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Use of Bed Materials in Dual Fluidized Bed (DFB) Systems

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Abstract

Dual Fluidized Bed (DFB) gasification is one alternative for the production of biofuels. In a DFB gasification process, the bed material plays a crucial role. Primary role of the bed material is to provide the heat needed for the gasification reaction. If the bed material, used in the system, is catalytically active it can improve the quality of the produced gas. In addition, inorganics originate from the biomass are retained in the system in the form of ash, which interacts with the bed material, thus representing catalytic potential. As a consequence of being circulated between oxidative and reductive environments, the bed material releases some inorganics into the gas phase, thereby influencing the final composition of the produced gas. The goal of the present work is to increase our understanding as to how changes in the bed material related to reactions with ash components can be utilized to improve the performance of the system. In this way, it should be possible to optimize the gasification step, thereby decreasing the cost of biofuel production. Moreover, by choosing naturally occurring bed materials not only the cost of the process is decreased, but also negative impact on the environment which comes with the disposal of the material.

This work deals with the application of catalytic bed materials in dual fluidized bed systems, both as a primary measure in the gasification process itself and as a secondary measure for the reforming of the raw gas. Applied directly in the gasification step, the bed material interacts with the inorganics derived from the fuel. As a result of this interaction, the bed material changes its physical and chemical properties, which has impacts for the gasification process. In the present study, four naturally occurring materials were evaluated. In the Chalmers 2–4-MW_{th} gasifier, the effects on the gasification process of interactions between the ash and the bed material were studied for quartz-sand and olivine. The effects on the process were evaluated with respect to: 1) the composition of the produced gas; 2) tar content; and 3) the physicochemical properties of the bed material. The studies yield information about the transport of inorganics between the reactors and their influences on the gas composition. Whereas the release of alkali during gasification implies a potential for enhancement of the gas quality, the presence of these same species represents a risk for agglomeration during combustion. In the Chalmers 12–MW_{th} boiler, ilmenite was tested as the bed material and as an alkali getter material. The adsorption of potassium to the ilmenite is shown to be non-reversible, and ilmenite shows great promise as a material for decreasing bed agglomeration in fluidized bed boilers. As a secondary measure, downstream of the gasifier, manganese ore was evaluated for its tar-reforming capability in a dual fluidized bed reactor system, in a process known as chemical looping reforming. This material has the ability to reduce tar levels by as much as 72%, while having high activity towards hydrogen production.

Keywords: DFB, CLR, bed material

List of Publications Included in the 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, Under Review*

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. *To be submitted*

Jelena Marinkovic is the principal author of Papers 1, 2 and 4. Angelica Corcoran is the principal author of Paper 3, which is the result of a Master's degree Thesis supervised by Jelena Marinkovic. Nicolas Berguerand and Fredrik Lind contributed with experimental work and editing for Paper 1. Pavleta Knutsson contributed to the work with ideas and discussions. Martin Seemann, who is the assistant academic supervisor, contributed to the discussion and participated in the experimental work and editing of all 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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1. Introduction

1.1. Dual Fluidized Bed

Energy produced from biomass has attracted strong interest as it represents a potential way of decreasing CO_2 emissions. Furthermore, increased production of energy from biomass might lead to an end to the dependence on fossil fuels [1-5]. Swedish government aim towards energy independence and has set the goal to have vehicles fleet that is fossil fuel free by the year 2030 and zero net emissions of greenhouse gases by the year 2050 [6].

Biomass gasification, which is a thermochemical process in which solid fuel is converted to gas, is a viable technical option to meet increasing demands for energy. The gas that is produced by biomass gasification contains CO, CO_2, CH_4, H_2, H_2O, and N_2, together with some light hydrocarbons. In addition, impurities, such as tars and inorganic compounds, are present. Depending of the gasification method and fuel used, the concentrations of the gaseous components and impurities vary. High levels of tar result in loss of the energy that is chemically stored. While condensation of these species in cold regions of the system results in clogging and leads to severe operational problems [2, 7-10], inorganics in the fuel, such as potassium, chlorine, and sulfur, cause corrosion problems and are detrimental to the catalysts acting downstream of the gasification process.

A schematic of the biofuel production process starting from biomass is shown in Figure 1, where each box represents several operational units. In order for the gas to be used in the final step (the product synthesis), it needs to fulfill specific requirements regarding purity, H_2/CO ratio, and CO_2 content. Optimization of the gasification part of the process is the first step towards decreasing the cost of the overall process, including increasing of the process efficiency and simplifying the gas conditioning process. A major factor is the type of bed material and its effects on both solid fuel conversion and gas composition.
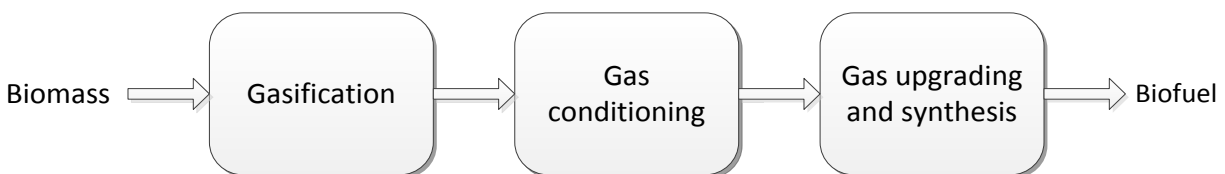

Figure 1. Schematic of biomass involvement in the biofuel production process *via* gasification

The present work deals with the interactions between the bed material and ashes and other impurities and their effects on the overall performance of a Dual Fluidized Bed (DFB) unit (Figure 2). The principle underlying the process is that the bed material that circulates between the two reactors provides the heat needed for the endothermic gasification reactions. By burning one part of the fuel, the material is heated in the combustion section and circulated to the gasifier, which is fluidized with steam. As the gasifier in this setup is separate from the combustion section of the system, the raw gas produced is not diluted with nitrogen.

The same principle can be applied downstream of the gasifier for secondary step-gas cleaning, with the employed bed material being catalytically active. In this Chemical Looping Reforming (CLR) unit, the catalyst reforms the raw gas in one reactor (reformer) and is then reactivated with diluted air in the other reactor (regenerator). The principle of the CLR is similar as Fluid Catalytic Cracking (FCC) used in oil industry as the catalytic material that is deactivated by the carbon deposits in one reactor circulates to the other reactor where deposits are removed. Being applied downstream of the gasification process, this system enables an optimization of the biomass conversion to the raw gas.
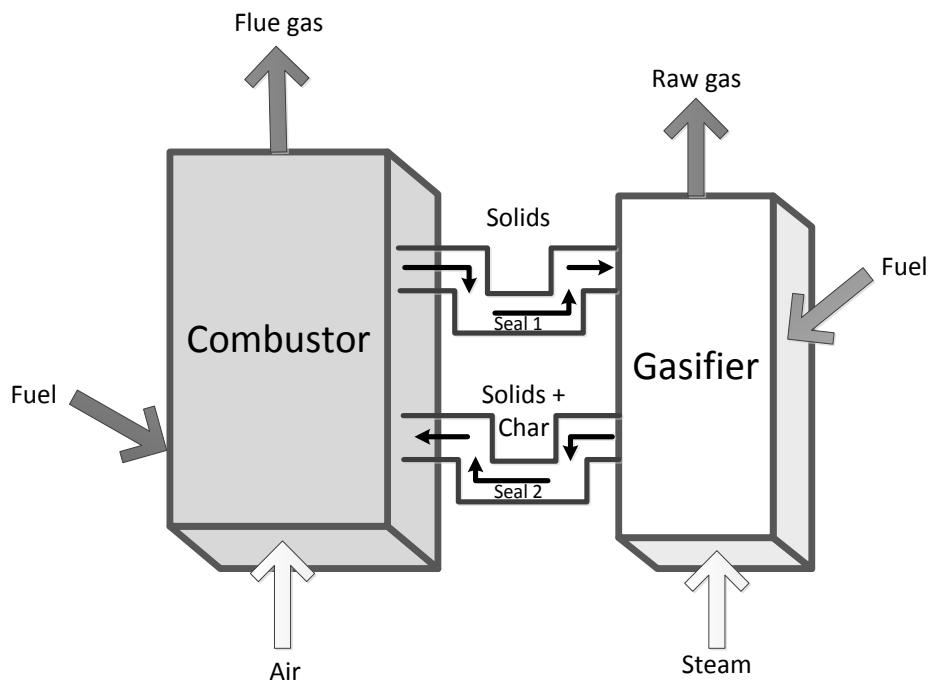

