass ash were not investigated. [75]. Naturally occurring MgO-based materials that are widely used for biomass gasification purposes include olivine and dolomite [76]. Both materials have shown to be active for tar decomposition, while the activity of olivine was found to increase following interactions with ash components [45-47, 77].

Titanium-based materials, in similarity to MgO, are mostly used as support materials for the catalyst. However, the use of TiO₂ as an additive in a straw combustion process has been performed with the aim of decreasing K vaporization [78]. In that investigation, KTi₈O₁₆ was detected as a resulting component and a reaction pathway through K₂CO₃ thermal decomposition and reaction of gaseous potassium with TiO₂ was proposed:



Besides the bed material, the composition of the ash and the presence of ash particles in the gas stream are of relevance, as described by Frandsen et al. [79] in a parametric study of wheat straw combustion. It was concluded that the process of formation of an alkali aerosol was very much dependent upon the chemical composition of the fuel and the presence of the particles in the flue

gas stream. The same group showed that the introduction of coarse fly ash particles into the flue gas stream could prevent the formation of K_2SO_4 and KCl aerosols. This outcome was attributed to the interaction of the gaseous K_2SO_4 and KCl with ash particles, e.g., heterogeneous condensation. By introducing additional particles, more of the surface was made available for salts to condense on, which reduced the possibility of aerosol formation. In the circulating fluidized bed reactor, this phenomenon can be very important.

1.5. Outline of the thesis

Even though the concept of DFB gasification has been ably demonstrated, for the commercial scale, this process still needs to be upgraded, as around 30% of the investment cost for the gasification section of a biofuel plant is allocated to the gas cleaning equipment. The goal is to derive a gas of higher quality from the gasifier, e.g., a gas that has a high yield of hydrogen and low tar and sulfur contents. One way of influencing the quality is to use an active bed material in the system. However, this has to be achieved at a reasonable cost. Therefore, the present work is motivated by the need to identify bed materials that are suitable for this purpose and a strong desire to increase our understanding of the relevant processes.

The work of this thesis, which is schematically depicted in Figure 8, focuses on the optimization of the biomass-to-biofuel route using an active bed material as a tool. Both primary measures (improvement of the gasification step) and secondary measures (upgrading of the produced gas) were investigated. The use of natural materials is emphasized given their wide availability and low cost of disposal. All the investigations discussed in this thesis were conducted at the Chalmers facility, using the Chalmers DFB gasifier and CLR unit. The performance profiles of the units, as a consequence of the change of bed material, were evaluated using analyses of the gas composition and of the tar content of the produced gas.

The potential for optimization of gasification as a primary step in biofuel production is investigated in Papers 2, 4, 5 and 7. Three natural materials, olivine, quartz-sand, and bauxite, were used in the Chalmers DFB gasification system, while ilmenite was investigated as a material for combustion purposes. The materials display different characteristics regarding alkali incorporation, oxygen-carrying capacity, and catalytic activity. All the materials are expected to be able to bond alkali, although the formed bonds are different in nature (chemical or physical), and this determines the tendency to release the alkali under reaction conditions. Quartz sand serves as an example of an alkali getter material with minimal oxygen-carrying capacity and minimal catalytic properties. In contrast, olivine has limited capacity as an alkali getter, can transfer limited amounts of oxygen, and is catalytically active towards tar species. Bauxite is known to bond selectively with potassium depending on the surrounding atmosphere. During the time of operation of the gasifier, bauxite showed significant oxygen-carrying capacity and catalytic activities for tar and char conversion.

The findings derived from the investigations presented in this thesis found a direct application on 20 MW SNG biomass gasification GoBiGas pilot plant. The specific set-up of the Chalmers gasifier, which allows the retention of inorganics in the system, and thereby enables rapid enrichment of the bed material with ash elements, prompted the realization of the importance of the presence of alkali in process. A collaborative project involving the addition of alkali salt and sulfur to the GoBiGas system, as a measure of the activation of the material, led to the successful start-up and running of the process unit.

Finally, the Fe-containing ore ilmenite was studied as a bed material with the goal of improving CFB boiler performance. The ability of ilmenite to minimize potassium release without forming low-melting-point eutectics in the boiler is described in Paper 3. The influence of the ash components in combination with the bed material on the performance of the system was the focus of all the studies. These investigation underline the importance of carefully selecting the bed material in combination with the fuel to be used in the process.

The use of the DFB set-up and a natural catalytically active material downstream of the gasification step is discussed in Papers 1 and 6. The Mn₃O₄-based ore behaves as an oxygen carrier and as a catalyst towards tar species, while feldspar is characterized as a material with low-level oxygen transport and activity towards specific tar compounds.

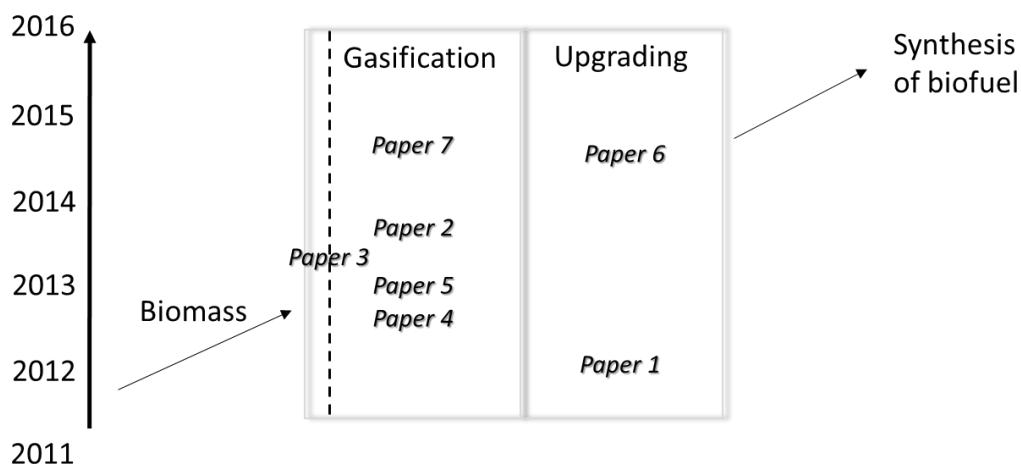


Figure 8. Schematic of the work of the thesis.

2. Method and Experimental Setup

2.1 The Chalmers DFB unit, measurement techniques, and bed materials tested

All the bed materials discussed within the scope of this study were investigated in the Chalmers DFB system. The Chalmers gasification unit comprises a 12-MW_{th} circulating fluidized bed boiler and a gasifier, which is a 2–4-MW_{th} bubbling fluidized bed, fluidized with steam. The two reactors are connected by loop seals, which are fluidized with steam. A schematic of the unit is shown in Figure 9. The circulating bed material, which is heated in the boiler, provides the heat needed for the gasification process. In the boiler, the bed material is heated by burning a portion of the fuel. Wood chips are used as the main fuel in the boiler, while wood pellets are used in the gasifier. The gasifier usually operates at a temperature of around 820°C. This set-up has also been used in the experiments performed for this thesis. After the gasification reaction, the remaining char is circulated together with the bed material to the boiler, where it is burnt. Raw gas produced in the gasifier is directed *via* the raw gas line to the boiler, where it is combusted. A detailed description of the Chalmers system is provided by Larsson et al. [80]. The specific set-up for raw gas recirculation enables greater retention of the ash elements in the system, resulting in a faster response of the system to the effects of mobile ash compounds.

In Figure 9, the letters A–D indicate the locations at which the bed material can be sampled. For the work presented in this thesis, sampling was carried out at Loop seal 1 (point B) and Loop seal 2 (point C). These two positions represent the entry and exit points of the gasifier. In Figure 10, the specially developed probe used for bed material sampling is shown. The sampling was done during the operation of the gasifier. The probe is equipped with a cooling system and works on the suction principle. The procedure starts with the injection of air to clear the pipe, followed by the application of suction pulses, until the probe is filled with the sample. The probe is then removed, allowed to cool, and the sample is collected. The sampled material was analyzed by the following four methods: Scanning Electron Microscopy and Energy Dispersive X-Ray spectroscopy (SEM/EDX); leaching analysis using Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS); dissolving analysis (performed by an accredited laboratory); and X-Ray Fluorescence (XRF) analysis. SEM/EDX was carried out using the FEI Quanta 200 Field Emission Gun ESEM, equipped with an Oxford Inca EDX system for chemical analysis. Line scanning and mapping were performed on chosen particles to determine the elemental compositions of the layers that were visible in the particle cross-sections. To draw conclusions regarding which elements were present in releasable form in the solid sample, e.g., in the form of salts, a leaching analysis with deionized water was conducted.

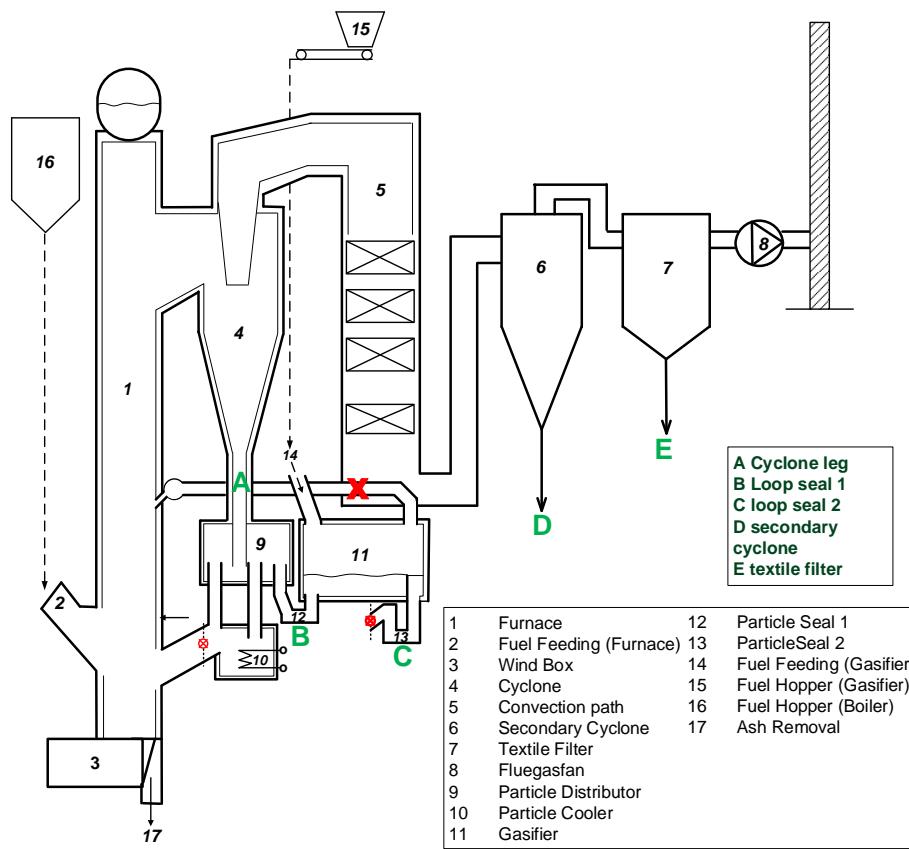


Figure 9. Schematic of the Chalmers Dual Fluidized Bed System. The red X corresponds to the sampling point, while the red circles represent connection points between Loop seal 2 and the down-comer to the boiler.

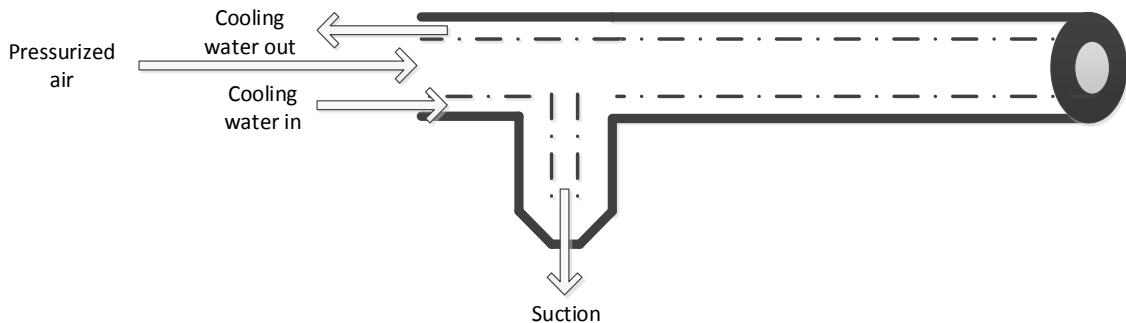


Figure 10. Schematic of the probe used for sampling the bed material.

For the experiments, one small stream of the produced raw gas was led through a heated line to the gas conditioning system, and thereafter to sampling and analysis. From the same line, the tar content of the gas was sampled (indicated by the red X in Figure 9). The composition of the permanent gases was analyzed by Varian CP4900 Micro-Gas Chromatograph (micro-GC). The tar in the raw gas was sampled using the Solid Phase Adsorption (SPA) method. The involved two types of amines, with and without inclusion of the carbon layer. The samples were further eluted and analyzed in a Gas Chromatograph equipped with Flame Ionization Detection (GC-FID). The procedures for sampling, elution, and analysis are described in detail elsewhere [81]. The identified tar components of the gases are discussed in the following groups: benzene; 1-ring components; naphthalene; 2-ring components; \geq 3-ring components; and heterocyclic aromatics. The samples that were acquired using the amine without a carbon layer showed lower accuracy levels for the benzene and 1-ring components, as compared to the samples acquired using the amine with a carbon layer. The results for the tar levels in the raw gas from the investigations are discussed accordingly. Each measurement point represents the average value calculated over approximately 30 minutes of analysis during stable operation of the gasifier. During the measurements, a known flow of helium was added to the gasifier so that the fuel conversion could be quantified. In parallel with some of the experiments performed within the scope of the thesis, another slipstream of the produced raw gas was directed to the High-Temperature Reactor (HTR) [82], where it was heated to 1700°C and converted into CO₂, CO, and H₂, thereby allowing quantification of the total carbon, hydrogen and oxygen.

Within the scope of this thesis, three natural materials, quartz-sand, olivine, and bauxite, were tested for suitability as bed materials in DFB gasification. The influences of these bed materials on the performance of the gasifier were evaluated with respect to gas composition, amount of tar in the gas, and cold gas efficiency. The fourth bed material, ilmenite, was assessed predominantly for its alkali-sequestering potential in the combustion unit. The focus of all the experiments was the interactions between the biomass ash and bed material, with emphasis on the interaction with potassium.

Quartz-sand

In the Chalmers gasification unit, quartz-sand is the standard bed material. Considering the relative inertness of amorphous silica as a heterogeneous catalyst, the influence on the produced gas composition is expected to be negligible. For this reason, quartz-sand can be regarded as a reference case for a material that acts exclusively as a heat carrier that provides the heat for the gasification process. However, as discussed above, ash-forming elements present in the biomass interact with the bed material and may change its properties. Interactions of quartz-sand with the ash and the retention of inorganics are described in Paper 4. In addition, the retention of sulfur and the phenomenon of its circulation within the system are discussed.

High-purity quartz-sand with the elemental composition listed in Table 1 was used in the experiment. The operational conditions presented in Table 2 cover two separate experiments: Case A, in which aging of the unit's inventory of sand was tested (I_A to V_A); and Case R, in which partial exchange of the sand was carried out (I_R to VII_R). To isolate the aging effect, no regeneration was carried out in Case A for 4 days. As shown in Table 2, the operational points (sampling time-points I_A to V_A) have comparable parameters and consequently, changes can be attributed to the aging effect. Between time-points IV_A and V_A , approximately 55 wt% of the bed inventory was exchanged by fresh quartz-sand. Case R, in which there was 20% wt. daily exchange of the quartz sand (I_R to VII_R) was used to study the phenomenon of elevated H₂S content in the raw gas.

Table 1. Chemical composition of the quartz-sand, as provided by the supplier.

Oxide	Weight%
SiO ₂	99.2
Fe ₂ O ₃	0.054
Al ₂ O ₃	0.17
LOI	0.1

Table 2. Operational conditions used in the aging experiment.

<i>Gasifier</i>			<i>Boiler</i>			
<i>Experimental point/day</i>	Temperature , [°C]	Fuel feed _{ar} , [kg/h]	Steam, [kg/h]	Temperature , [°C]	Fuel feed _{ar} , [kg/h]	Bed circulation, [kg/h]
I_A	814	294.39	160	856	2067.17	17576
II_A	824	294.00	160	867	2036.11	16777
III_A	817	299.74	160	867	2031.12	NM*
IV_A	821	293.05	160	871	1935.42	15457
V_A	827	293.28	160	870	1857.78	17426
I_R	833	391.09	209	860	1900.58	20400
II_R	827	393.00	262	860	1923.77	19100
III_R	829	397.11	311	860	1810.08	23100
VII_R	784	394.38	211	825	1560.13	16300

*NM, not measured.

Olivine

Olivine, which is a natural material, has been studied by several groups for its catalytic activity in the biomass gasification process. The focus of the study conducted at the Chalmers facility, as

described in Paper 2, was on the effect of biomass ash on the activity of the olivine bed material. For this experiment, raw olivine with the composition listed in Table 3 was used. The entire experiment lasted for 9 days, whereby no exchange of the bed material was conducted during the first 4 days, in order to observe the influence of the ash on the performance of the olivine (aging). Thereafter, approximately 22% of the material was exchanged with fresh olivine (operational point VII). Considering the possible variability of the fuel used as feedstock, additional tests involving the introduction of sulfur and silica into the system were performed: i) introduction of 800 g of elemental sulfur to the boiler during Day VII; and ii) a two-step experiment in which approximately 500 kg of the bed inventory was exchanged with fresh silica sand on two occasions overnight. The changes were determined in the period from Day VIII to Day IX. During all the operational days, the temperature, as well as the fuel feed and steam flow in the gasifier were kept constant. The operational parameters used in the study are presented in Table 4.

Table 3. Chemical composition of raw olivine.

Wt. %	
MgO	49.6
SiO₂	41.7
Fe₂O₃	7.4
Al₂O₃	0.46
Cr₂O₃	0.31
NiO	0.32
L.O.I.**	0.6

Table 4. Operational parameters used in the olivine study.

Date	Operational point/Day	Description of the bed inventory	Temperature in the gasifier [°C]	Solid circulation [t/h]	Fuel flow [kg/h]	Fluidization level [kg _{steam} /h]
25 Feb	I	Olivine	818	11.6	291	161
26 Feb	II	Olivine	813	12.0	300	160
28 Feb	IV	Olivine	814	12.4	299	161
03 Mar	VII	Replacement of olivine	820	15.8	300	160
03 Mar	VII_S	Sulfur addition	820	15.8	300	160
04 Mar	VIII	Olivine/Sand	812	15.4	298	160
05 Mar	IX	Olivine/Sand	813	12.5	297	160

To confirm the importance of alkali in the process, an experiment with the same olivine bed was done in which the activation was triggered by the addition of potassium. The test started from fresh olivine and K₂CO₃, and S was introduced into the system as an “activation procedure”. Over a period of 18 h, the system was fed around 6 kg of solid K₂CO₃ and 7 kg of elemental S, excluding the amounts of K and S fed with the fuel. After activation of the olivine, an additional 3.5 kg of K₂SO₄ was fed to the gasifier, to test its eventual decomposition. In Table 5, the operational conditions used in the experiment are listed.

Table 5. Operational conditions used for triggering the activation of olivine in the Chalmers system.

Description of the bed inventory	Temperature in the gasifier [°C]	Solid circulation [t/h]	Fuel flow [kg/h]	Fluidization level [kg _{steam} /h]
Potassium-loaded olivine	Olivine/K/S	808	15	298

Bauxite

According to the literature, bauxite, as an Al₂O₃-based material, should display a behavior different to that of SiO₂-based materials when interacting with alkali elements in the system. Even though bauxite has been tested as an alkali getter material for the combustion systems, its applicability is limited due to partially reversible interactions with alkalis. The nature of the bonds between bauxite and alkali has been shown to be physical, which if suitably controlled in a system, such as the Chalmers DFB gasifier, could be utilized to improve the gasification process by controlling the uptake and release of active alkali compounds. Investigation of bauxite as a bed material in the Chalmers gasification system is described and discussed in Paper 5. The chemical composition of the material as received is listed in Table 6. The experiment lasted for 9 days in total, during which quartz sand was added occasionally as compensation for the material lost during the operation through attrition. To determine the effect of aging, the measurements taken on the first and the last day of the operation with bauxite were used. As the main operational parameters (Table 7) were similar, a comparison could be made in regard to the aging of the material in the system.

Table 6. Chemical composition of bauxite as received.

Bauxite	Weight %
Al ₂ O ₃	88.50
SiO ₂	6.50
Fe ₂ O ₃	1.10
TiO ₂	3.00
CaO	0.02
MgO	0.02
Na ₂ O	0.02
K ₂ O	0.03

Table 7. Operational parameters used in bauxite study.

Operational parameter	Bauxite (Day 1)	Ash-enriched bauxite (Day 9)
Steam flow to the gasifier, kg/h	160	160
Fuel feed, kg/h	295	294
Temperature in the gasifier, °C	823	818
Temperature in the boiler, °C	854	860
Solid flow circulation	15.4	17.8

Ilmenite

This study was performed in the context of a combustion experiment in the Chalmers facility [53] to investigate the effects of oxygen transport on the combustion process. Focusing only on the combustion part of the process and addressing the potential problems of corrosion and agglomeration, a study of the interactions between ilmenite and ash components is described in Paper 3. The time-frame for the experiment encompassed 4 consecutive days, starting with a 100% quartz sand bed. On each day, a certain amount of the sand was exchanged for ilmenite. Samples of the bed material were extracted from the system after 1 h, 24 h, 48 h, and 72 h of operation (Table 8). Thus, it was possible to observe the build-up of the ash layer around the ilmenite particle over time. The extracted samples were analyzed to gain information about the physical and chemical changes.

Table 8. Extraction schedule for bed materials.

Sample	Timing of sample extraction (h)	Percentage ilmenite in bed material
I	1	20 wt%
II	24	17 wt%
III	48	40 wt%
IV	72	40 wt%

2.2 The Chemical Looping Reforming unit

An alternative and/or complementary measure to the usage of active bed materials in the gasification unit is the application of these materials in a secondary conversion step. For the investigation of raw gas upgrading with active bed materials, two types of reactors were used: a dual fluidized bed CLR reactor; and a tube reactor. In Figure 11a, the set-up of the CLR reactor is shown. The system consists of a reformer reactor (FR), which comprises a CFB, and a regenerator reactor (AR), which is a BFB. The two reactors are connected by two loop seals, which are fluidized with helium. The air reactor is fluidized with diluted air to remove any carbon deposits that are formed in the FR. The raw gas produced in Chalmers gasifier is fed into the reforming reactor *via* a heated line. The tube reactor, which is a simple bubbling fluidized bed, is depicted schematically in Figure 11b. The connection to the raw gas line and electrical oven is the same as that for the dual fluidized bed CLR reactor. Even though one reactor system is used, it is possible to alternate the fluidization media between the raw gas and the diluted air, thereby simulating the CLR process. After passing through the unit, in both set-ups, the gases were sent to the gas conditioning system and onwards to the gas analysis. For the analysis, a micro-GC and a Non-Dispersive Infrared Analyzer were used. Tar samples taken from both the raw and reformed gases were analyzed and compared. The bed materials, fresh and used, were analyzed to follow the physicochemical changes.

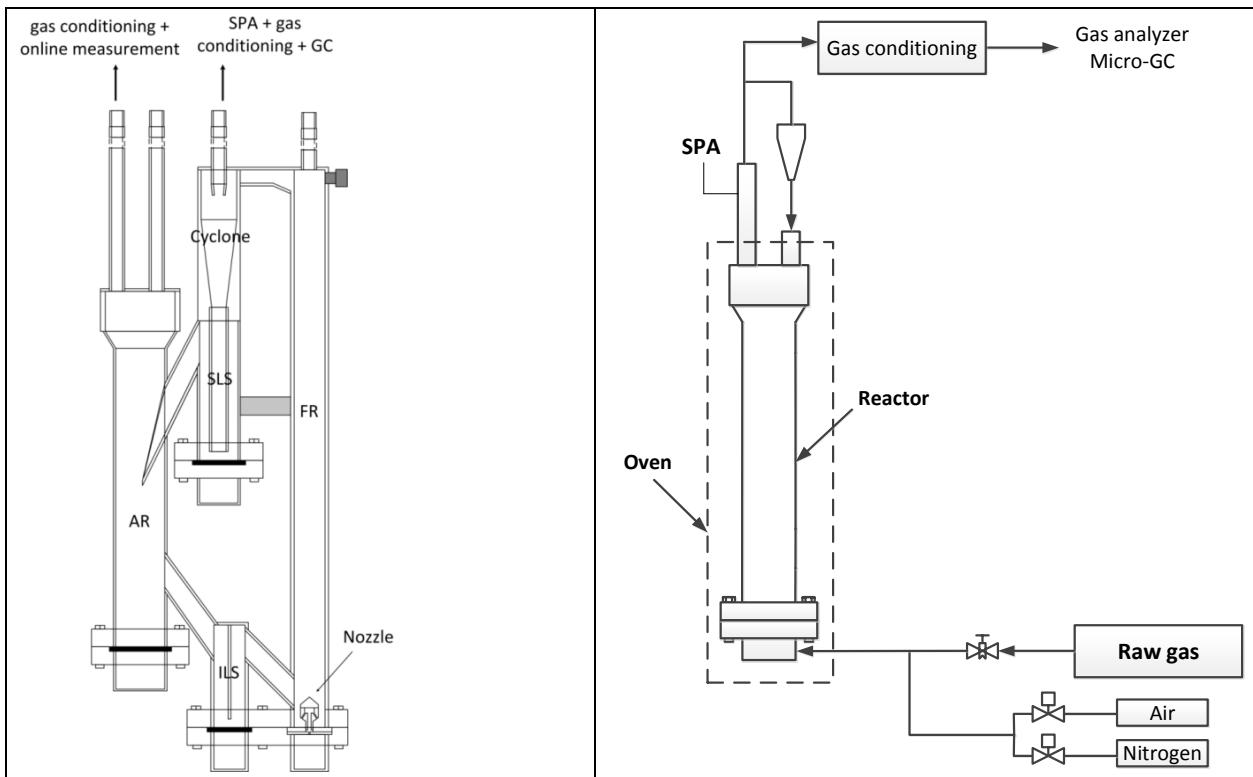


Figure 11. Schematics of the CLR (left panel) and tube reactor (right panel).

Manganese ore

Manganese ore has been evaluated as a catalytic material for the secondary step for the conversion of the raw gas produced by biomass gasification. The tests were done in the dual fluidized bed CLR reactor (Figure 11a), and the results and discussion thereof are presented in Paper 1. The diameters of the particles used were in the range of 45–90 µm. The elemental composition of the fresh ore is given in Table 9. The gasifier was operated at a temperature of 815°C. The catalytic performance of the used ore was evaluated at 800°C, 850°C, and 880°C. To burn off the eventual carbon deposits and minimize the transport of oxygen by the bed material from the AR to the FR and the consequent burning of the gas, the AR was fed with a stream of nitrogen-diluted air that contained 2.2% oxygen.

Table 9. Elemental composition of the fresh manganese ore.

Element/Compound	Weight %
Mn	45.0 min
Fe	6.0 max
SiO ₂	11.0 max
Al ₂ O ₃	9.5 max
ZnO	0.3 max
P	0.085 max
S	0.050 max
K ₂ O	2.6 max
BaO	3.0 max
C	0.60 max
B	< 15 ppm

Feldspar

Feldspar is a naturally occurring ore with the general formula: (K, Na)AlSi₃O₈. Considering its wide availability, limited oxygen transport capacity, silica and alumina base, and similarity to FCC catalysts, feldspar is an attractive material for testing as an agent for the secondary cleaning / upgrading step for the raw gas. In the test, feldspar in the size range of 125–180 µm and with the composition listed in Table 10 was used. Evaluation of its catalytic performance towards tar reforming was performed at three temperatures: 700°C, 800°C, and 900°C. For each test, 200 g of feldspar bed were fluidized with raw gas for 2–3 hours. Then, the fluidization media was changed to nitrogen. At the end of the experimental run, samples of the spent bed materials were collected and examined with the aim of determining the eventual physicochemical changes to the feldspar, as compared to the fresh state.

Table 10. Elemental composition of fresh feldspar.

Chemical Composition	Weight (%)
SiO₂	67.5
Al₂O₃	18.8
K₂O	8.4
Fe₂O₃	0.11
CaO	1.2
Na₂O	4.3
TiO₂	0.01
P₂O₅	0.08
MgO	0.04
MnO	<0.0078

3. Evaluation of bed materials

3.1. Natural ores in the Chalmers DFB system

In this section, the main results from the experiments on the aging of the different bed materials, i.e., quartz-sand, olivine, and bauxite, in the Chalmers DFB gasification system are presented. Performance of the gasification system is commonly described in terms of several parameters, such as cold gas composition, concentration of condensable hydrocarbons, cold gas efficiency, and carbon conversion rate [83]. These parameters were evaluated in this thesis. The results are further discussed regarding the aforementioned parameters and for the comparison of different cases. For combustion purposes, ilmenite was tested as an alkali getter, focusing on the interactions of the bed particles with the biomass ash elements. In all the performed investigations, the interaction between the bed material and potassium was emphasized. In the tests that were carried out in relation to gasification, alkali is considered to be the element triggering the activation of the material, while in the tests done in relation to the combustion process, the bed material was used as a preventive measure against agglomeration.

Quartz sand

When investigating an active bed material, a base case with a non-active material is desirable. High purity quartz-sand can be utilized for this purpose. With the aim of studying the influence of biomass ash on the otherwise inert silica-sand in the gasifier of the Chalmers DFB gasification system, an experiment was carried out in which there was no exchange of the bed inventory over four consecutive days of operation. The tar content of the raw gas was analyzed based on the changes in yields of specific tar groups: naphthalene; 2-ring components; 3-ring components and heavier hydrocarbons, and phenolic components. The results given in Figure 12 are shown in g/kg_{daf} fuel. From Day I_A to Day IV_A, there were decreases in the yields of all the tar groups. The greatest changed occurred in the level of the phenolic species, which decreased by 21%, and the total tar yield decreased by around 10%. Simultaneous changes in the produced gas composition are presented in Figure 12b as yields of permanent gases versus time of operation (days) in the aging experiment. The right-hand y-axes correspond to the yields of H₂S in the raw gas, while the yields of H₂, CO, CO₂, CH₄, and C₂H_X are shown on the left-hand y-axes. Increases in the H₂ and CO₂ yields were observed with aging of the sand in the system (points I_A to IV_A in Figure 21). The concentrations of CH₄ and light hydrocarbon were constant, while a steady increase in H₂S yield occurred over the time of operation. After regeneration of the bed inventory (point V in Figure 21), the composition of the raw gas was similar to that measured on the first day of operation.