Figure 2. Schematic of the Chalmers Dual Fluidized Bed Unit

1.2. Biomass and ash

The conversion of biomass, with associated physical and chemical changes, is schematically presented in Figure 3. Initially, the fuel particle is heated, dried, and devolatilized. Subsequently, one or more ash particles are produced when the remaining char is combusted.
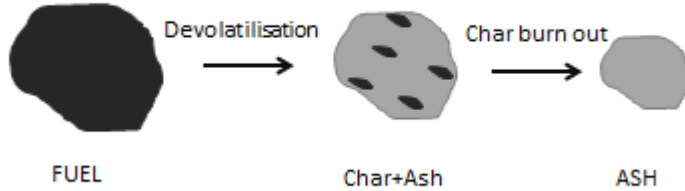

Figure 3. Schematic of the fuel to ash conversion process

The content and elemental distribution of the biomass ash varies according to the origin of the biomass and the part of the plant used. The ash content can range from 0.5 % wt. for wood, up to some percent in straw [11, 12]. In general, biomass ash has a relatively low melting point and, therefore, the gasification process in the DFB has to be operated at relatively low temperatures (<950°C). The main ash-forming elements are Ca, Si, K, Na, S, Cl, Al, Fe, P, Mg, and Mn. These elements, their levels, and associations exert significant influences on the performance of the process and may raise environmental issues [13, 14]. High levels of silicon and potassium are recognized as being problematic for the process, as their interactions tend to form a mixture that has a low melting point [15, 16]. Even though biomass can have a very low level of ash, it can cause severe problems within the system. Agglomeration due to ash melting can cause bed defluidization and shut-down of the process, with consequent increased maintenance costs [17]. Moreover, potassium released in the form of chlorides represents a high risk for corrosion, while potassium released in the form of sulfate may create deposits on heat transfer surfaces [18].

The interactions between the ash-forming elements and the pathways of their release are highly dependent upon the composition of the fuel. Valmari et al. [19] have studied the ash distributions that occur during combustion of biomasses of different origins. They tested willow, forest residue, and waste wood and concluded that potassium, instead of forming the chloride or sulfate species, tends to react with silicon from 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 content in the fuel or in the bed material leads to the formation of potassium silicates rather than potassium sulfate [20, 21]. However, studies carried out by Novakovic et al. [22] in a fixed bed reactor showed that the presence of Ca can influence the potassium silicates creation and prevent it.

Sulfur derived from the biomass is released during both the devolatilization and char conversion phases. Depending on the prevailing gas atmosphere and ash composition, the sulfur ends up in the produced gas as H_2S, COS, SO_2 or organic sulfur components (thiophene, dibenzothiophene, etc.) [23]. The sulfur content of biomass is significantly lower than that of coal. However, even low contents that result in some hundreds of parts per million (ppm) sulfur in the produced gas, exceed the limits that most catalysts downstream of the gasifier can handle before affecting theirs activity. Most synthetic processes require a sulfur-free gas [24]. To achieve this, guard beds, which are commercially available, are commonly used. In the process, sulfur is released in the form of H_2S or SO_2, which can further react with alkali metals and create sulfides and sulfates, depending of the environment in the reactor. Thus, the presence of alkali and alkali earth metals in the biomass allows the retention of sulfur in the ash [25] . The formation of sulfates of potassium and calcium in an oxidizing environment follows reactions (1), (2) and (3) [19]:

$$2KCl + H_2O + SO_2 + \frac{1}{2}O_2 \leftrightarrow K_2SO_4 + 2HCl \tag{1}$$

$$2KOH + SO_2 + \frac{1}{2}O_2 \leftrightarrow K_2SO_4 + 2H_2O \tag{2}$$

$$2CaO + SO_2 + \frac{1}{2}O_2 \leftrightarrow CaSO_4 \tag{3}$$

A study of the combustion of the biomass done by Nordin et al. [25] has shown 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 interactions between Ca, K and Si and those between S, K and Ca, Knudsen et al. [26] concluded that sulfur retention in the ash is a function of the Si/(Ca+K) ratio. They also concluded 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. This is due to the creation of K- and Ca-silicates, which prevent sulfate formation.

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

1.3.   Bed materials

In DFB systems, the bed material is an essential factor in the overall process. The primary role of the bed material in the process of indirect gasification is to deliver the heat needed for the gasification reaction. Furthermore, the bed material can be viewed as a tool for increasing the quality of the produced gas by facilitating a high level of fuel conversion and low contents of tar, sulfur, and alkali.

Any bed material employed in a DFB system undergoes temperature- and environment-dependent variations. Figure 4 shows a simplified schematic of the pathway of the bed material during one cycle in the system. In the boiler, the material is in a predominantly oxidative environment. However, in the gasifier, the bed material enters an oxidative environment in the steam-rich zone at the bottom, whereas it encounters a highly reducing environment rich in volatiles in the freeboard. In the Chalmers unit, fuel is fed in at the top of the gasifier and the aforementioned zones can be clearly distinguished.

The main criteria to be considered when selecting a bed material are illustrated in Figure 5. In particular, the mechanical and chemical properties of the bed material have to be considered, although the overall economic aspect is decisive.
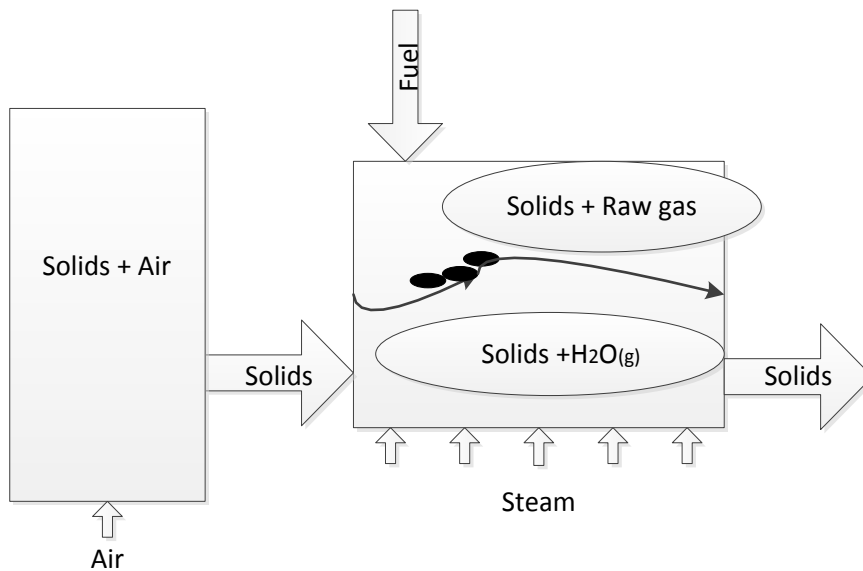

Figure 4. Schematic of the pathway taken by the bed material during one cycle in the Chalmers DFB system
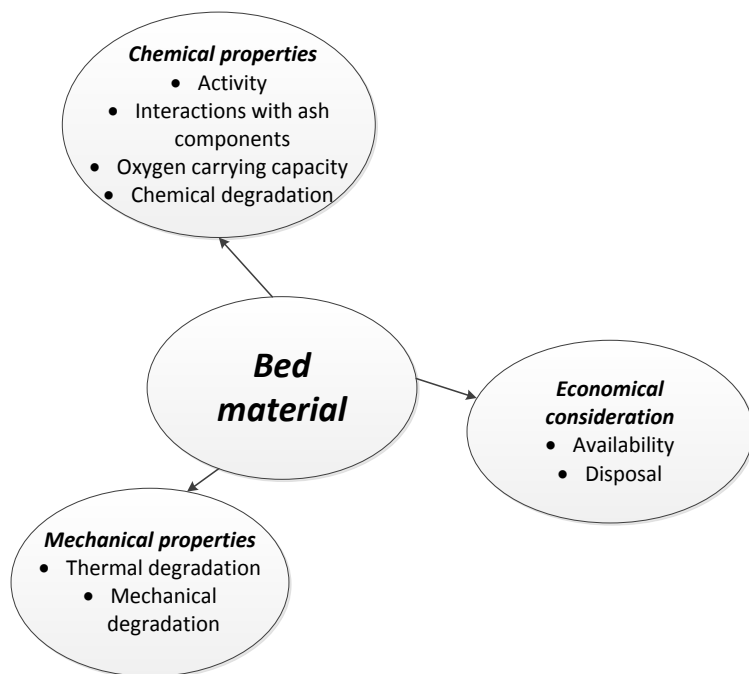
Figure 5. The most important criteria for selecting a bed material

1.3.1 Chemical properties

Activity of the bed material

As previously mentioned, the main function of the bed material is to transfer heat. However, in the case of a catalytically active bed, the chemistry within the system is influenced and consequently, the nature of the produced gas. 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. In Papers 1 and 2, these two different approaches are explored. In Paper 1, the effect of manganese ore on the upgrading of the raw gas produced in the gasifier is studied in the CLR system, located downstream of the gasifier. In Paper 2, the use of olivine as a bed material in the gasifier is discussed.

The activity of the bed material can be a determinant of the rate of fuel conversion and the composition of the produced gas. Various bed materials have been tested in the past, being either added directly to the gasification process or used as active agents for secondary cleaning of the gas (Figure 6). In Figure 6, the spectra of activities, in relation to fuel conversion and both tar and sulfur removal, are shown for different bed materials. The bed materials are metal-, metal-oxide- and alkali-salt-based compounds combined with the support material. The main roles of the support materials are to reduce the sintering rate, provide a large surface area, and in some cases,

to participate in the reaction itself. Al_2O_3, SiO_2, TiO_2, ZrO_2, MgO, CeO_2, and zeolites (microporous solids based on alumino-silicate) are the most commonly used support materials.
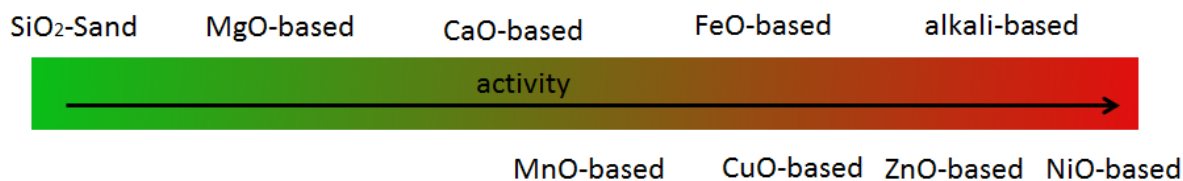

Figure 6. Schematic of the activity spectrum for a range of oxide-based bed materials

Silica sand, which is commonly used as the bed material in fluidized bed systems, is not expected to influence the chemical reactions within the system so as to increase the quality of the produced gas, e.g., a high hydrogen yield and low tar content. For that purpose, numerous naturally occurring materials and synthetically produced materials have been studied [3, 7, 10, 29-31].

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, 32-36].

Alkali-based catalysts (K_2CO_3, K_2O, Na_2CO_3) have been studied in different process set-ups for the purpose of catalytic gasification. Potassium increases the rate of carbon conversion [3, 37-40]. Moreover, K_2CO_3 is active against tar species [7, 41]. In the study of Hauserman et al. [42] linked increased reactivity of the fuel following the addition of wood ash as the catalyst, as compared with the non-catalyzed process to the presence of the alkali metals in the ash.

Oxygen carriers

When an active bed material in the form of a metal oxide is used, it has the ability to transfer oxygen from an oxidizing to a reducing environment. The reduction of the bed material in the volatile zone of the gasifier results in the combustion of valuable gas components, thereby lowering the heating value of the produced gas [43].

Bed material-ash interactions

When interacting with the biomass ash components, the bed material tends to cause agglomeration. Depending of the biomass ash content and composition and the type of bed material used in the system, agglomeration can be more or less severe [15, 16, 44].

Interactions between ash components and bed particles can occur on the physical level or chemical level. These interactions result in layer formation around the particle. Zevenhoven-Onderwater et al. [45] concluded that these layers are formed *via* three alternative modes of interaction: i) the particle is simply a carrier of the ash layer (the layer contain elements that originate exclusively from the fuel); ii) a chemical reaction between the particles and ash elements (the layer contains elements that originate from the fuel and bed material); and iii) a combination of the first two interactions.

In a DFB system, the bed material together with the ash is eventually distributed as: 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) [19]. When silica sand is used, certain ash components can interact chemically with the bed particles. Potassium released from the biomass can diffuse into the sand particles, creating an 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 [15, 16, 46]. 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:

$$SiO_{2(s)} + 2KCl_{(g)} + H_2O_{(g)} \rightarrow K_2SiO_{3(l)} + 2HCl_{(g)} \tag{4}$$

$$SiO_{2(s)} + 2KOH_{(g)} \rightarrow K_2SiO_{3(l)} + H_2O_{(g)} \tag{5}$$
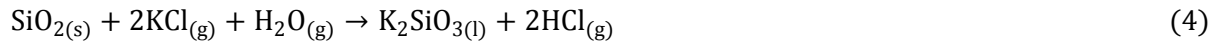
The reactions result in a melted layer around the particle., The thickness of the layer increases with increasing ash content of the fuel, as well as increases in the duration of the operation [47, 48].

 He et al. [47] studied the interactions between biomass ash and a quartz-sand bed in different reactor setups, i.e., Bubbling Fluidized Bed (BFB) and Circulated Fluidized Bed (CFB) boilers. In the study [47] was shown that the composition of the ash layer around the particle is a function of the bed material used and the fuel composition, but is also dependent upon the reactor set-up. The formation of melted potassium-silicate was proposed as the first step in the ash coat build-up. In addition, calcium derived from the fuel was shown to react with melted potassium-silicate, resulting in the release of potassium and the formation of Ca-silicate with a higher melting point. However, an analysis of the material, in the same study, showed different elemental distributions within the layers for the BFB and CFB systems. SEM/EDX of cross-sections of particles extracted from the BFB boiler revealed a silicate-layer rich in Ca, while for the particles extracted from the CFB boiler, two layers were observed: an inner layer rich in potassium and an outer layer rich in Ca.

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. Besides silicate formation, agglomeration is in the literature also connected to the combustion of a fuel with a high content of phosphorus, in which case alkali phosphates are created [22].

Some studies have shown a positive impact of the interactions between the bed material and ash. Olivine, which is a well-investigated material, changes its activity when exposed to calcination, and also when it interacts with ash elements [3, 49, 50]. However, the mechanism of olivine activation remains unclear. The interactions of bed material with ash components are described in Paper 2 for olivine with the focus on gasification conditions, and in Paper 3, the interactions of ilmenite with ash components are outlined in relation to the operation of the boiler.

Chemical degradation

Catalytic materials are necessary in the process of biofuel production. Depending of the desired final product, noble metal based catalysts are used in the process downstream of the gasification. Commonly used catalysts are sensitive to the presence of impurities that originate from the gas. Sulfur derived from the gasification gas acts as a poison for the active sites in the bed material. The adsorption of sulfur by the catalyst is strong and often leads to the complete deactivation of the material [51]. Even though sulfur level in the raw gasification gas is relatively low, acceptable level of the H_2S in the gas that is to be further processed has to be ≤1 ppm [52].

1.3.2 Mechanical properties

In general, mechanical damage results in the loss of mass or function of the bed material. Loss of mass is caused by attrition and fragmentation. Since fluidized beds are discussed in this work, resistance to attrition is one of the most important properties of the bed material.

Heavy hydrocarbon species present in the gas can affect the performance of the bed material. Condensed hydrocarbons can be physically deposited on the surfaces of the particles, which results in loss of activity due to the blockage of the active sites and the pores in the structure of the material [51].

Depending on the operational conditions and temperature of the process, the material can sinter, leading to the evaporation of metals from the material and, consequently, the loss of active sites. In the interaction with ash from the fuel, this phenomenon can be enhanced [53, 54], resulting in the formation of deposits and severe problems for the system.