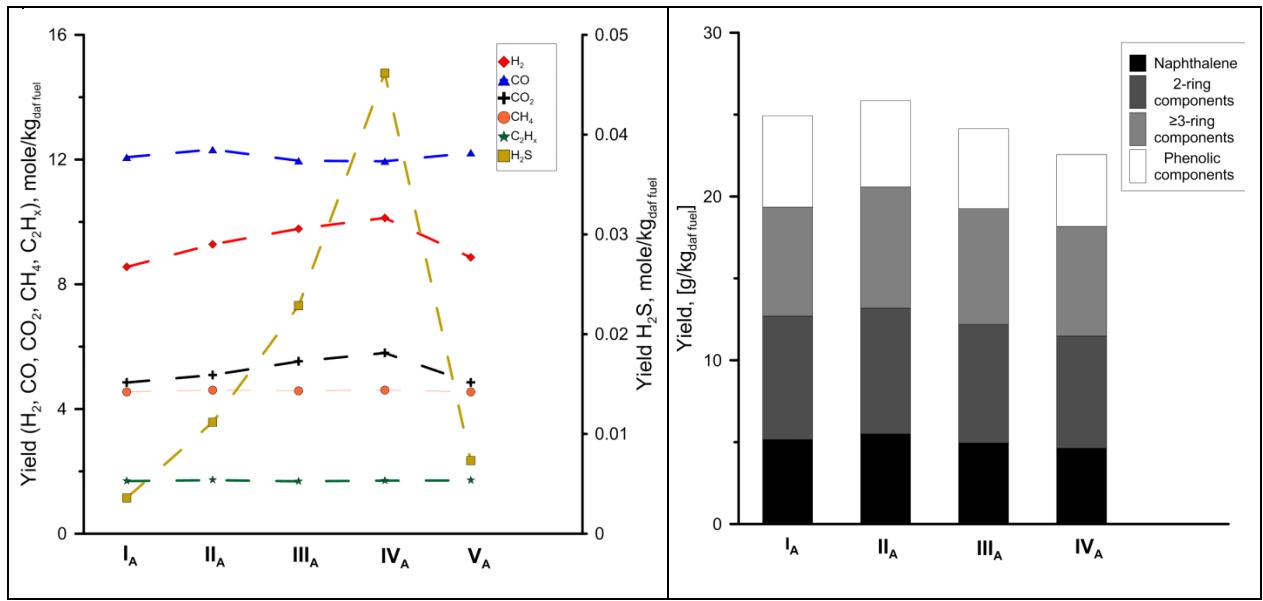


Figure 12. (a) Left: Composition of the dry raw gas obtained during the experiment (mol/kg_{daf} fuel); (b) Right: Composition of the tar components in the raw gas, presented as groups (g_{tar}/kg daf fuel).

The observed increase in H₂S yield in the raw gas is a common phenomenon in the Chalmers DFB. In Figure 13, the measured yields of sulfur in the produced raw gas (in the form of H₂S) from two different experiments are shown: (i) a case with regeneration of the bed material, with the experiment being performed in a separate study; and (ii) a case without regeneration of the bed material, performed within the study of aging of the quartz-sand bed. In the regeneration case around 20 wt.% of the bed inventory was exchanged on a daily basis. Between points III_R and VII_R, only the boiler was in operation for 3 days. The y-axis is in mole S/kg_{daf} fuel. In the same figure, the amount of sulfur that enters the system *via* the fuel feed to the gasifier is shown. In both cases, with and without regeneration of the bed material, already on the second day of the operation, the amount of sulfur in the gas exceeded the amount that was present in the fuel that was fed into the gasifier. This increasing trend was noted throughout the experiment. During both experiments, the SO₂ concentrations in the exit flue gases from the boiler were also monitored online. Given the specific set-up of the Chalmers DFB system, whereby raw gas is re-directed to the boiler where it is burnt, it is reasonable to expect a relatively high level of SO₂ in the boiler flue gas. However, the concentrations of SO₂ recorded in the boiler flue gases during the two experiments (bed regeneration and bed aging) were <10 ppm for all the days of operation. These low levels of SO₂ can be attributed to the aforementioned sulfation reactions (see Section 1.2), in which the generated sulfate reacts with the particles in the gas stream.

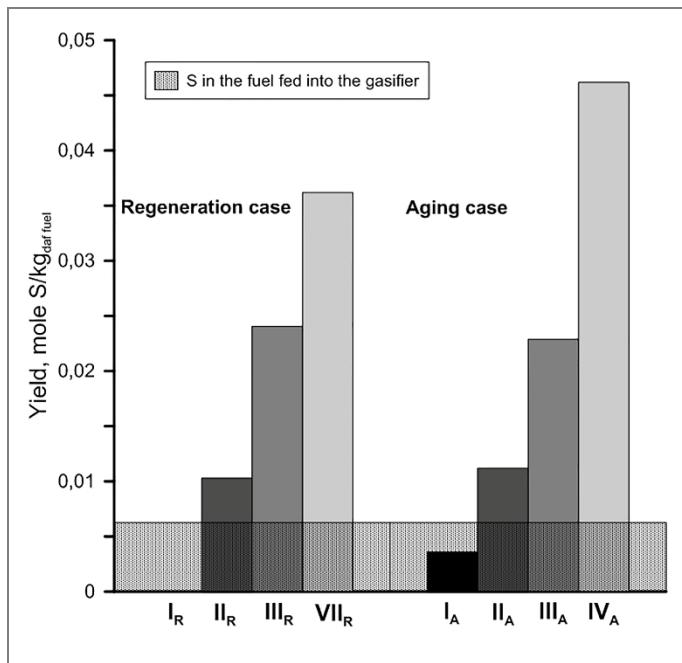


Figure 13. Measured levels of S emissions in the form of H₂S in the dry raw gas, and the amounts of sulfur added to the system with the fuel; kg of S/h vs. days of operation of the gasifier.

The results of the elemental analyses of the samples collected in the regeneration experiment were obtained by XRF. The results of the analyses performed for points II_R, III_R, and VII_R and results are shown in Figure 14a for the solids samples extracted from Loop seal 1. In Figure 14b, the differences between the elements in the samples extracted at Loop seal 1 and Loop seal 2 for the point III_R are presented. There was enrichment of the quartz bed with ash components over time. Comparing the samples from Loop seal 1 and Loop seal 2 (Figure 14b) for the day with the highest ash accumulation, it is clear that there are decreases in the percentages of all the ash components, with the exception of silicon. This indicates that attrition of the ash coating of the bed particles is occurring in the gasifier. Taking together the difference noted for sulfur in the results of the XRF analysis and the observed increased concentration of H₂S in the raw gas (Figure 13), one can conclude that the sulfur content in the bottom bed material is lost in part through attrition and in part through release to the gas phase.

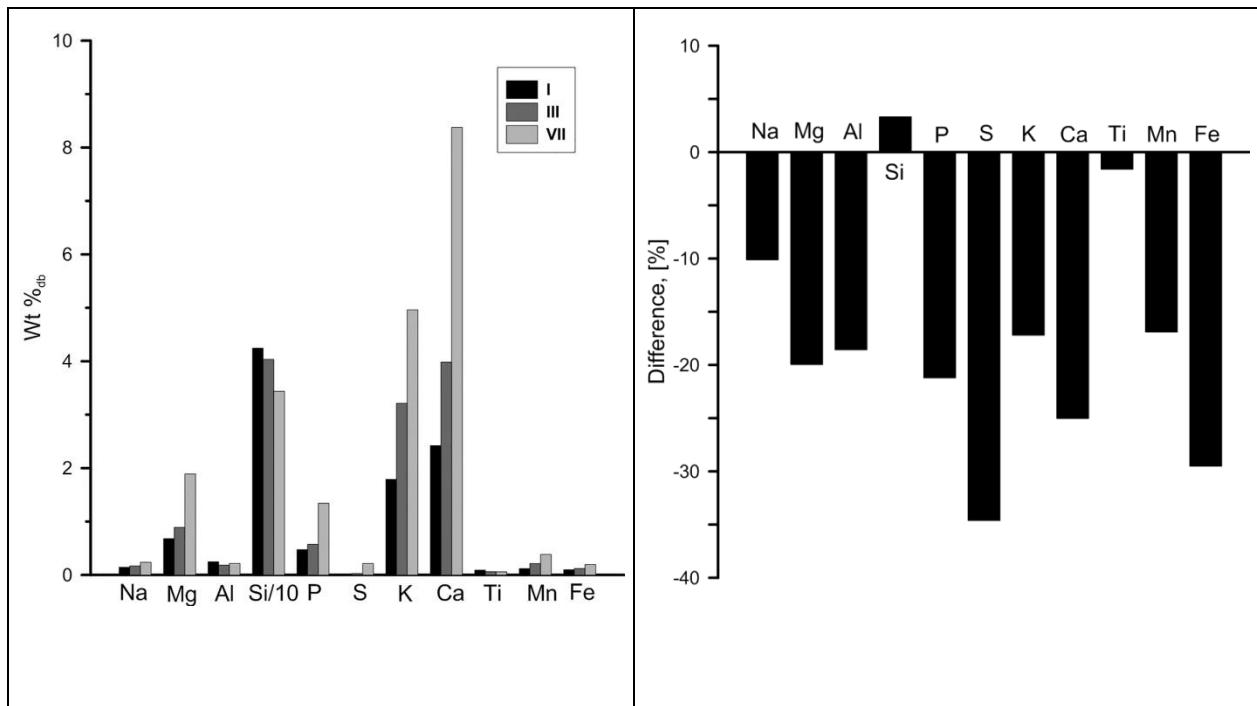


Figure 14. Results of the XRF analyses. *Left panel:* Elemental compositions of the bed material samples collected on Days I, III, and VII in the regeneration case; *Right panel:* Percentage differences in elemental compositions between the Day III samples collected at Loop seal 1 and Loop seal 2.

To characterize the elemental distribution in the cross-section of the particle and the association of sulfur within the material, SEM/EDX analyses of the particle cross-sections were performed. The results of the line scan of the ash layer around a particle extracted from Loop seal 1 is shown in Figure 15. The analyzed particles were from the regeneration experiment, collected on Day III_r. Sulfur was detected in the outer layer of the ash coat. Potassium, as expected from reports in the literature [21, 68], had diffused into the core of the quartz particle, thereby forming potassium-silicate. Calcium was detected as a small fraction in the inner layer and as a larger fraction in the outer layer. As sulfur was located in the calcium-rich part of the ash layer, it appears to be associated with calcium. XRD analysis was used to determine the phase in which sulfur originated in the sample. However, due to the low level of sulfur (lower than the confidence threshold of the equipment), these results cannot be used for the discussion. If sulfur is linked to the calcium-rich layer in an oxidative environment it should be in the form of sulfate [84, 85]. Circulating to a reductive environment, such as that prevailing in the upper part of the gasifier (volatile zone), stable CaSO₄ would be decomposed to calcium sulfide and/or calcium oxide, as described in previous studies [86, 87]. In the gasifier, part of the sulfur is released to the gas phase and part is retained in the form of sulfide, which circulates back to the boiler where it is re-oxidized.

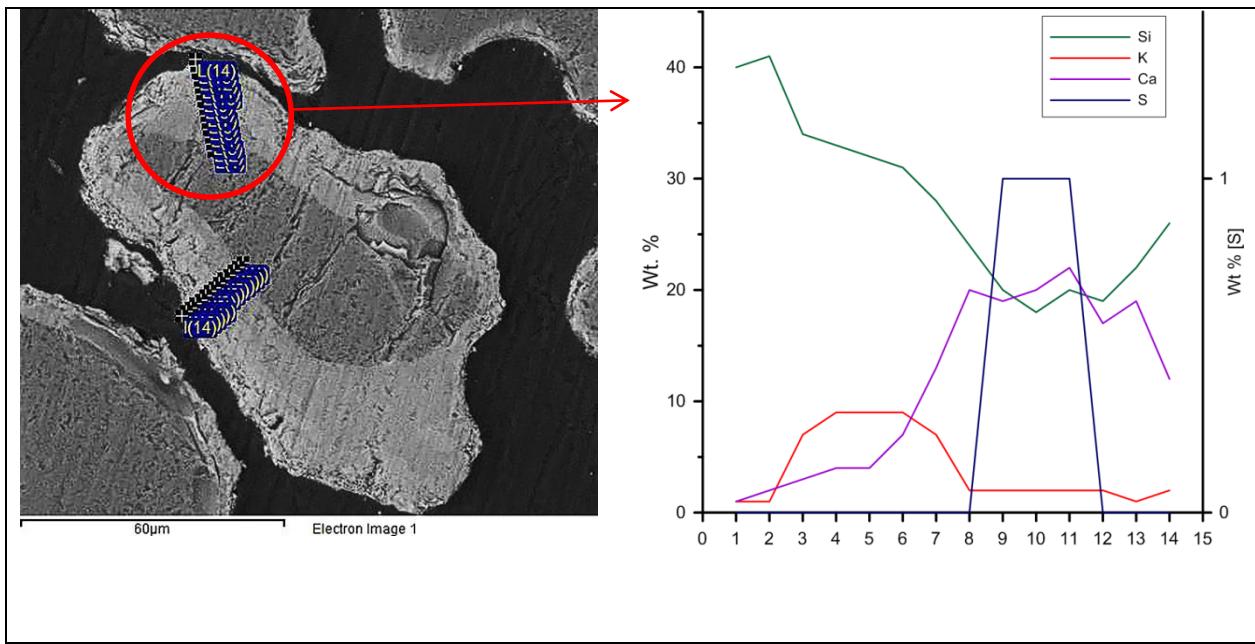


Figure 15. Line scan over an ash-coated particle obtained from Loop Seal 1 and the elemental concentrations (in wt.%). On the x-axis, the value of 1 represents the location near the interface of the quartz particle-ash layer, while the value of 14 represents the outer surface of the ash layer.

Olivine

Aging of olivine

Olivine has been widely tested as an active bed material for gasification purposes. To exert its activity, olivine has to be activated, which is usually accomplished by calcination prior to use. In the study carried out at the Chalmers facility, raw olivine was used and its activation by ash element enrichment was the main focus.

The change in the activity of olivine following its enrichment with ash elements was investigated for 4 days over a period of 2 weeks with respect to: 1) the yields of the specific tar groups (Figure 16a); and 2) the yields of gaseous components in the produced gas (Figure 16b). As shown in Figure 16a, the total tar amount decreased and all the tar species were affected. Compared with the first day of operation, at the peak of the activation (on Day IV), the total tar yield had decreased by 30%. Considering this significant decrease in tar yield, the increase in the yield of H₂ (Figure 16b) can be attributed to steam reforming reactions. However, the increases in the levels of CO₂ and H₂O occurred concomitant with a decrease in the level of CO, which points to the WGS being the relevant reaction. Following the partial exchange of the bed with fresh olivine (Day VII), the overall activity of the bed material towards tar decomposition decreased. This may have been due to dilution of the activated bed material in the system. However, the composition of the gas was not significantly affected. In contrast, the addition of quartz-sand (Day VIII) generated a much stronger

effect than would have been expected from simple dilution. The tar yields increased in a non-proportional manner for all the groups, and the gas composition was similar to that measured on the first day of the experiment. After sulfur was added (VII_S) to the boiler, the total tar yield decreased by 20% and the H₂S yield in the raw gas increased. From the increase in the H₂S level in the raw gas it can be concluded that sulfur was transported from the boiler to the gasifier.

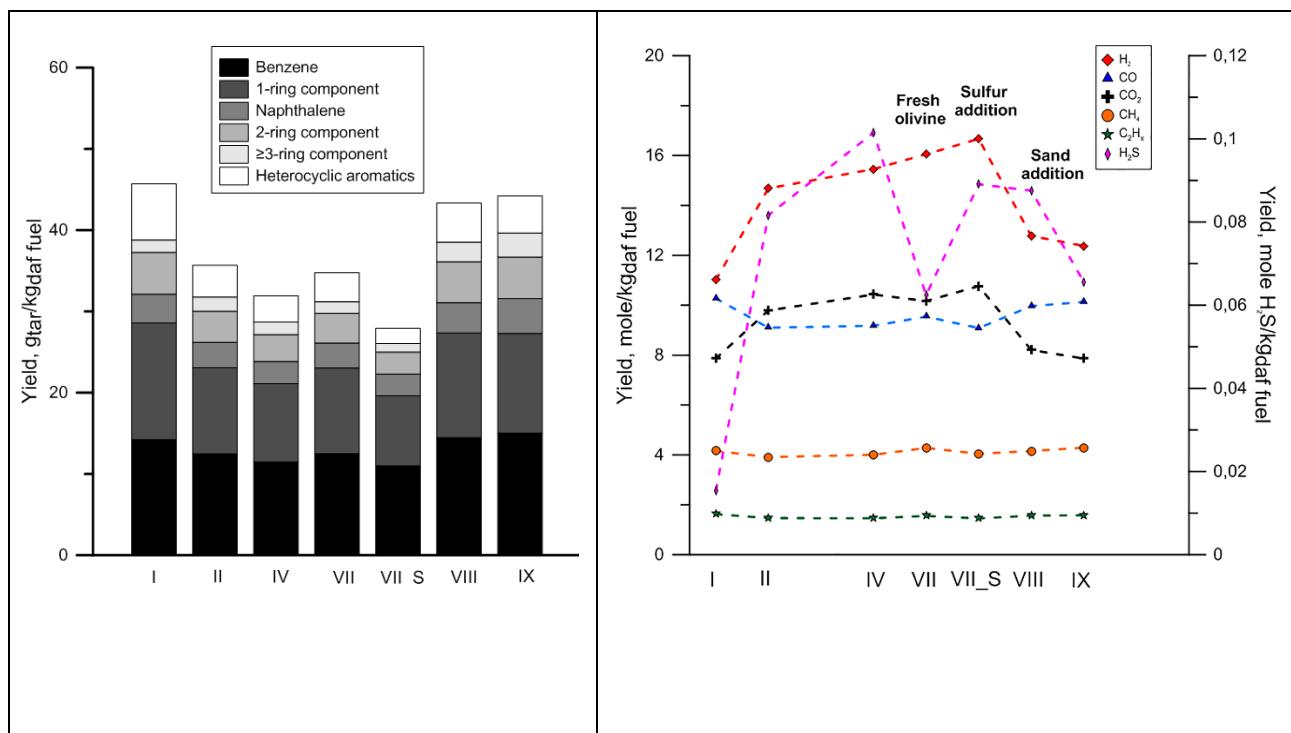


Figure 16. (a) Levels of tar components in the raw gas, presented as yields of specific tar groups (in gtar/kg daf fuel) over time.
***VII_S** represents an experiment in which sulfur was added to the system. **(b)** Composition of the dry raw gas obtained during the experiment (in mol/kg daf fuel).