1.3.3 Economical considerations: availability and disposal of the bed material

Considering the potential degradation of the bed material over time and the cost of replacement, as well as environmental laws related to the disposal of the used material, the use of natural ores instead of synthetically produced materials seems to be a convenient solution. Natural ores based

on active oxides (see Figure 5), such as olivine, dolomite, calcite, and ilmenite, have been researched in terms of their applications to the thermochemical conversion of solid fuels [55-59].

Olivine [$(Mg,Fe)_2SiO_4$] is a naturally occurring material. It has been studied extensively for *in situ* gas cleaning in gasification, both in pure form and mixed with an active component, such as Ni or Fe [3, 5, 31, 60]. However, to ensure its desired catalytic effect against tar species, olivine needs to be activated. While several studies have been carried out on this topic, the mechanism of olivine activation remains unclear, although it is commonly attributed to the migration of Fe to the surface of the particle and to interactions with inorganics from the ash and the formation of the CaO layer [49, 60, 61].

The natural iron ore ilmenite ($FeTiO_3$) has been widely tested as a catalytic material in Chemical Looping Combustion (CLC) due to its oxygen-carrying ability [62]. Moreover, in CLC, ilmenite has been studied for its ability to drive the reforming of biomass-derived raw gas. Lind et al. [55] demonstrated the reforming capability of partially reduced ilmenite and reported a tar conversion of 60% when 100% ilmenite was used in a DFB system . 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 [35, 55].

In addition to the main bed material, additives can be present in fluidized bed systems. Bauxite, kaolin, and dolomite are commonly used for alkali adsorption and the prevention of corrosion [27, 28, 63]. This topic is covered in detail in Paper 3, where ilmenite is discussed as an alkali-binding material.

Logically, there has to be eventual disposal of the process materials. The mode of disposal depends on the origin of the material and its toxicity. Considering that biomass ash contains plant nutrients, the use of ash as a fertilizer or soil amendment agent has great potential. However, ash also contains some hazardous elements, such as heavy metals. According to environmental regulations, the concentrations of these elements in leachable form need to be below a certain level to meet the requirements for landfilling. Alternatives uses for ash include the production of ceramics and construction materials [14]. Figure 7 shows the elements that are present in the ash, in the order of increasingly problematic disposal (from green to red).

C O H Ca K N Si Al Mg P Na Fe Mn Cu Cl S Mo Hg Pb As Zn Ba Cr Sb Ni Cd

Figure 7. Distribution of the elements in ash, in the order of increasing difficulty with proper disposal (from green to red).

As shown in the figure, Ni-based catalysts, which are often used as catalytic materials for gas upgrading, not only are costly to manufacture, but also require specialized and costly disposal. Reflecting on the materials studied in the thesis, olivine can be problematic to dispose. Even though it is not classified as hazardous waste, olivine contains some amount of chromium and nickel. Consequently, despite the fact that it is mineral rock and have low price on the market compared to the synthetically produced materials, in the final step, its disposal, olivine can bring some additional costs. A trade-off between catalytic activity and economical and environmental issues has to be made in this situation.

1.3.4 Aim

Even though several studies have been performed previously on various bed materials, there remains an urgent need to identify suitable bed materials for optimization of the gasification step, to ensure the production of higher quality gas from a gasifier, e.g., a high yield of hydrogen and low tar and sulfur contents. Moreover, this has to be achieved at a reasonable cost. The need to identify such bed materials and a desire to increase our understanding of the relevant processes involved motivate the present work.

The main objective of the work is to investigate how changes in the bed material related to interactions between the ash and material influence the performance of the system. Increased fuel conversion and upgrading of the gas are the goals. By understanding these interactions, it will be possible to choose suitable combinations of bed material and fuel for the process.

In this work, the use of natural materials is emphasized. Natural ores are mixtures of various minerals and behave accordingly. In this study, four materials were applied, i.e., quartz sand, olivine, ilmenite, and manganese ore.

In Paper 1, the possibility to use manganese ore as the material in the second step (gas upgrading) was investigated. The Mn_3O_4-based ore behaves as an oxygen carrier and catalyst towards tar species. The performance of the material was researched in the CLR unit, located downstream of the Chalmers gasifier.

Papers 2 and 4 investigate the use of two natural materials, olivine and quartz-sand, in the DFB gasification system. Both materials are expected to be able to bond alkali. Sand has minimal both oxygen-carrying capacity and catalytic properties. In contrast, olivine can transfer limited amounts of oxygen and is catalytically active towards tar species. The influence of the ash components on the performance of the system was the focus of both studies.

Ilmenite, which is an iron-titanium oxide-based ore, is an oxygen carrier and alkali getter material, and depending of the degree of its reduction, it shows catalytic properties. The ability of ilmenite to minimize potassium release in the boiler is described in Paper 3.

2. Experimental

2.1   The Chalmers DFB unit and measurement techniques

All the bed materials were evaluated in the Chalmers facility. The Chalmers Unit comprises a 12-MW_{th} circulating fluidized bed boiler and the gasifier, which is a 2–4-MW_{th} bubbling fluidized bed, fluidized with steam. A schematic of the unit is shown in Figure 8. The flexibility of the set-up allows operation of the boiler either independently of the gasifier or together when the gasifier is coupled to the system *via* two loop seals. The heat needed for the gasification process is delivered by the bed material, which is heated in the boiler and circulated to the gasifier. Fuel is fed at both the combustion and gasifying sides. 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 and pressure of 1–2 kPa. The char that remains after the gasification reaction is sent 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. [64]; in the same study, the process was evaluated and reported for a case in which the system was run with silica-sand as the bed material.

In Figure 8, letters A–D indicate the locations at which the bed material can be sampled. For the work presented in Papers 2 and 4, sampling was carried out at Loop seal 1 (point B) and Loop seal 2 (point C). These two sites represent the entrance and exit points of the gasifier.
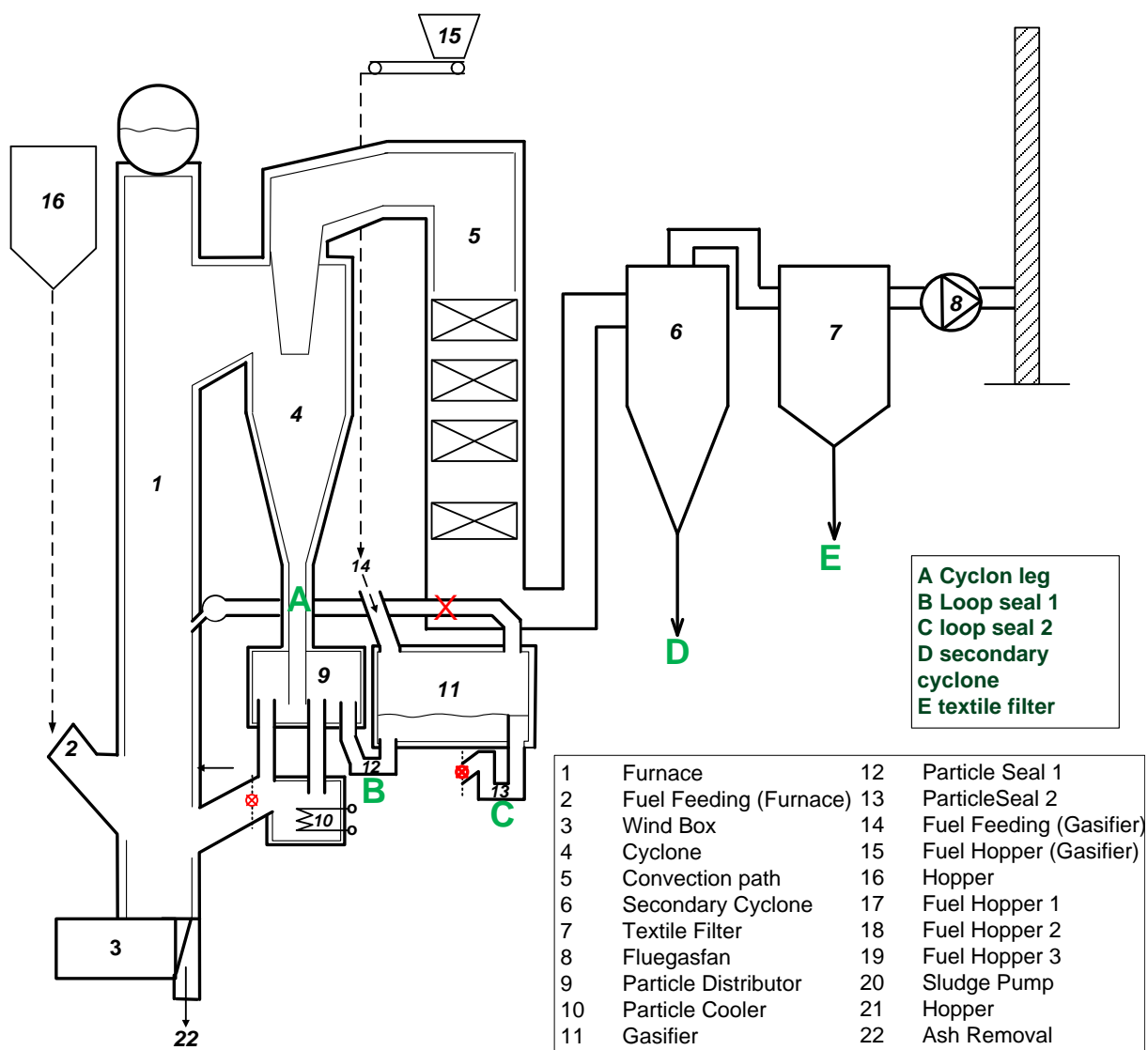
Figure 8. Schematic of the Chalmers Dual Fluidized Bed System. Red sign X correspond to the sampling point while red circles represents connection point between loop seal 2 and down-comer to the boiler.

During process operation, the composition of the raw gas was monitored online and tar samples were taken. Sampling was from a slipstream that led from the raw gas line (indicated by a red X in Figure 8).

For the analysis of the gas, Varian CP4900 Micro-Gas Chromatographs (micro-GC) were used. Sampling of the tar species from the system was performed using the Solid Phase Adsorption (SPA) method. Eluted samples were then analyzed in a Gas Chromatograph equipped with Flame Ionization Detection (GC-FID). The procedures used for sampling and analysis can be found

elsewhere [65]. For the purpose of this study, all the samples were analyzed with the same equipment and according to the same procedure. The identified components of the gases are grouped as follows: benzene; 1-ring components; naphthalene; 2-ring components; 3-ring and higher components; and heterocyclic aromatics.

Bed material samples were acquired using specially developed probes that were inserted into the seals during process operation. A schematic of the probe is shown in Figure 9. The probe is equipped with cooling system and works on a suction principle. The procedure starts with air injection to clear the pipe, followed by suction pulses, until the probe is filled with the sample. The probe is then removed, allowed to cool, and the sample is collected. Sampled material was further analyzed by Scanning Electron Microscope and Energy Dispersive X-Ray spectroscopy (SEM/EDX), using Inductively Coupled Plasma Sector Field Mass Spectrometry (ICP-SFMS). In addition, leaching of the solid material with deionized water was carried out.
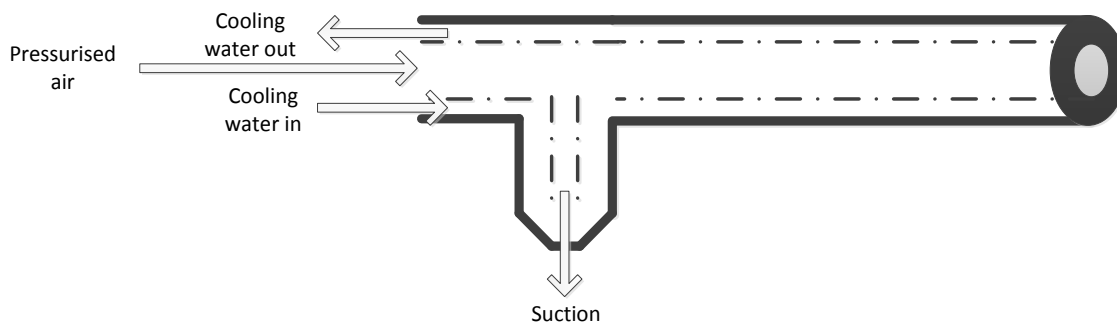

Figure 9. Schematic of the probe used for sampling the bed material
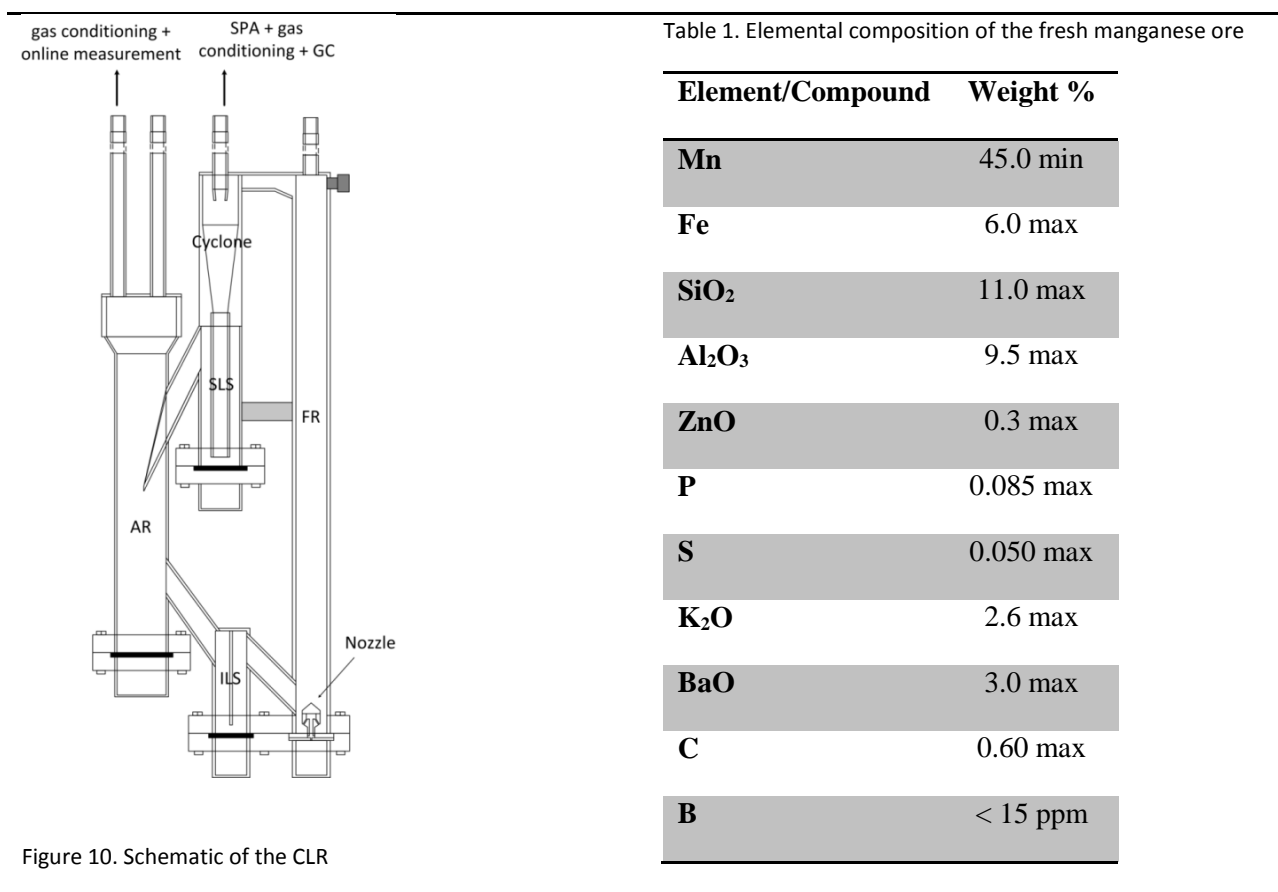
2.2   The Chemical Looping Reforming unit

In Paper 1, the use of manganese ore as a material for upgrading the gasification gas is described. The effect of the material was evaluated by coupling the CLR unit to the above-mentioned slipstream of raw gas downstream of the gasifier. In Figure 10, 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 eventual carbon deposits formed in the FR. The raw gas is fed to the reforming reactor *via* a heated line.