Complete elemental analyses of the bed materials extracted from the system during the experiments showed that there was significant retention of inorganics in the bottom bed material. Figure 17 shows the results of the analyses for the respective oxides. An interaction between olivine and the ash components is evident from the increased contents of inorganics in the samples. The decreases

in the levels of ash components observed on Day VII are related to the regeneration of the bed inventory with fresh material and the removal of a portion of the bottom ash.

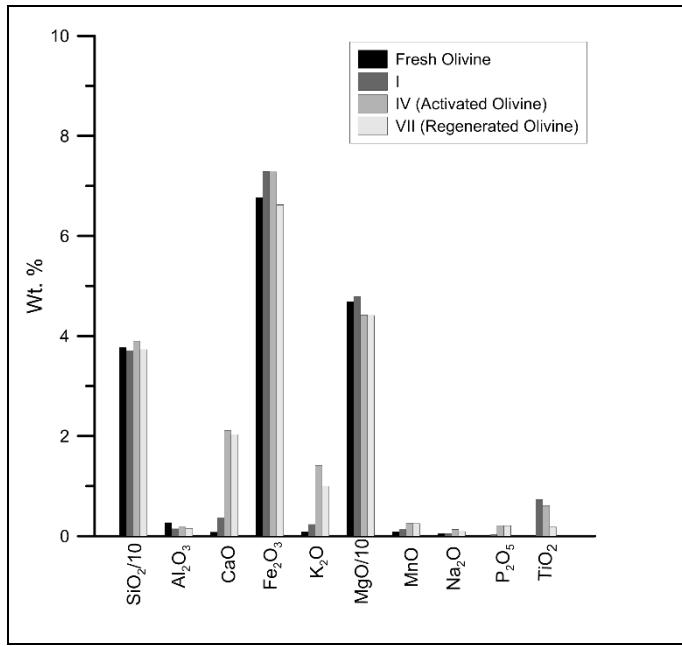


Figure 17. Bed material compositions, expressed as wt.% of oxides.

The solids extracted after 4 days of operation were analyzed by SEM/EDS. The results are presented in Figure 18. In line with the findings of Kirnbauer et al. [47], a Ca shell was formed on the surfaces of the particles. However, the iron layer described by Lancee et al. [46] was not observed in the present study. The reason for this may be that unlike in the previous study, the material in the present work was not calcinated before the experiment. A mapping analysis of the samples after the addition of sand to the system (Figure 18) revealed that the majority of the potassium was associated with silica-sand particles in the form of a melted layer. Potassium, as expected, diffused into the core of the silica-sand, as confirmed by the spot analysis (shown in the same figure). Considering the significantly lower level of silicon in the olivine, an association between potassium and the silica-sand particles is not surprising. However, potassium was observed in the thin outer layer on the olivine particles.

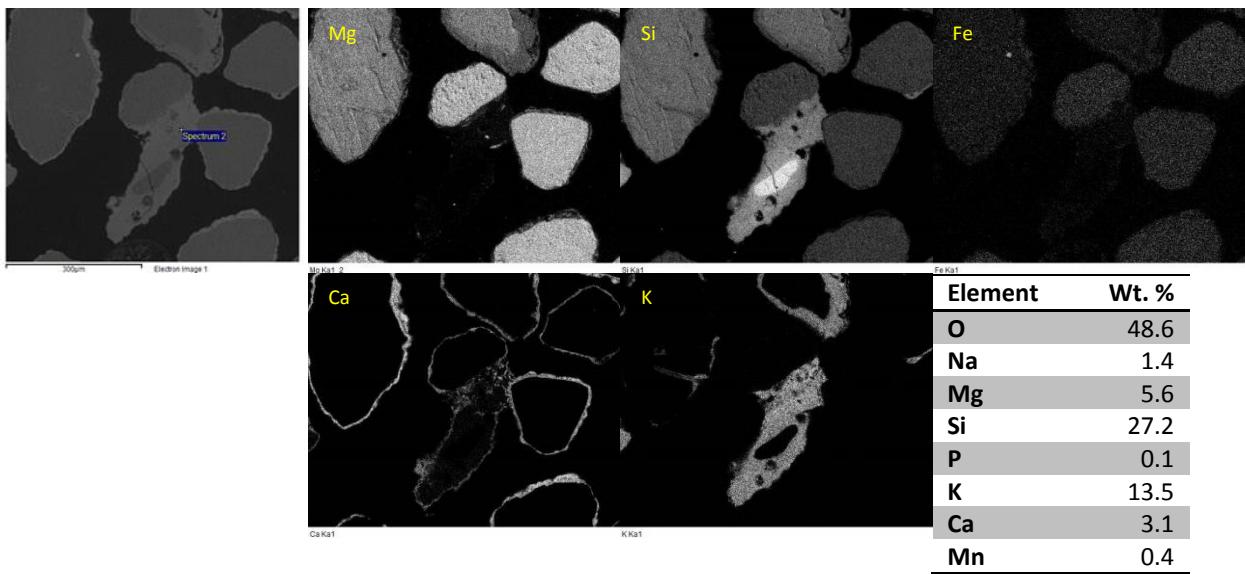


Figure 18. SEM/EDX analyses of used olivine particles mixed with sand. Inset table: elemental analysis of the chosen spot.

To confirm the presence of potassium in salt form, an additional leaching test with deionized water was performed for the particles extracted on Day IV. Indeed, the leachate was found to contain approximately 520 mg of K per kg olivine. Considering the non-uniformity of the ash coating on the particles, this result cannot be discussed in a quantitative sense. However, the analysis provides supplementary information regarding the source of the potassium release.

Even though the boiler was operating all the time at above stoichiometry, increased levels of CO emissions from the boiler were detected from the second day of the operation. An interesting observation is that for each day that fuel was introduced into the gasifier, the level of CO emission from the boiler decreased, as shown in Figure 19. Hindiyrati et al. [88] performed a study that combined experimental work and chemical modeling and that looked at the influence of the K-salt on CO oxidation. That study found that alkali could act as a strong inhibitor of CO oxidation under atmospheric pressure and in the temperature range of 773–1373 K. Due to the specific set-up of the system and re-circulation of the raw gas to the boiler, all the sulfur from the fuel that is converted into H₂S in the gasifier will be oxidized to SO₂ in the boiler. This addition of SO₂ to the boiler may be the reason for the decreasing levels of CO in the flue gas that were observed each time that the gasifier was introduced into the operation. The addition of sulfur-containing compounds to the boiler caused a decrease in the level of gaseous alkali in the gas through the sulfation reaction, followed by K₂SO₄ condensation at the surfaces of the bed particles. Silica-sand addition to the system (Fig. 20) resulted in a similar decrease in CO emissions, which implies that the same species was affected as in the case of sulfur addition. The decrease in CO level caused by silica-sand addition was found to be permanent, which suggests that the inhibiting component for CO oxidation is non-reversibly bound to the sand in the boiler.

Since the addition of sulfur to the boiler affected the performance of the gasifier, it seems reasonable to conclude that the added sulfur reacts with the K and bed material in the boiler and is transported by circulation to the gasifier. Subsequent decomposition of the transported K_2SO_4 leads to more KOH and K_2CO_3 becoming available for the reactions within the gasifier. The increased level of H_2S in the raw gas after sulfur addition accords with the hypothesis. In summary, the main effects of the sulfur in the system is to bind potassium and to make it mobile in the system.

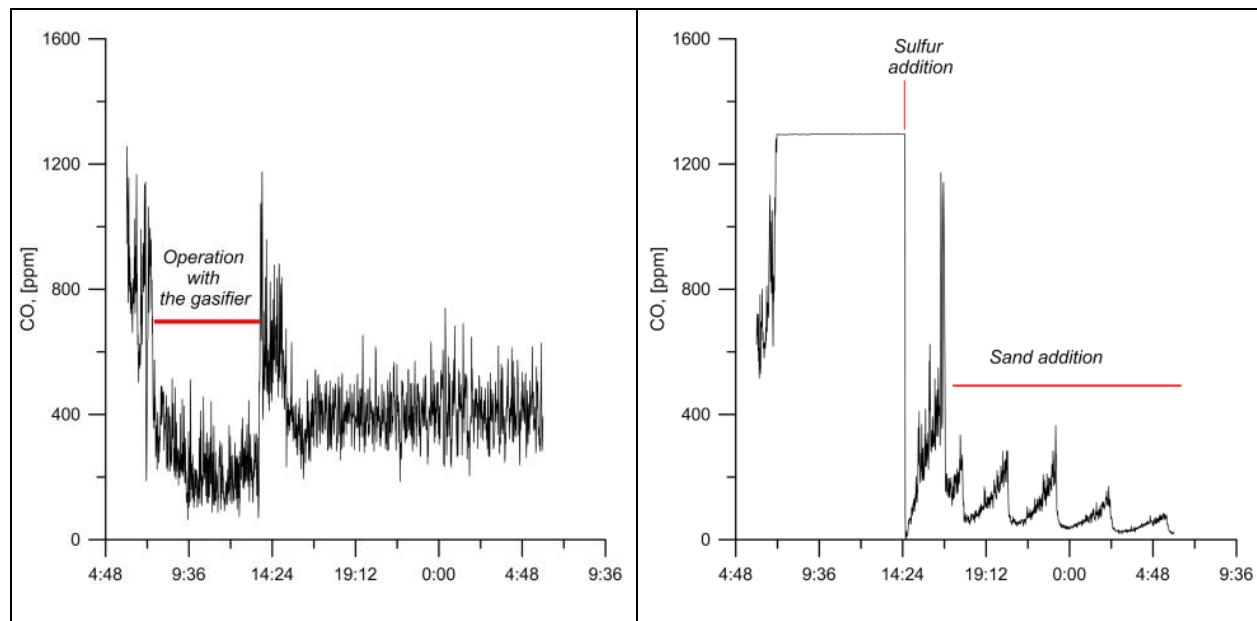


Figure 19. CO concentrations in the flue gases during gasifier operation with olivine as the bed material. Left panel: Effect of gasifier operation; Right panel: Effects of sulfur and silica sand additions.

Triggered activation of olivine

Based on the hypothesis established during the investigation of olivine aging, potassium is identified as a key element in the activity of olivine. With the aim of testing this hypothesis and the possibility for ‘triggered’ (instantaneous) activation, potassium salts were added into the gasifier.

The activation of olivine was accomplished within one day of operation, resulting in a 52% decrease in the total tar yield and a shift in the raw gas composition. The results of the SPA analysis are presented in Figure 20a, wherein the yields of specific tar groups are presented on the y-axes. The addition of K_2CO_3 (5 kg + 1 kg) decreased the yields of all the tar groups, with the exception of the phenolics, the levels of which remained unchanged. With continuous feeding of sulfur overnight (referred to as ‘activated olivine’ in Fig. 20), the tar yield decreased even more, including in this instance the yields of phenolic species. In Figure 20b, the composition of dry produced gas is shown. The addition of K_2CO_3 resulted in increases in the H_2 and CO_2 yields, while the yields of CO , CH_4 and C_2H_x decreased. In contrast, the yield of C_3H_x increased somewhat. After sulfur feeding overnight, the trend of change in the gas composition was the same. During the experiment,

in parallel, the oxygen-transport capacity of the olivine (kg of O per kg of olivine) was determined using a High-Temperature Reactor (HTR). The method used for this measurement is described elsewhere [82]. A modest increase in the olivine oxygen-transport capacity, from 0.11 wt.% to 0.18 wt.% was observed.

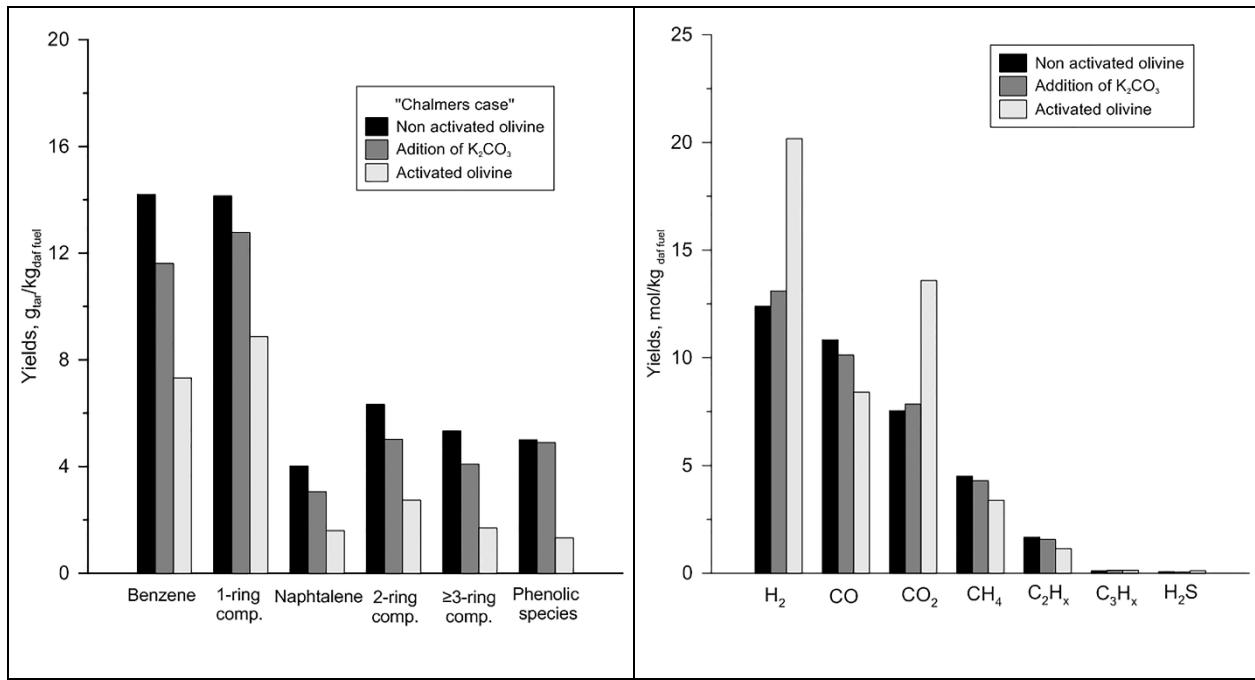


Figure 20. (a) Levels of tar components in the raw gas, presented as the yields of specific tar groups (in g_{tar}/kg daf fuel) versus time. **(b)** Compositions of the dry raw gases obtained during the experiment.