For the purpose of this study, a natural manganese ore with a particle diameter in the range of 45–90 µm was tested in the system. The elemental composition of the fresh ore is given in Table 1.

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 850°C. To burn eventual carbon deposits and minimize oxygen transport by the bed material from the AR to the FR and consequent burning of the gas, the AR was fed with a stream of nitrogen-diluted air that contained 2.2% oxygen.

After the unit, the gases from the reformer and regenerator were sent to the gas conditioning system and onwards to the gas analysis. The stream from the reformer was analyzed by a micro-GC, while the stream from the regenerator was analyzed in a Non-dispersive Infrared Analyzer. Tar samples were taken from both the raw and reformed gases and analyzed. Bed materials, fresh and used, were analyzed to follow the physicochemical changes.

Figure 10. Schematic of the CLR

Table 1. Elemental composition of the fresh manganese ore

Element/Compound	Weight %
Mn	45.0 min
Fe	6.0 max
SiO_2	11.0 max
Al_2O_3	9.5 max
ZnO	0.3 max
P	0.085 max
S	0.050 max
K_2O	2.6 max
BaO	3.0 max
C	0.60 max
B	< 15 ppm

2.3 Olivine

In Paper 2 study, the use of olivine as the bed material for gasification is described. In focus are the interactions between olivine and the ash elements in the Chalmers DFB. The amount of the material that was circulating through the system was approximately 4 tons. Starting from the raw olivine, a gasification experiment was run for 9 days. During the first 4 days, no exchange of the bed material was conducted, in order to observe the influence of the ash on the performance of the olivine. Thereafter, approximately 22% of the material was exchanged with fresh olivine (operational point VII). During Day VII, 800 g of elemental sulfur were added to the boiler. This was done to observe the effect of sulfur on the system. To study the influence of silicon, a two-step experiment was carried out in which approximately 500 kg of the bed inventory was exchanged with fresh silica sand on two occasions during the night. The changes were determined during Days VIII and IX. During all the days of operation, 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 2.

Changes that occurred in the system were detected by means of the composition and tar analyses of the produced gas. Furthermore, bed material was extracted at two points in the system (points B and C in Figure 8) and analyzed. Based on the results of these analyses, thermodynamic modeling was performed with the FactSage software. For the composition of the input stream of the activated olivine, the results of the ICP-SFMS analysis on Day IV were used, while for the raw gas stream, the composition detected by the micro-GC was used. The temperature was chosen according to the operational conditions during the experiment.

Table 2. 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

2.4 Ilmenite

A study that focused on the interactions between ilmenite and ash components is described in Paper 3. This study was performed in the context of a combustion experiment in the Chalmers facility [43]. The experiment started with only sand in the system. The boiler was operating for 4 days, whereby on each day a certain amount of sand was exchanged by ilmenite. Solid samples were taken on several occasions: after 1 h, 24 h, 48 h and 72 h of operation (Table 3). Thus, it was possible to observe the build-up of the ash layer around the ilmenite particle. Extracted samples were analyzed to gain information about physical and chemical changes.

Table 3. Extraction schedule for bed materials

Sample	Time of extraction	State of bed material
I	1 hour	20 wt% ilmenite
II	24 hours	17 wt% ilmenite
III	48 hours	40 wt% ilmenite
IV	72 hours	40 wt% ilmenite

2.5 Quartz-sand

Quartz-sand is the standard material used in the Chalmers DFB system; its interactions with the ash and the retention of inorganics are described in Paper 4. The focus is on the effect of the aging of quartz-sand on the gasification process, e.g., the composition of the produced gas. 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 given in Table 4 was used in the experiment. The operational conditions used are presented in Table 5. As shown in Table 5, the operational points (sampling time-points, I_A to V_A) have comparable temperatures, steam-to-fuel ratios, and rates of circulation of bed solids. Wood pellets were fed into the gasifier, and wood chips were fed into the boiler during that run. In the study, no regeneration was carried out for 4 days. Between time-points IV_A and V_A, approximately 55 wt% of the bed inventory was exchanged by fresh quartz-sand.

In the same table, given are operational conditions for the separate experiment done with 20% wt. daily exchange of the quartz sand (I_R to VII_R). Results of this experiment were used for the observation of the phenomenon of an elevated H_2S content in the raw gas. The H_2S content in the raw gas was monitored online, and solid samples were extracted from the system at points B and C (see Figure 7) for each operational time-point. The samples were further analyzed by SEM/EDX and XRF.

Table 4. Chemical composition of the quartz-sand provided by the supplier

Oxide	Weight%
SiO_2	99,2
Fe_2O_3	0,054
Al_2O_3	0,17
LOI	0,1

Table 5. Operational conditions used in the aging experiment

Gasifier				*Boiler*		
Experimental point/day	Temperature, [ºC]	Fuel feed_ar, [kg/h]	Steam, [kg/h]	Temperature, [ºC]	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	1900.584	20400
II_R	827	393.00	262	860	1923.768	19100
III_R	829	397.11	311	860	1810,08	23100
VII_R	784	394.38	211	825	1560.132	16300

*NM, not measured.

3. Results

3.1.   CLR - secondary upgrading of the gas

Figure 11 lists the concentrations of the tar group species for the raw and reformed gases when manganese ore was used as the catalyst. The temperatures used in the study were 800°C, 850°C, and 880°C. As shown in Figure 11, the benzene fraction increased in the reformed gas for all the tested temperatures. However, due to the inherent inaccuracy of the measurement for benzene [65], this change cannot be discussed or be used for drawing any conclusions. The reduction of the phenolic fraction in the raw gas is significant for all cases compared to the raw gas. In contrast, the naphthalene fraction is higher in the reformed gas. The observed trend leads to the conclusion that 2-ring components and 3-ring and higher components convert to naphthalene, which is further decomposed at elevated temperatures (Figure 11b). As a result, the maximum total tar conversion measured in this experiment was 76%, excluding the benzene fraction.

Figure 12 shows the compositions of the raw and reformed gases. The concentrations of gas species for each experimental point are presented. As the concentration of N_2 in the raw gas is constant, the decrease in N_2 concentration observed for the dry reformed gas indicates an increase in the dry gas flow. This may be due to reactions that result in the production of a permanent gas in the FR. As presented in the figure, for all tested temperatures, the concentrations of H_2 and CO_2 are higher in the reformed gas than in the raw gas, while the concentration of CO is lower. The increase in the concentration of H_2 can be partly explained by the conversion of tars (Figure 11) and light hydrocarbon (C_2H_x)-reforming reactions that are favored at elevated temperatures. A change in the CO_2 pattern indicates that besides hydrocarbon and CO oxidation through oxygen transport from the catalyst, the Water-Gas Shift (WGS) occurs in the FR. Consequently, some H_2 is formed *via* this reaction. The concentrations of measured light hydrocarbons, C_2H_x and C_3H_x, are decreasing with a temperature increase.
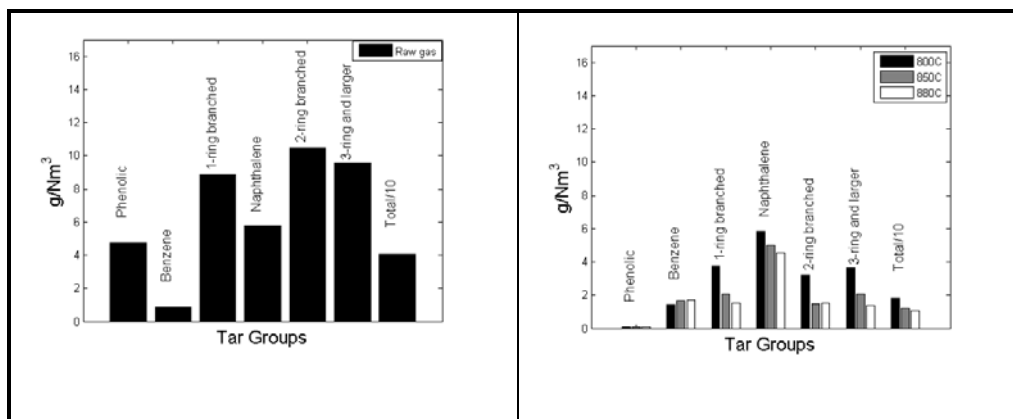

Figure 11. Concentrations of individual tar groups in g/Nm³ in the (a) raw gas (left panel), and (b) reformed gas (right panel).
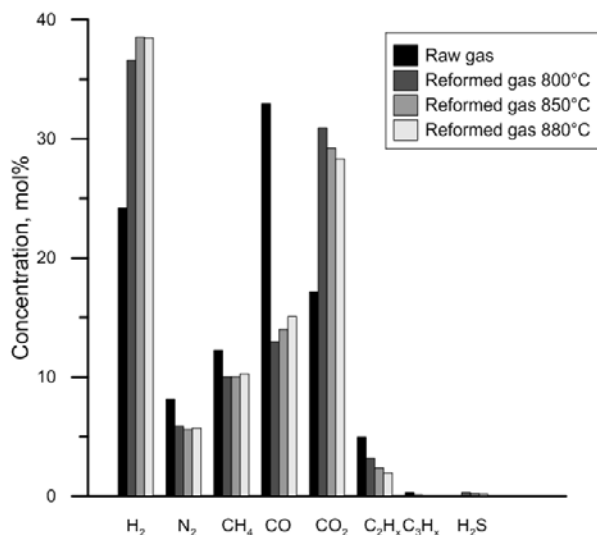
Figure 12. Compositions of the raw gas and reformed gas at the tested temperatures

Figure 13 shows the SEM/EDX images of particles after exposure to CLR. Agglomeration is evident in the analyzed sample. 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. However, in the presence of a silicon particle, potassium creates a layer around it. A possible explanation for this is the formation of potassium-silicate. Due to the high affinity 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 [66], 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. Based on these results, it can be concluded that the mixing of manganese ore and quartz-sand should be avoided in this application.
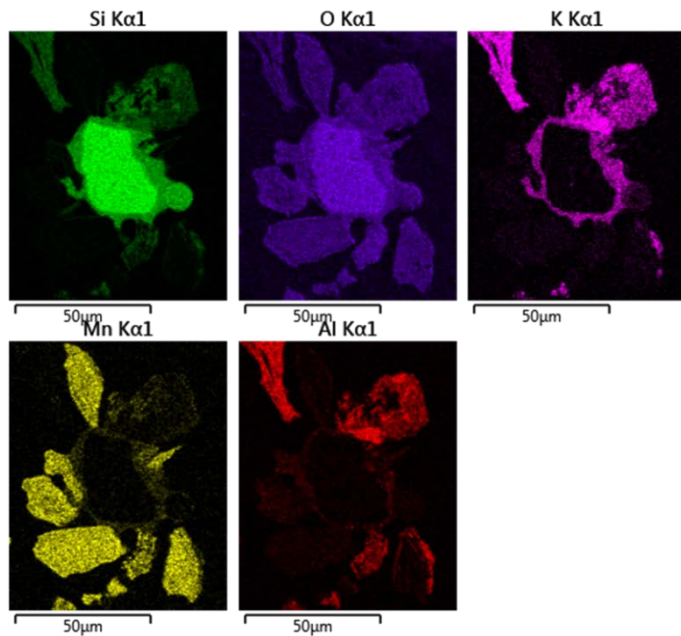
Figure 13. SEM/EDX images of cross-sections of the used manganese ore

3.2. Olivine

The influence of ash components on olivine activation was studied in a continuous gasification experiment without any exchange of the bed inventory. To observe the effects of problematic species, i.e., sulfur and silicon, two separate experiments were performed by adding relevant amounts of sulfur and quartz-sand to the system.

Elemental analysis of the bed material extracted from the system during the experiments showed that the level of retention of inorganics in the bottom bed material was significant. Figure 14 shows the results of the analyses for the respective oxides. An interaction of olivine with the ash components is evident from the increase in the content of inorganics in the samples. The decrease in the levels of ash components observed on Day VII may be related to the regeneration of the bed inventory with fresh material and the removal of one part of the bottom ash.
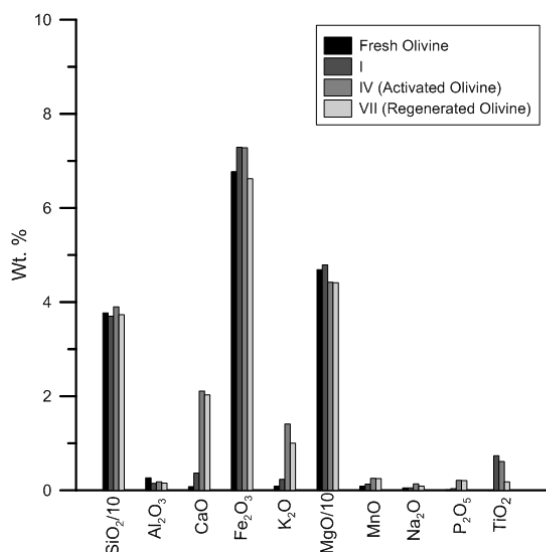
Figure 14. Bed material compositions expressed as wt% of oxides

Solids extracted after 4 days of operation were analyzed by SEM/EDS. The results are presented in Figure 15. In line with the findings of Kirnbauer et al. [49], a Ca shell was formed on the surfaces of the particles. However, the iron layer described by Lancee et al. [61] was not observed in the present study. The reason for this may be that the material in the present work was not calcinated before the experiment, as was the case in the previous study. Potassium is observed only as a melted layer between the particles and in the cracks in the particles. In Figure 15, the results of spot analyses of the melted layer and the particle are presented. The melted layer consists mainly of Si, K, and Mg (point 2 in top-left panel). Spot analysis of the particle outer part reveals Mg and Si as the major components and K as the minor component (point 3 in bottom-left panel).

A mapping analysis of the samples after the addition of sand to the system is shown in figure 16. The majority of the potassium is found to be associated with quartz-sand particles in the form of a melted layer. Potassium appears to diffuse into the core of the quartz-sand, which is confirmed by the spot analysis (shown in the same figure). Calcium remains in the outer layer of the olivine particles.
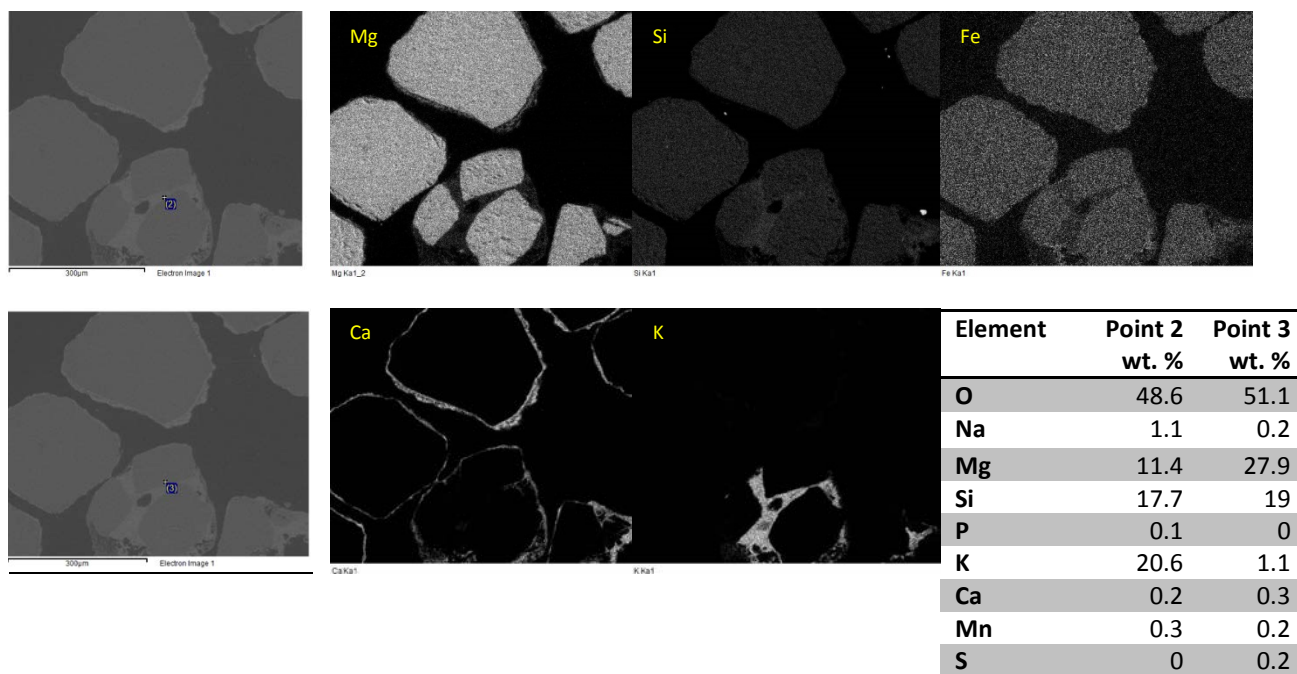
Figure 15. SEM/EDX analyses of used olivine particles. Inset table: elemental analyses of the chosen spots.