To draw conclusions regarding the presence of potassium within the particle, SEM/EDX analysis of a cross-section of one randomly chosen particle was carried out. Figure 21 shows a line scan over the particle, and the results in wt.% are listed in Table 11. From this table, it is clear that potassium can be found in the outer part of the olivine particle, which is in line with the hypothesis derived from the olivine aging experiment, i.e., the occurrence of interactions between K₂SO₄ and the surfaces of the particles in the freeboard of the boiler. Furthermore, leaching of the solids extracted from the reactor before and after triggered activation of olivine resulted in an increase in the level of potassium (from 159 mg to 1923 mg of K per kg of olivine). The presence of potassium in salt form accords with the aforementioned conclusion.

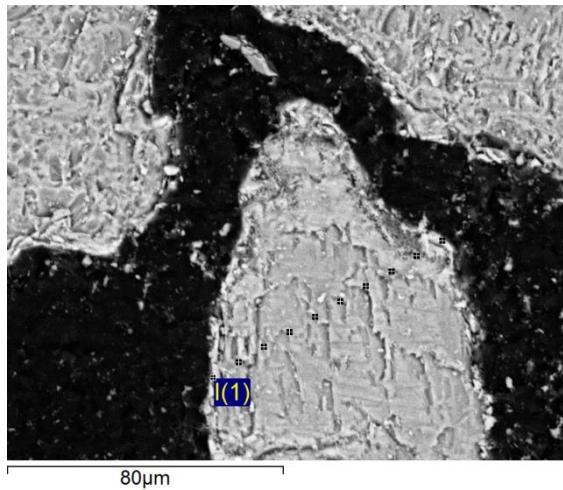


Figure 21. EDX image of a randomly chosen olivine particle extracted from the Chalmers gasifier.

Table 11. Line scan analysis of the activated olivine particle. Units are percentage of weight.

Spectrum	O	Mg	Si	P	S	Cl	K	Ca	Mn	Fe	Total
I(1)	69	14	13	0	0	0	1	1	0	2	100
I(2)	61	17	17	0	0	0	1	1	0	3	100
I(3)	66	16	16	0	0	0	0	0	0	2	100
I(4)	66	16	16	0	0	0	0	0	0	2	100
I(5)	67	16	15	0	0	0	0	0	0	2	100
I(6)	60	17	19	0	0	0	1	0	0	3	100
I(7)	65	16	16	0	0	0	1	0	0	2	100
I(8)	62	16	17	0	0	0	3	0	0	2	100
I(9)	61	16	13	0	0	0	4	3	1	2	100
I(10)	63	13	10	1	1	1	3	5	1	2	100

During the experiment, the same problem with increased CO emission from the boiler occurred as in the olivine aging experiment. In Figure 22, the profile of the CO concentration in the flue gas during the experiment is shown. Even though the salt addition was performed at the gasification side of the system, it had an effect on the operation of the boiler, in that the concentration of CO was affected. The addition of 5 kg of K_2CO_3 provoked an instantaneous and rapid increase in the CO concentration in the flue gases from the boiler, reaching CO levels higher than those allowable for boiler operation. This implies the dissociation and decomposition of the K_2CO_3 , whereby potassium is released from the bed material to the gas phase and by re-circulation of the raw gas sent to the boiler. The CO emission level was decreased by manual addition of sulfur into the boiler. The addition of 1 kg of K_2CO_3 resulted in the same effect on the system, albeit with a lower intensity. Overnight, sulfur was fed continuously into the system and the resulting CO emission level was negligible.

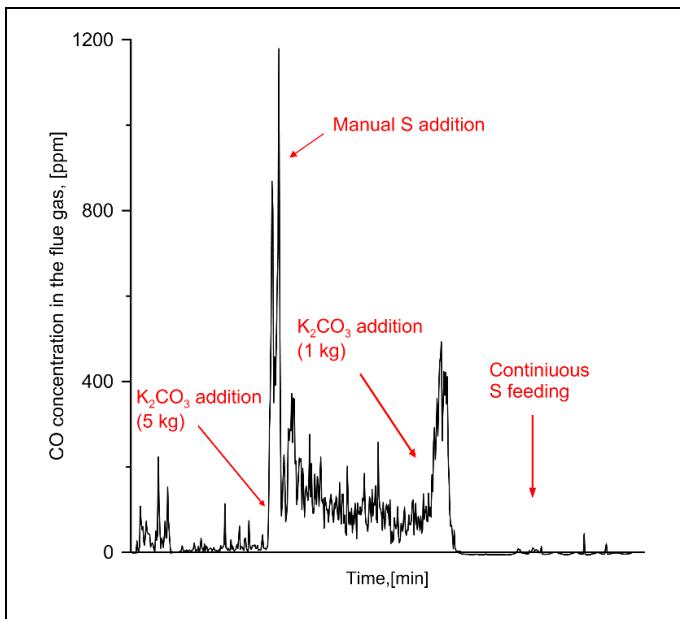


Figure 22. CO concentration in the boiler flue gas, [ppm]

To test the hypothesis that the decomposition of K_2SO_4 to active potassium in gaseous form is the main catalytic pathway in the system, a separate experiment was done in which 3.5 kg of K_2SO_4 was added to the gasifier second day of the experiment, at which point the olivine was already active. In Figure 23a, the responses of the system are presented in terms of the tar yields; the bars show the results of the analyses of three amine samples taken during the addition of the salt. The minimum yield of tars measured was 11.7 g_{tar}/kg_{daf} fuel. Compared to the corresponding level at the beginning of the operation (i.e., with non-activated olivine), this value represents a decrease of 76%. Indeed, all the tar groups showed reduced yields. However, this effect was partially lost after a short period of time. The changes in the permanent gas compositions, caused by sulfate addition, are shown in Figure 23b. Monitored were the levels of CH_4 , CO, CO_2 . The left y-axis relates to the concentrations of CH_4 and CO, while the right y-axis relates to the CO_2 concentration. With the addition of the salt, the concentrations of CO and CH_4 decreased, while that of CO_2 increased.

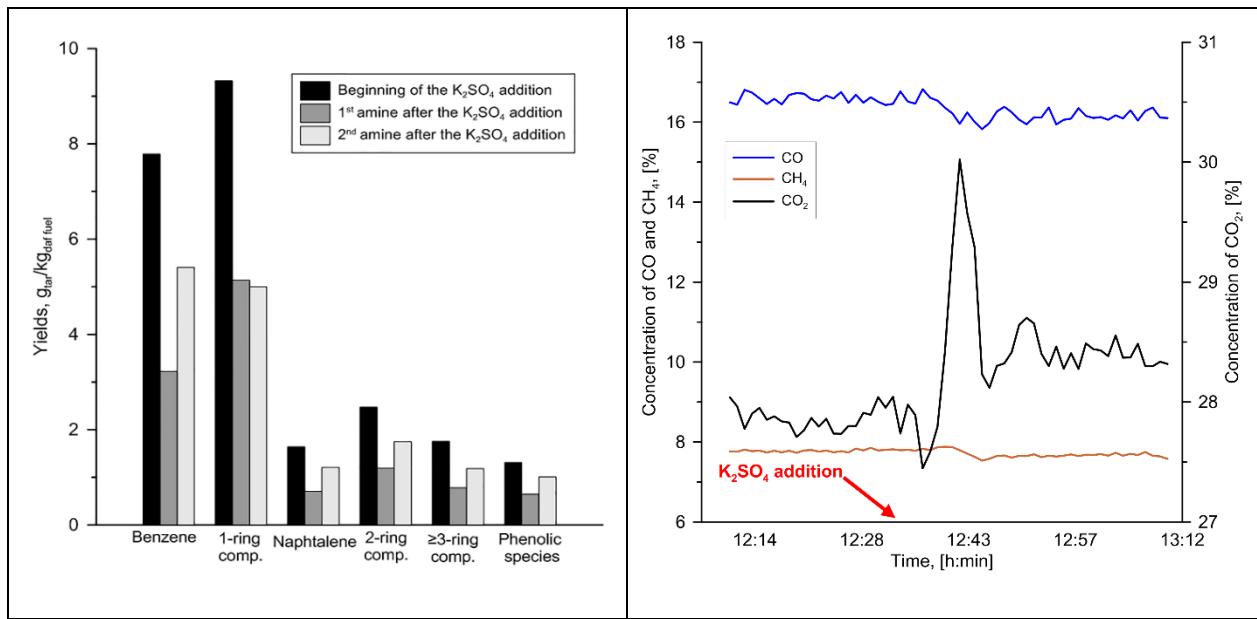


Figure 23. Influence of K₂SO₄ addition on the (a) tar content and (b) gas composition of the raw gas.

Bauxite

Due to the fact that the interactions between bauxite and alkali are very different to those between SiO₂-based materials and alkali, the uptake and release of active alkali elements in different zones of the system can be expected. This phenomenon was in focus in the study carried out with bauxite as the bed material in the Chalmers DFB unit.

The measured compositions of the dry gases produced during the experiment with bauxite as the bed material are presented in Figure 24. The results are in the form of yields of components in the dry raw gas. With increasing residence time of bauxite in the system, the yields of carbon, hydrogen, and oxygen in the gas increased. More specifically, the yields of H₂ and CO₂ in the produced gas increased, while those of CO and CH₄ decreased. The ratio of hydrogen to CO increased with the time of the operation from 1 to 2. The yields of light hydrocarbons decreased overall. However, the levels of C₂H₆ and C₃H₆ slightly increased and those of C₂H₄ and C₂H₂ decreased. As indicated by the gas yields the carbon conversion rate, defined in terms of kg of carbon in the cold gas per kg of carbon in dry ash-free fuel, increased from 0.60 to 0.74 with aging of the bauxite. The results of a separate study that included the HTR [82], which was done in parallel to this experiment, provided evidence of significant char conversion in the case of ash-enriched bauxite. However, the cold gas efficiency (CGE) of the produced gas showed a moderate increase (from 0.60 to 0.63) with the aging of the bauxite, which is comparable with the value obtained with the CGE when the system was operated with silica-sand [80]. An additional laboratory-scale experiment was done to test the oxygen-carrying capacities and activities towards the WGS reaction of both samples. A significant increase in the oxygen-transport capability, from 0.07 wt.% to 0.25 wt.%, and an increasing trend towards enhancing the WGS reaction were

observed with ash enrichment of bauxite. This increase in oxygen-transport ability may explain the low calorific value of the produced gas, even though there was increased carbon conversion.

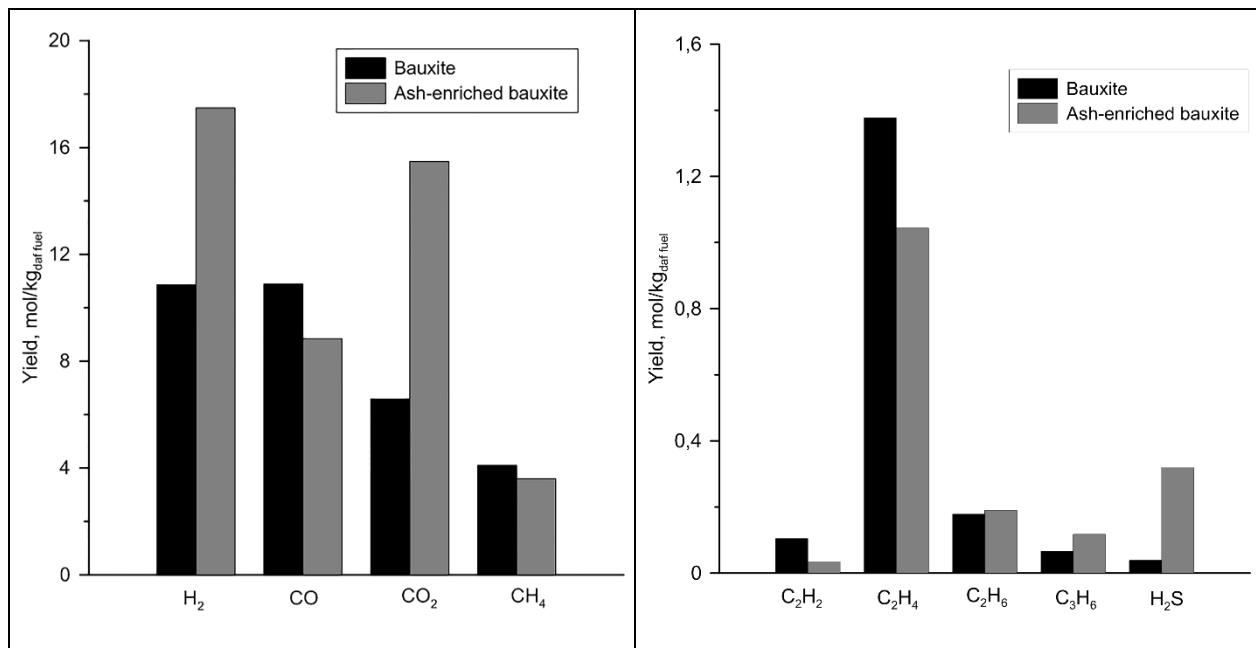


Figure 24. Yields of permanent gases, in mol/kg dry ash free fuel

The measured tar contents in the raw gases from the beginning of the operation and when bauxite was enriched with biomass ash are presented in Figure 25. Benzene and 1-ring components are excluded from the discussion due to the low accuracy of the method used to measure those two groups. The yields for the four presented groups decreased with ash enrichment of the bauxite. The most affected were the phenolic species. Overall, comparing the yields of tar species at the beginning of the operation and after ash enrichment of the bauxite, and excluding the BTX fraction, a decrease of about 40% was noted. Considering that no increase was noticed for any of the tar groups, it can be concluded that bauxite has a catalytic effect on the primary tar species, e.g., decomposing the primary tars or preventing their creation.

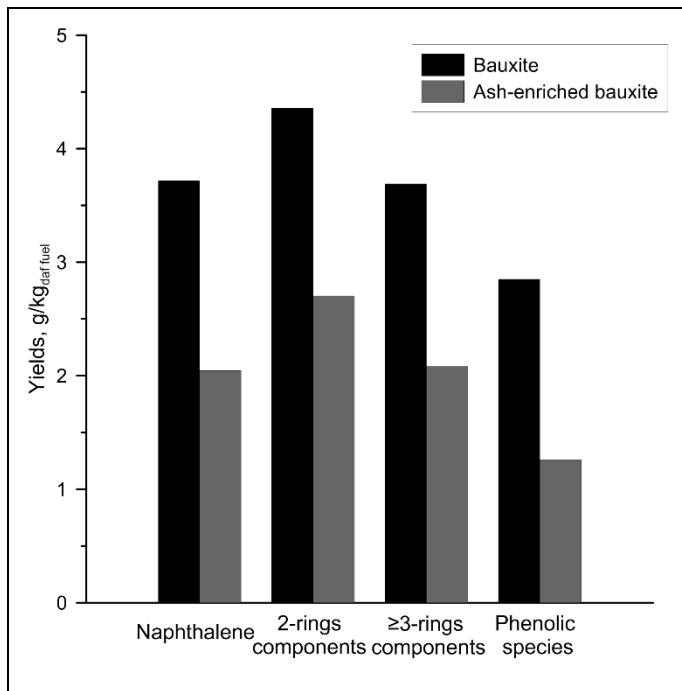


Figure 25. Yields of tar components measured in the raw gas [g/kg _{daf fuel}] and presented as specific groups.

By complete chemical analysis of the samples extracted for the two discussed cases, as shown in Figure 26, a significant enrichment of bauxite in the ash components over the time of the operation of the system becomes evident. The observed increase in the level of Si is due to the addition of quartz-sand to the system. The levels of both Ca and K showed significant increases in the bed material with time, starting from the fresh bauxite. Since bauxite is known to be an alkali-sorbent compound, the presence of K is not surprising.

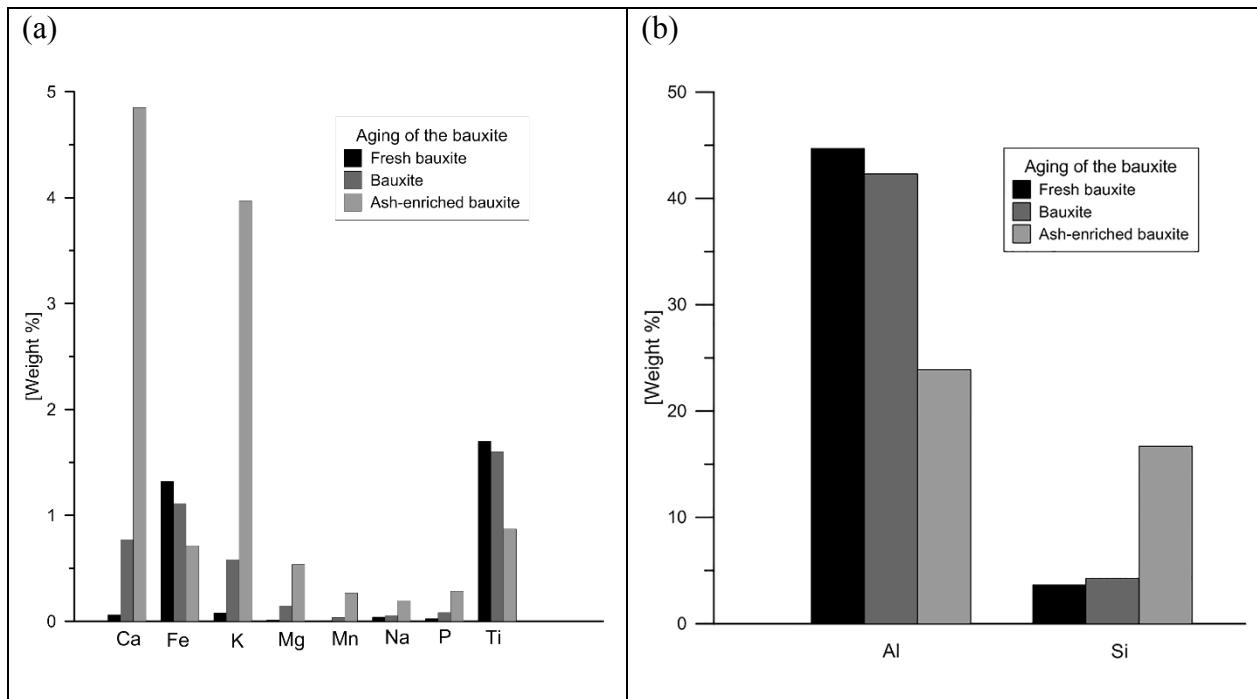


Figure 26. Elemental analyses of the solid samples extracted from the Chalmers DFB system: (a) minor elements [wt.%]; and (b) major elements [wt.%]. Remain amount up to 100% correspond to the oxygen.

To determine which ash elements are released within the system, a leaching analysis with deionized water was conducted for the same samples. The results for K and Ca, which are potentially active elements in the system, are presented in Figure 27. The concentration of leachable K increased around 12-fold, while the concentration of Ca increased only 1.7-fold. Such an significant increase and the possibility of release is in line with findings reported in the literature, which describe bauxite as an alkali getter with the ability to reversibly adsorb the alkali from a flue gas stream [27, 72]. Moreover, recovery of the sorbent was accomplished through use of boiling water, which resembles reasonably well the atmosphere in the bottom of the gasifier. The potential for K release from the bauxite bed in the steam fluidized gasifier may explain the increase in overall activity, and especially the increase in carbon conversion observed in the present experiment.

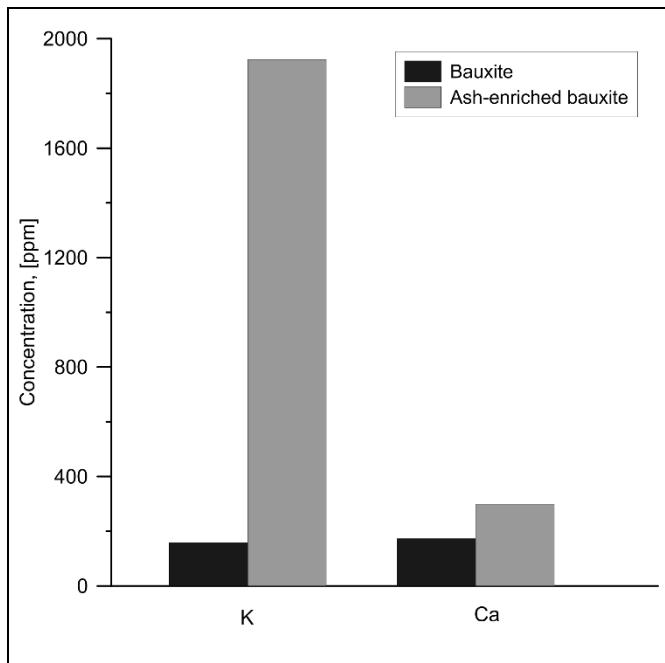


Figure 27. Concentrations of K and Ca in the leachates from the gasifier using bauxite as the bed material, with samples taken at the beginning of the operation and after ash enrichment of the bauxite.

Ilmenite

The fourth type of material tested within the scope of this thesis is a TiO_2 -based material, ilmenite. In the literature, TiO_2 has been described as causing a decrease in K vaporization in the process of straw combustion. Therefore, the focus of our investigation was the interactions between ilmenite and biomass ash, particularly with regards to potassium and calcium.

The SEM/EDX images of the ilmenite particles extracted from the system after 1 h and 24 h of operation are shown in Figures 28 and 29, respectively. At the start of the operation (Figure 28), potassium was detected as a thin layer on the ilmenite particles. However, with the aging of the ilmenite in the system, the potassium appeared to diffuse into the core of the ilmenite particle (Figure 29). The particle core was rich in Ti, while Fe was located at the surfaces of the particles, and Ca was found to form two layers.

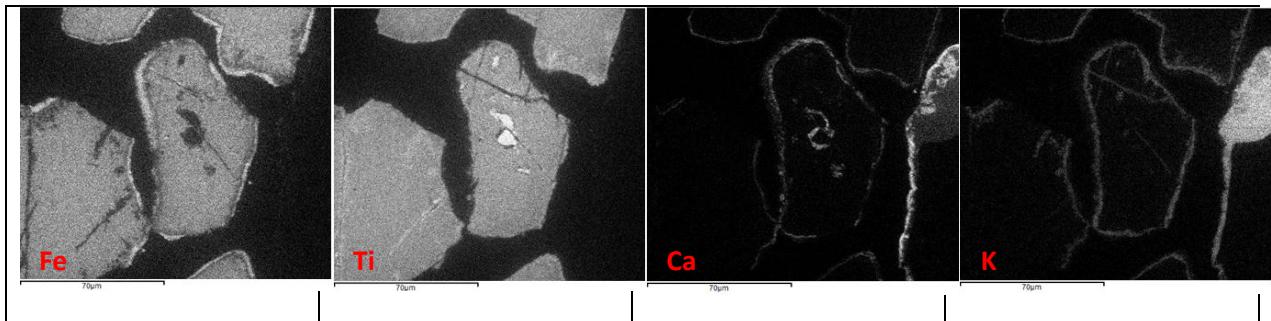


Figure 28. EDX maps of the distributions of iron, titanium, calcium, and potassium in the cross-section of an ilmenite particle from sample I collected from the gasifier after 1 h of operation.

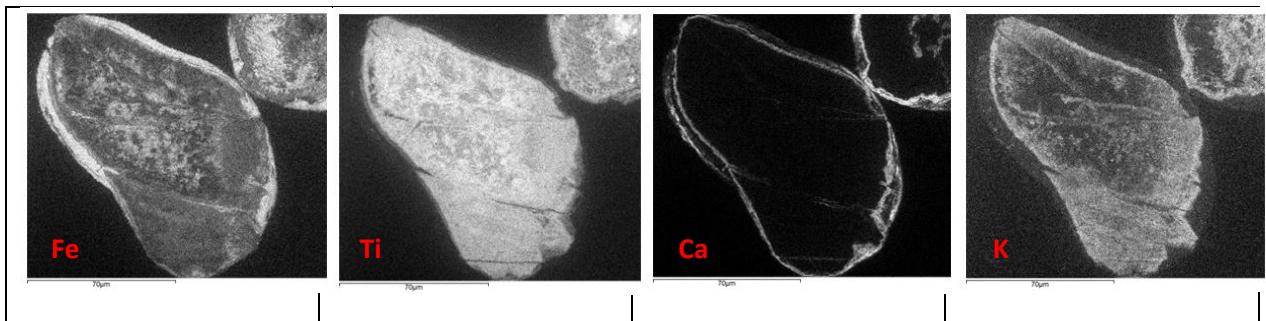


Figure 29. EDX maps of the distributions of iron, titanium, calcium, and potassium in the cross-section of an ilmenite particle from sample II collected from the gasifier after 24 h of operation.

To understand the interactions between potassium and the ilmenite particles, leaching with deionized water was carried out on the particles extracted during the process. Thereafter, the particles were analyzed by SEM/EDX and the results are presented in Figure 30. As the elemental distributions within the particles were the same and the analysis of the leachate showed that both K and Ca were leachable only to a certain extent, it can be concluded that the K is stored permanently inside the particle, where it is chemically bonded to TiO_2 .

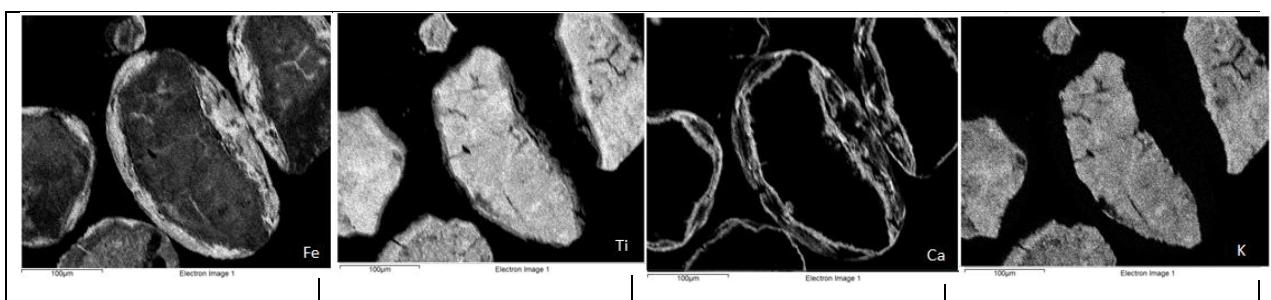


Figure 30. EDX maps of the distributions of iron, titanium, calcium, and potassium in the cross-section of an ilmenite particle from sample II leached for 72 hours.

In addition, the XRD analysis of the particles before and after the leaching procedure showed no differences in composition. In both cases, the samples contained $\text{KTi}_8\text{O}_{16}$. In light of the presented results, ilmenite offers great potential as an alkali getter material for the combustion process.

Comparisons of the tested bed materials

Depending on its composition, a bed material can affect the gasification process catalytically or/and thermally. In addition, the material can have the ability to transfer oxygen by moving from the combustion side to the gasification side of the unit. This affects both the total fuel conversion rate and the final composition of the produced gas. When comparing the tested materials throughout the experiments, the most important changes monitored were those related to: i) oxygen transport; ii) activity towards tar reforming; iii) activity towards CH_4 reforming; iv) activity towards carbon conversion; and v) activity towards the WGS reaction.

A summary of the effects observed during the activation of the tested materials is presented in Table 12. As it can be concluded that following enrichment by ash elements, all the bed materials showed activities in relation to gas shifting and tar decomposition. Quartz-sand was found to be the least active of the tested materials. Alkali-enriched olivine was the most active material in the gas phase, while bauxite, while influencing the gas composition, also displayed the ability to increase the level of char conversion. This implies that bauxite is active both above and in the bed. Bauxite also showed significant an enhanced ability to transport oxygen, which negatively affected the calorific value of the produced gas. Through analyses of the solids extracted from the system, it was concluded that the particles in all the tested cases have an outer layer rich in calcium. Potassium has detected in the cores of the silica-sand and bauxite particles, whereas it was present in the outer ash layer of the olivine particles.

Table 12. Summary of the effects of various bed materials on the performance of the Chalmers DFB gasifier.

Active effect	Quartz-sand	Olivine aging	Olivine 'triggered'	Bauxite
Ash enrichment	Yes	Yes	Yes	Yes
H ₂ /CO	Increased (from 0.7 to 0.9)	Increased (from 1.1 to 1.7)	Increased (from 1.1 to 2.6)	Increased (from 1.0 to 2.0)
CH₄ reforming	No	Yes	Yes	Yes
Tar species	Modest decrease in all groups; the greatest difference noted for the phenolics	Significant decrease in all groups; greatest difference noted for the phenolics	Significant decrease in all groups; greatest difference noted for the phenolics	Significant decrease in all groups; greatest difference noted for the phenolics
Oxygen transport	Equally low	Modest increase	Modest increase	Significant increase
Carbon conversion to cold gas [kgC, coldgas/kgC daf fuel]	0.62	0.64	0.68	0.74
SEM/EDX	K in the core in form of silicate; Ca shell around the particle	K difficult to find (due to the sand addition, the majority of the K reacts with the quartz-sand); Ca forms the shell around the particles	K in the outer layer of the particles; Ca forms the shell around all the particles	K found to be linked to Al in the bauxite particles; Ca forms a shell around the particles

The increased activities of all the bed materials tested within this thesis, which is shown to be a consequence of ash accumulation in the system, can be discussed in terms of the presence of the three most active elements: K, Ca, and Fe. All these elements are known to be active in the biomass conversion process. The influences on the WGS reaction and tar reforming may be a consequence of the presence of K, Ca and/or Fe [89-91], while the level of carbon conversion is known to be significantly affected by the presence of the alkali [3, 38-41]. The ability of a bed material to transport oxygen from the combustion side to the gasification has negative implications for the DFB gasification unit in that it decreases the value of the produced gas. In this context, Fe-oxide and Ca-sulfate are known to have high oxygen-carrying capacities.

Potassium in the system can chemically and/or physically interact with the bed material. Physical interactions can occur in the form of adsorption and/or heterogeneous condensation on the surface of the particle. By comparing the compositions of the three tested material, it can be concluded that the silicon content is highest in quartz-sand. Moreover, the particle analysis shows that potassium is found to the greatest extent within the core of the quartz-sand particle. The bonds that are formed between potassium and silicon are chemical in nature, and it seems unlikely that potassium can be released from the potassium-silicate structure. In the case of bauxite, both alumina and silicon have

affinity to react with potassium. However, the types of bonds formed have different natures: physical and chemical. Physically bonded (adsorbed) potassium is mobile and can be released in a steam-fluidized gasifier. Being released in the bed, the gaseous potassium is available to react with the char that remains after pyrolysis. In the case of olivine, SEM/EDX analysis shows very little potassium within the particle, even though the complete elemental analysis confirms its presence. Moreover, the leaching analysis shows that potassium is present in leachable form, which indicates the occurrence of a potassium-salt. Reaction of the bed material with added sulfur in the boiler, which simultaneously influences the level of CO emissions, indicates a sulfation reaction. K_2SO_4 formed in the freeboard of the boiler can be adsorbed by heterogeneous condensation on the surface of the bed particles and can be carried by the circulation to the gasification side of the unit. This stable sulfate is decomposed in a reductive environment, such as that prevailing in the volatile zone, which implies that olivine is primarily active above the bed, in the gas phase. The hypothesis regarding K_2SO_4 formation and decomposition is in line with the observed absence of SO_2 emissions from the boiler, an increase in the level of H_2S in the raw gas, and increased activity in the gasifier after sulfur was added. Sulfur turns out to be an important element in the system due to its involvement in the transport of potassium.

Calcium formed a shell around the particles of all the tested bed materials. Again, depending of the presence of Si, Ca may form a sulfate or silicate in an oxidizing environment [68]. If it is a sulfate, it can be reduced to CaO or CaS in the gasifier, and thus becomes involved in the oxygen transport and tar reduction reactions. By building the layer around the particles, Ca may also prevent additional diffusion of K into the core of the particle, which could be beneficial for the transport of the releasable form of potassium, e.g., potassium in salt form.

Iron-oxide is known to be active towards tar reforming and it is able to transport significant amounts of oxygen. However, to express these activities, iron has to be available for the reaction, i.e., to be in the contact with the gas. In DFB systems, Fe can migrate from the core to the surface of the particle, and this phenomenon may contribute to the increased oxygen transport observed with aging of the material in the system. However, for an application to gasification, this property is not beneficial as it will result in burning of the valuable gas. Among the tested materials, olivine has a much higher content of Fe in its original composition than does bauxite. Therefore, if the majority of the transported oxygen originates from the Fe-oxide, one would expect higher levels of transported oxygen in the olivine case. Surprisingly, bauxite showed superior oxygen transport ability to olivine.

Taking into account the activity of the material and the nature of the interactions with ash elements, potassium has the greatest effect on gas quality. Depending on the heat balance of the system, char gasification may or may not be desirable. If char gasification is necessary, bauxite may be the material of choice. However, the strong oxygen transport capability of bauxite places a limitation on its use for gasification purposes. If the most important consideration is gas quality, i.e., low tar content, activated olivine should be selected. Operation with bauxite or olivine does not result in the production of a gas with the appropriate properties to allow it to be used directly in the synthesis

step. However, investigations carried out within scope of this thesis highlight the key events in the process: the uptake and release of the alkali within different zones of the system. We also show that the addition of the specific elements facilitates manipulation of the chemistry in the gasifier.

Application of the findings on the GoBiGas pilot plant gasification unit

Constructed by Göteborg Energy AB, GoBiGas pilot plant [92] is aiming for the production of the 20MW Substitute Natural Gas (SNG) by biomass gasification. The unit is composed of two fluidized bed reactors: the combustor, which is the heat source for the gasification reaction, and the gasifier where gas is produced. The combustor is circulating fluidized bed, which use air as fluidization media. Gasifier is bubbling fluidized bed, fluidized with steam. As bed material, in the system calcinated olivine is used, which has been proven to be a suitable material for biomass gasification process [3, 32, 51, 55, 93-95].

The unit started with the operation in the year 2014 with the main struggle to keep the tar level in the produced gas under control and avoid clogging of the coolers located downstream the gasification unit. Even though calcinated olivine, which has been considered as active towards tar decomposition is used, in the first months of commissioning problematic of unacceptably high levels of the tar could not be overcome. Based on the findings at Chalmers, which are described in this thesis, the bed was enriched with potassium to increase the activity. The activation procedure involved addition of a water based solution of 40 %_{wt} K₂CO₃. The enrichment of the bed with potassium had a strong effect on the composition of the produced gas and tar levels, enabling the normal operation of the unit and the first successful delivery of the SNG to the gas grid in December 2014. To improve the performance even further, elemental sulfur was added into the combustor together with the potassium-salt which pushed the tar concentration to even lower levels. However, it has been noticed that olivine can be deactivated again with an increased tar level in the gas as a consequence. This has been observed mainly after a stop and necessary cooling and heating up of the process under inert conditions.

In figure 31, a correlation between yield of total tar in the dry gas and concentration of CH₄ previously presented in work of Larsson et al. [96] is shown. The correlation is derived based on measurements done in the GoBiGas unit, and can be used as a quick assessment of the tar yield based on the measured CH₄ concentration. As it can be seen from the figure, the activation of the bed by potassium salt has influenced on both the tar and CH₄ concentration. Depending on the degree of activation of the material, three operational zones can be distinguished in the figure: Non-activated, Deactivated and Activated olivine. The operation with non-activated olivine bed corresponds to a very high tar concentration, in which case the plant was operated only for a few hours before problem with clogging of the cooler appeared. The deactivated olivine bed which is represented by the middle zone in the figure corresponds to relatively high tar concentration and

the plant could be run for approximately 100 hours under those conditions before it had to be stopped. Finally, the activated zone in the figure corresponds to the standard and unhindered operation of the plant with 1200 h of the operation with minor clogging of the cooler. Within this case K-activated (addition of K_2CO_3 solution) and K, S-activated (simultaneous addition of K_2CO_3 and S) olivine is considered.

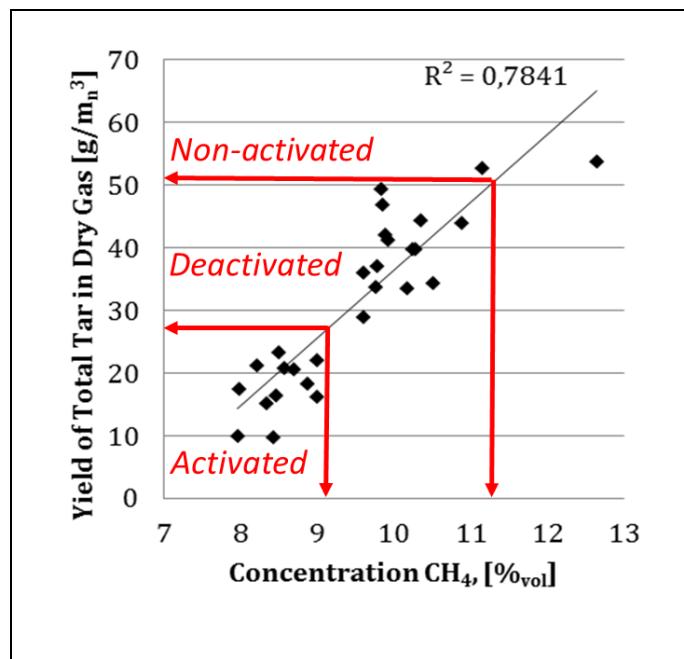


Figure 31. Yield of tar as a function of the CH_4 concentration in the dry gas produced in GoBiGas unit [96].

Specifically, looking on tar groups of the same measurements showed in Figure 31, it can be concluded that the activation of the material affected all tar groups where the strongest effect was on phenolic species, which were decreased almost to zero (see Figure 32). In total, a 62% decrease in tar concentration was accomplished by activation of the olivine compared to the beginning of the commissioning of the plant (looking on the activation with solely K_2CO_3 addition). The gas composition measured for the same points are presented in Table 13. An increase of H_2 and CO_2 and a decrease of the CO and CH_4 concentrations occurred with the activation of the bed. The effect of sulfur addition intensifies that trend, but has showed not to be permanent (see Figure 33) and after its termination, the gas composition was the same as before addition. This is not surprising and goes in line with the hypothesis established in the experiment done in Chalmers unit. Decomposition of the K_2SO_4 , that is formed in the combustor, in the gasifier results in loss of potassium and sulfur via the product gas stream.

The trends, both for tar and gas composition observed in GoBiGas unit, are matching those observed in the Chalmers system even though the operating parameters are somewhat different.

For example, the gasification temperature in the GoBiGas unit is significantly higher (870 °C) compared to one used at Chalmers (820 °C). Also, the olivine used in Chalmers system was not calcinated prior use. Regardless of those differences, the same effect of the K-salt has been noticed, which confirm the ability of olivine to transport the active element, potassium from the boiler to the gasifier and to release it.

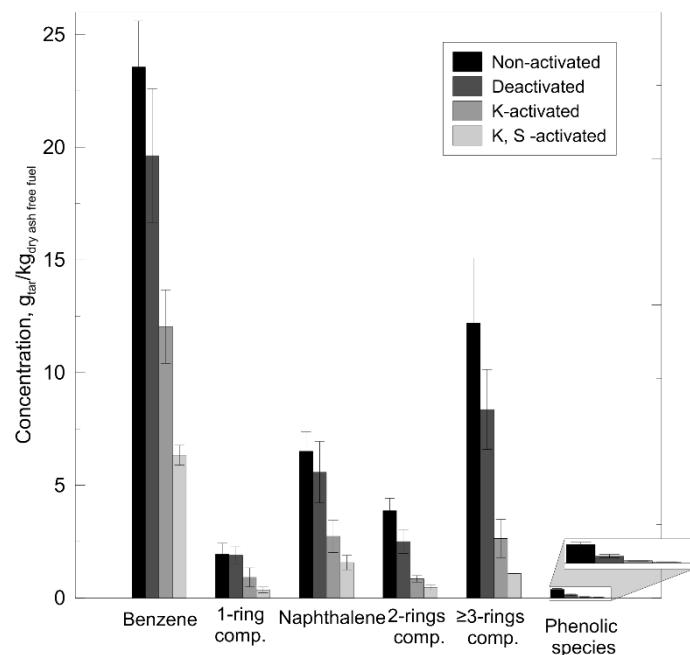


Figure 32. Concentration of the specific tar groups presented as a mean value with standard deviation-results of SPA analysis.

Table 13. The composition of the product gas produced in the GoBiGas gasification unit showed as a range of the concentrations for different measurements

	H ₂ , vol %	CO, vol %	CH ₄ , vol %	CO ₂ , vol %
Not activated	28.6-30.7	27.2-34.9	10.9-12.6	15.7-20.2
Deactivated	31.5-37.1	19.0-23.9	9.6-10.5	22.7-30.0
K-Activated	38.9-41.9	21.3-24.3	8.0-9.0	19.8-26.5
K, S-Activated	42.1	23.2-24.1	8.0-8.4	23.2-24.1

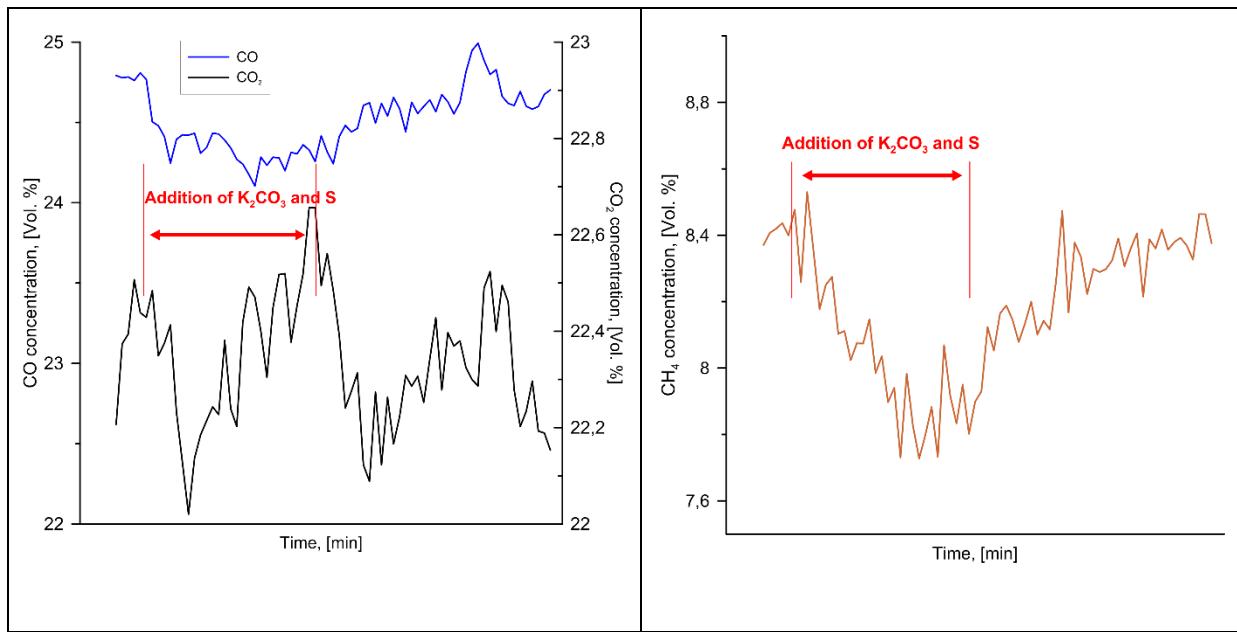


Figure 33. Effect of the sulfur addition on the concentration of CO, CO₂ and CH₄ in the produced gas

3.2. Natural ores for secondary upgrading of the gas

For the gas produced by gasification to be usable in the fuel synthesis step, it has to be of appropriate composition and purity (i.e., low tar and H₂S contents). Therefore, cleaning and upgrading of the gas downstream of the gasification unit is commonly included in the process. In this section, the results of tests done in relation to the secondary step (gas upgrading) will be presented. Two materials were tested, both of which are naturally occurring: manganese ore and feldspar.

Manganese ore

The effects of manganese ore on the various tar species in the raw gas are presented in Figure 34. The temperatures used in the study were 800°C, 850°C, and 880°C. Comparing the results presented in Figure 34, it is evident that the benzene fraction increases in the reformed gas for all the tested temperatures. However, due to the low level of accuracy of the technique used for measuring benzene [81], this change cannot be discussed or be used for drawing any conclusions. The reduction in size of the phenolic fraction in the raw gas is significant for all the cases compared to the raw gas. In contrast, the naphthalene fraction is larger in the reformed gas. The observed trend leads to the conclusion that 2-ring components and ≥3-ring components are converted to naphthalene, which is decomposed further at higher temperatures. As a result, the maximum total tar conversion rate measured in this experiment was 76%, excluding the benzene fraction.

The changes that occurred in the composition of the dry raw gas are shown in Figure 35. The concentrations of the gas species for the reformed gas at the three different temperatures of operation are presented, as well as the composition of the dry raw gas produced by gasification. As the concentration of N₂ in the raw gas is constant, the decrease in N₂ concentration observed for the dry reformed gas indicates an increase in the dry gas flow, which is probably a consequence of the production of a permanent gas in the FR. As can be seen from the figure, for all the tested temperatures, the concentrations of H₂ and CO₂ increased in the reformed gas compared to the raw gas, while the concentration of CO decreased. An increase in the concentration of H₂ can be explained in part by the conversion of tars (Figure 34) and light hydrocarbon (C₂H_x)-reforming reactions that are favored at elevated temperatures and partly by formation *via* the WGS reaction. The concentrations of measured light hydrocarbons, C₂H_x and C₃H_x, decreased with increase in temperature.

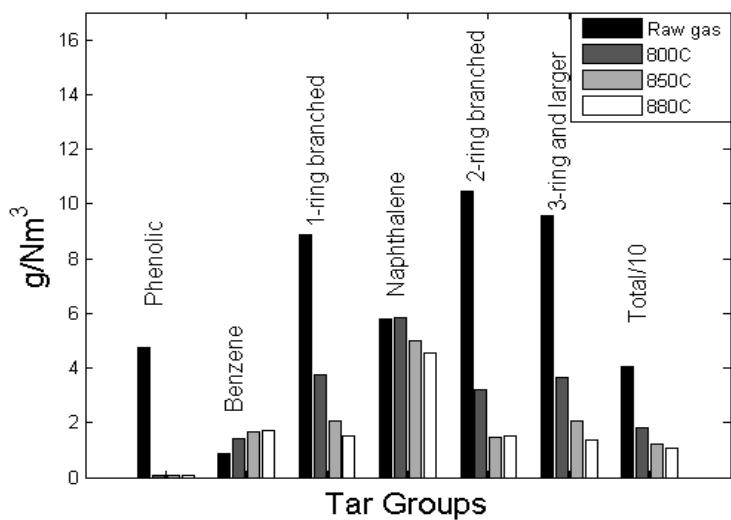


Figure 34. Concentrations of the individual tar groups and total tar concentration (in g/Nm³) in the raw gas, as well as in the reformed gases at 800°C, 850°C, and 880°C.

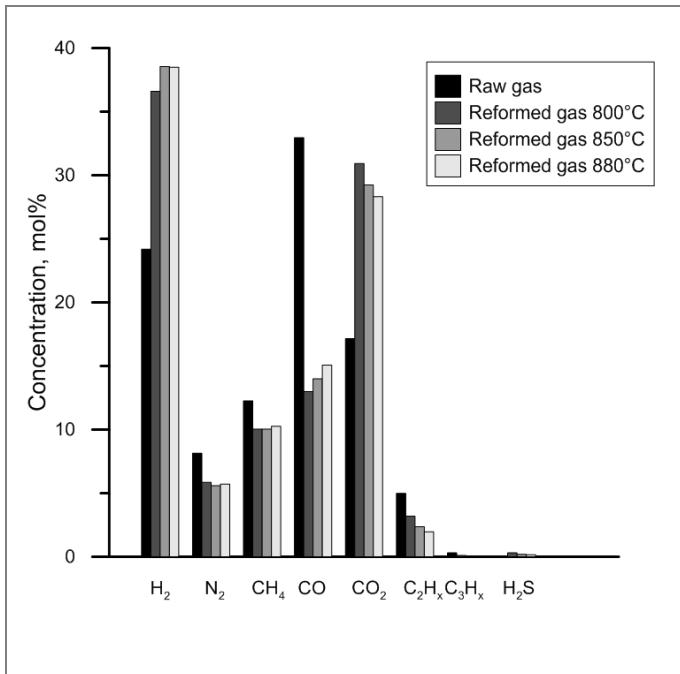


Figure 35. Compositions of the raw gas and reformed gases at the tested temperatures.

Figure 36 shows the SEM/EDX images of the manganese ore particle cross-sections after the experiment in the CLR. In the images, several manganese ore particles and one quartz-sand particle are shown. It is clear from the images that the potassium in the manganese ore is associated with aluminum and silicon, probably in the form of alumino-silicate. The agglomeration evident in the analyzed sample is triggered by the presence of the quartz-sand particle, which together with potassium has formed a layer of potassium-silicate. Given the strong propensity of potassium to react with silicon, the potassium most probably migrates from the ore towards the silica particle. Potassium incorporation into the silicate structure starts already at temperatures above 700°C [97], and the temperature used in the CLR system is sufficiently high to enhance the formation of the sticky eutectic mixture of potassium-silicate. The formed layer initiates agglomeration by bringing together several particles. From these results, it can be concluded that the mixing of manganese ore and quartz-sand should be avoided in this application.

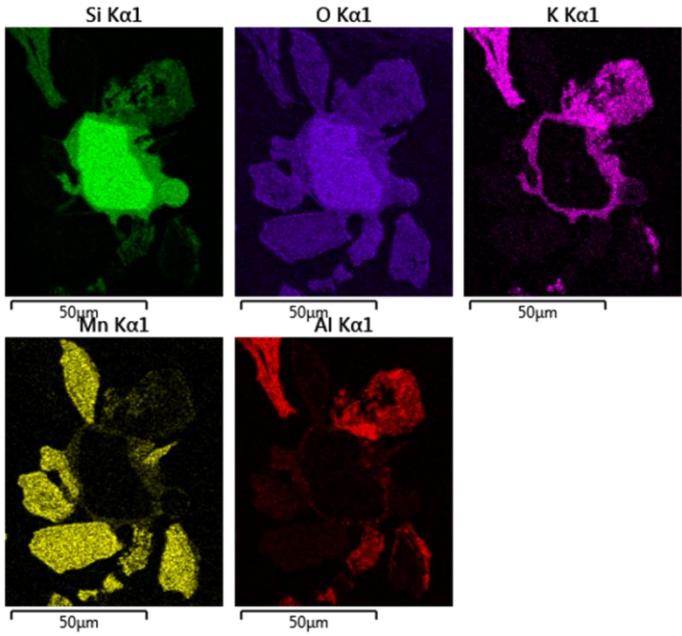


Figure 36. SEM/EDX images of cross-sections of the used manganese ore from the CLR.

Feldspar

The results of the tar sampling from both the raw gas and reformed gas obtained during the experiment with feldspar are shown in Figure 37. The yields of six tar groups are presented. It is noteworthy that the overall tar yield does not show a significant decrease, although the composition of the tar species in the reformed gas has been modified towards the formation of stable pure ring structures (Benzene and Naphthalene), as compared to the raw gas. Increasing the temperature from 800°C to 900°C caused a decrease in the levels of the heavy tar species, which was most probably the reason for the increase in benzene yield. Phenolic compounds are almost completely reformed at 900°C.

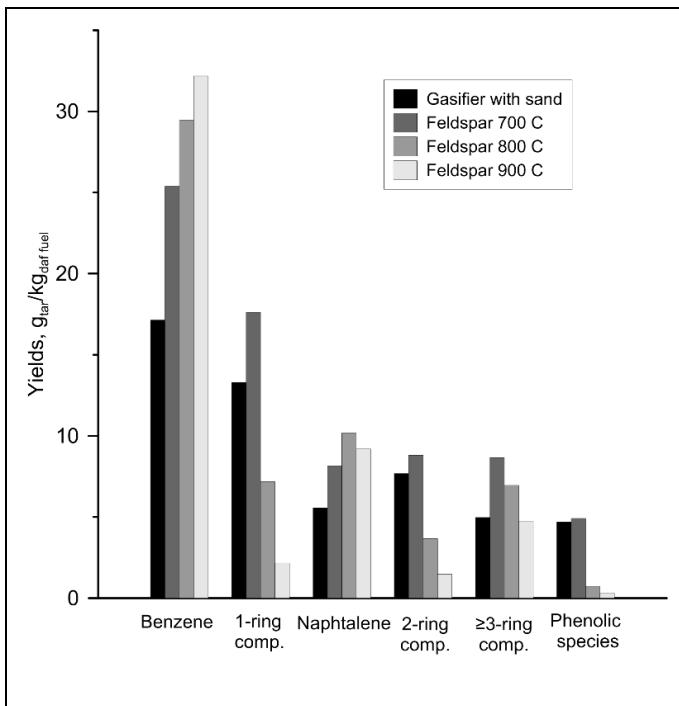


Figure 37. Comparison of the tar yields between the inlet and outlet of the CLR, [g_{tar}/kg daf fuel].

Figure 38 shows the yields of gaseous components that exited the gasifier and exited the reformer for the three tested cases. The values shown are in mol/kg dry ash-free fuel. The trend, which is towards increases in the H₂ and CO₂ yields, is enhanced with temperature increases. In contrast, the CO yield decreases. The H₂/CO ratio increases to 3. At 900°C, the CO yield increases, which may be attributed to the stripping of branched tars. The same is true for the CH₄ yield. Feldspar also shows activity related to the decomposition of alkenes, which is of importance for the downstream fuel synthesis process.

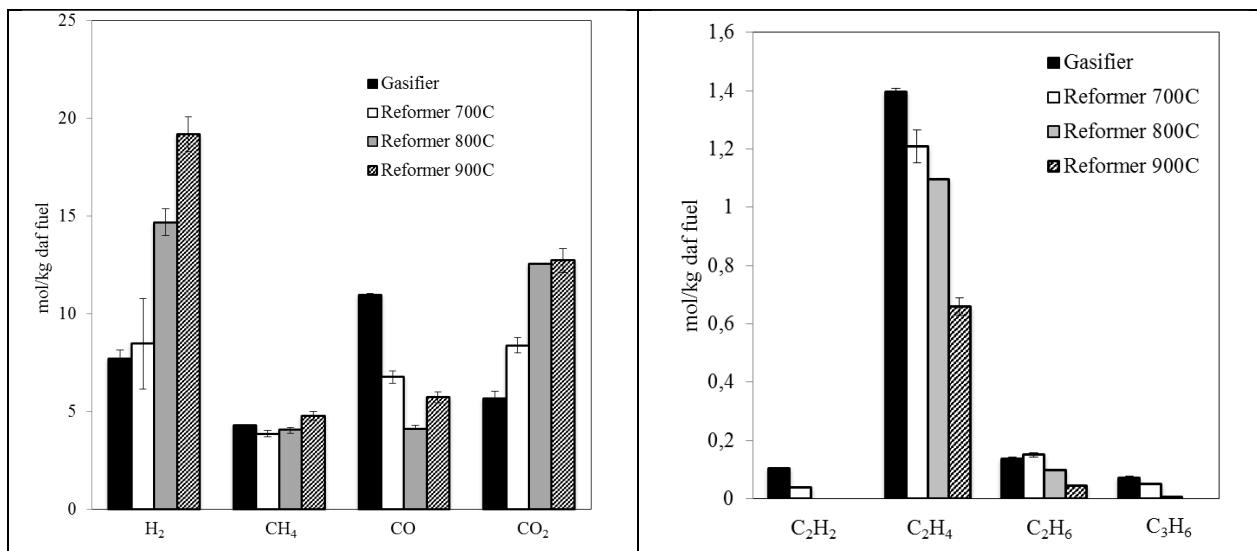


Figure 38. Compositions of the dry gases exiting the gasifier and reformer for all the tested temperatures, given in yields [mol/kg daf fuel].

To determine whether the material experienced physicochemical changes, both fresh and used feldspar samples were subjected to SEM/EDX analysis. Images of randomly chosen feldspar particles are presented in Figures 39 and 40, while the elemental distributions derived from the line scans are listed in Tables 14 and 15. The particles show no changes related to alkali release, and even the integrity of the material appears to be intact. Considering that the analysis shows no change in the alkali content of the particles, it is not possible to link the activity of the material to the presence of releasable alkali. However, since potassium-doped catalysts are known to be catalytically active towards tar decomposition, a role for the alkali in the performed investigation cannot be completely ruled out.

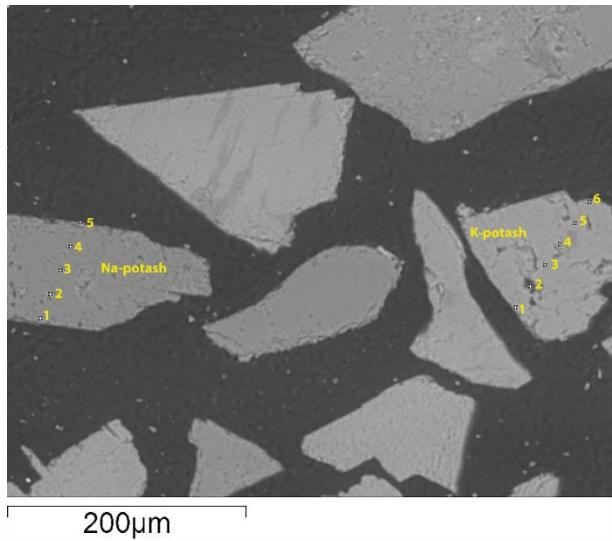


Figure 39. SEM image of fresh feldspar particles.

Table 14. Elemental analysis of fresh feldspar particles. Units for the values in the table are percentage of weight.

Fresh material	O	Na	Al	Si	K	Total
K-potash						
1	71	2	5	17	5	100
2	71	0	6	18	6	100
3	59	0	8	24	9	100
4	57	0	7	25	10	100
5	58	0	7	25	10	100
6	65	0	6	20	8	100
7	58	0	8	25	9	100
Na-potash						
1	63	6	8	14	0	100
2	64	6	8	15	0	100
3	65	6	7	15	0	100
4	64	6	7	15	0	100
5	79	3	3	4	0	100

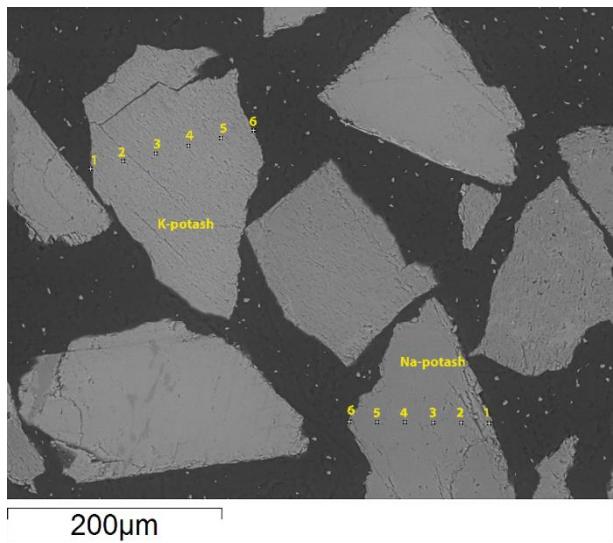


Figure 40. SEM/EDX image of used feldspar particles.

Table 15. Elemental analysis of the used feldspar particles. Units for the values in the table are percentage of weight.

Used material	O	Na	Al	Si	K	Ca	Total
K-potash							
1	68	2	7	18	5	0	100
2	59	2	8	23	8	0	100
3	58	2	8	23	9	0	100
4	57	2	8	25	9	0	100
5	58	2	8	24	9	0	100
6	59	2	8	23	8	0	100
7	81	0	4	12	4	0	100
Na-potash							
1	67	3	7	18	3	2	100
2	64	5	8	20	2	2	100
3	64	5	8	22	0	2	100
4	65	5	8	22	0	2	100
5	66	5	8	20	0	2	100
6	85	0	4	11	0	0	100

4. Concluding remarks

Considering that the bed material is critical component of the DFB gasification process, its careful selection is crucial for optimization of the ‘biomass to biogas’ route. In order for a bed material to be used as a tool for improving the gasification process, it needs to have catalytic properties and to be able to deliver gas, thereby decreasing the costs associated with the downstream process. Thus, optimization of the biofuel production process can be achieved through an eventual reduction in the number of operational units required for the production of gas of the desired composition.

In three separate studies, in which aging of the bed material in the DFB gasification system was investigated, the responses of the system were evaluated with respect to decreased tar yield, alteration of the permanent gas composition, char conversion, and increased oxygen transport of the bed material. Enrichment of the bed material by biomass ash components influences the performance of the gasification unit. In this context, three elements are identified as being important: K, Ca and Fe. Even though each of these elements was expected to exert some influence, K transport from the combustion side to the gasification side of the unit emerges as the key effect. The transport and possible release of K in the gasifier are highly dependent upon the amounts of Si and S in the system. The presence of S has a positive effect, as it interacts with K in the oxidative environment and is transported in the form of sulfate to the gasification side of the system. In the presence of Si, K is chemically bonded into the silicate structure, such that its release in any part of the system is disabled. The Ca in the ash layer, apart from its known catalytic activity towards tar, can contribute to forming a diffusion barrier for the K to react with the core of the bed particle.

In the combustion process, in order to decrease the agglomeration and to avoid problems with corrosion, the aim is to decrease the level of alkali in the flue gas. Therefore, a bed material that is able to store permanently these problematic species needs to be chosen. In addition, chemical reactions between the alkali and bed material should not lead to the formation of low-melting-point mixtures.

We conclude that in a DFB system in which the material alternates between different environmental zones, as is the case in the presented Chalmers set-up, the establishment of a balance between the levels of K, Ca, S, and Si in the system is of great importance. Among the tested materials, bauxite has a positive influence on fuel conversion. However, the strong oxygen-transport ability of bauxite limits its use as a bed material for gasification purposes. Olivine, if it is fully saturated with alkali, ensures the best performance of the unit, in terms of the quality of the produced gas. Ilmenite, which was tested as a bed material for the combustion process, has a tendency to store potassium in the particle cores. This is beneficial with respect to avoiding agglomeration in biomass-fired and waste-fired boilers. Regarding the complexity of the chemical reactions that occur between the bed material and inorganics in the different zones of a DFB gasification unit, we observed the uptake and release of inorganics from the fuel by the bed, which highlights the importance of carefully selecting the combination of fuel and bed material to be used in the system.

The results obtained and the conclusions drawn for the investigations conducted with the Chalmers DFB gasifier, especially those involving olivine are of great importance. The knowledge gained from these experiments has been transferred to the pilot plant-scale gasifier at GoBiGas, enabling the start-up of the unit, which was not previously possible due to the low quality of the produced gas.

If a secondary cleaning step is necessary in the process chain, natural ores are the bed materials of choice. With a suitable combination of bed material and operational conditions in the DFB system (CLR system), simultaneous removal of tar and H₂S might be possible, while the regeneration step would prolong the lifetime of the bed material. Both manganese ore and feldspar, which have been tested in the work of this thesis, show abilities to influence the gas composition and affect the WGS reaction. However, the levels of cleaning employed resulted in a tar concentration in the gas that still exceeds the level allowable for a biofuel synthesis process.

5. Nomenclature

BB	Bubbling Bed
CFB	Circulating Fluidized Bed
CHP	Combined Heat and Power
CLC	Chemical-Looping Combustion
CLR	Chemical-Looping Reforming
DAF	Dry Ash-Free (Fuel)
FCC	Fluid Catalytic Cracking
GC	Gas Chromatograph
IR	Infrared
PSD	Particle Size Distribution
SEM	Scanning Electron Microscopy
ICP-SFMS	Inductively Coupled Plasma Sector Field Mass Spectrometry
SNG	Substitute Natural Gas
SPA	Solid-Phase Adsorption
WGS	Water-Gas Shift
HTR	High-Temperature Reactor

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