Element	Point 2 wt. %	Point 3 wt. %
O	48.6	51.1
Na	1.1	0.2
Mg	11.4	27.9
Si	17.7	19
P	0.1	0
K	20.6	1.1
Ca	0.2	0.3
Mn	0.3	0.2
S	0	0.2

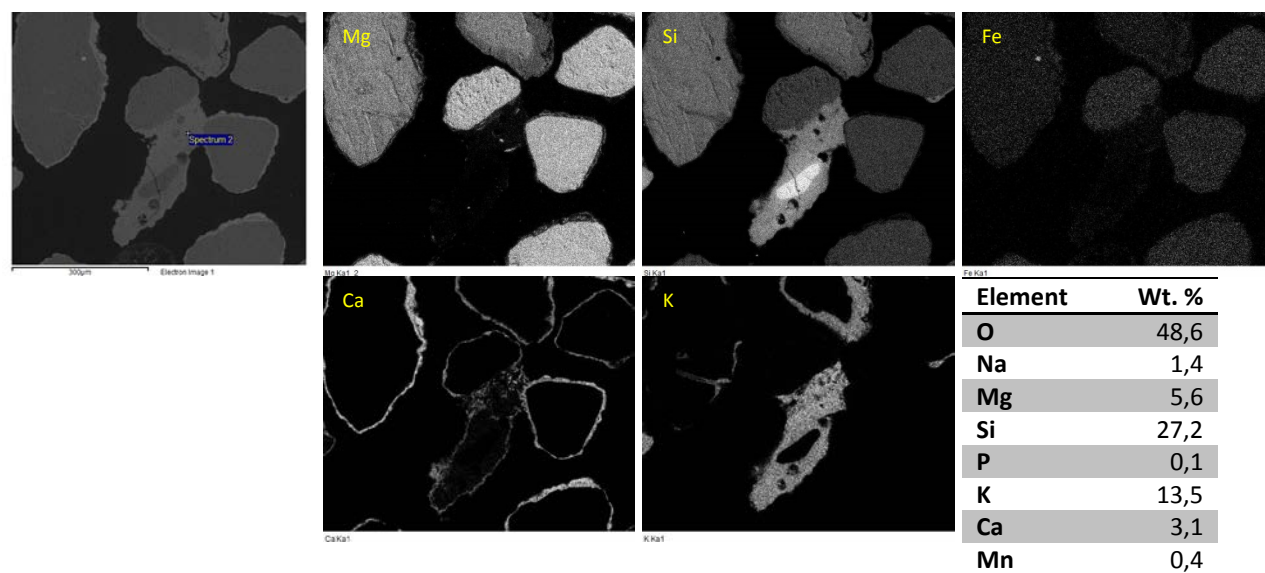| Element	Wt. %
O	48,6
Na	1,4
Mg	5,6
Si	27,2
P	0,1
K	13,5
Ca	3,1
Mn	0,4

Figure 16. SEM/EDX analyses of used olivine particles mixed with sand. Inset table: elemental analysis of the chosen spot.

To improve our understanding of the possible transformations of the material and its influence on the process, equilibrium calculations were done for different parts of the system (see Figure 3).

Three cases were considered:

1. Reaction between the activated olivine and flue gas, representing the boiler environment (T=880°C);
2. Reaction between the solid alkali solution from the first case and the steam, as an indication of the bottom of the bed in the gasifier (T=800°C); and
3. Reaction between the solid alkali solution from the first case and the raw gas, as an indication of the freeboard in the gasifier (T=790°C).

The results of the calculation are presented in Table 6, with the most stable phases in the system being included. Presented are the results for K, Ca, S, Fe and Si, since it is expected that these have the greatest impacts on the chemistry within the system. All the components, except some fraction of the sulfur, are predicted to be in the solid and slag phase. The model predicts that potassium is distributed between the slag form and solid salt. The presence of potassium in the slag form was confirmed by the SEM/EDX analysis (see Figure 15). As it is in the slag form, the potassium is not readily released. However, potassium in the salt form, K_2SO_4, can be transformed in the environment of the upper part of the gasifier to form KOH and K_2CO_3. The catalytic activities of these potassium species towards carbon gasification [67] and tar reduction [41] are well-known. However, whether the tar decrease is due to the suppression of tar formation or the catalysis of tar decomposition remains unclear [41].

Table 6. Equilibrium calculation for the reaction between activated olivine and air in the boiler

	Gas phase	Slag_liquid phase	Solid phase	OlivA phase
K		$K_2O/Na_2O/SiO_2/Al_2O_3$	K_2SO_4	
Ca			$CaMgSi_2O_6/Ca_3(PO_4)_2/CaSiTiO_5$	$CaMgSiO_4/CaFeSiO_4$
S	SO_2/SO_3		K_2SO_4	
Fe			Fe_2O_3	$MgFeSiO_4$
Si		$K_2O/Na_2O/SiO_2/Al_2O_3$	$CaMgSi_2O_6/CaSiTiO_5$	$MgMnSiO_4/CaMgSiO_4/CaFeSiO_4/Mg_2SiO_4/MgFeSiO_4$

To confirm the presence of potassium in the salt form, an additional leaching test was performed for particles extracted on Day IV. Indeed, 52 mg K per kg of olivine was leached out. Considering the non-uniformity of the ash coating on the particles, this result cannot be discussed in a quantitative sense. However, the analysis yields supplementary information regarding the possibility of potassium release.

Figure 17 shows the results obtained for 6 days during a span of 2 weeks with respect to the: yields of the specific tar groups (Figure 17a); and yields of gaseous components in the produced gas (Figure 17b). Furthermore, in Figure 17b, points from an olivine run during a different season are added, to illustrate the repeatability of the experiment. The olivine that was used in the earlier experiments originated from the same mine, but was of somewhat different particle size. However, the operational parameters were similar in both cases.

As shown in Figure 17a, the total tar amount decreased and all the tar species were affected. The highest obtained reduction was measured on Day IV and compared with the first day of operation, when the total tar yield decreased by 30%. Considering this significant decrease in tar yield, the increase in the yield of H_2 (Figure 17b) can be attributed to steam reforming reactions. However, the fact that the increases in the levels of CO_2 and H_2O are concomitant with a decrease in the level of CO point to the WGS being the relevant reaction. Day VII represents the results obtained after regeneration of one part of bed inventory with fresh olivine. The overall activity of the material towards tar decomposition decreased. Bearing in mind the previous studies, in which the activity of olivine was linked to the formation of an iron layer and calcium layer on the surfaces of the particles, the observed result is anticipated [49, 60, 61], due to the dilution of the activated bed material in the system. However, the composition of the gas was not significantly affected. In contrast, quartz-sand addition (Day VIII) did generate a much stronger effect than was expected from simple dilution.

The addition of sand caused 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. Moreover, from the SEM/EDX images, it is obvious that the quartz-sand reacts with potassium to a significant extent. The predominance of silicon causes the formation of potassium-silicate, a structure that does not allow the release of potassium. Consequently, less potassium is available for reaction with the raw gas. This leads to the conclusion that potassium plays an important role in determining the activity of olivine.

Sulfur addition (VII_S) to the boiler resulted in a decrease of the total tar yield by 20% and an increased H_2S yield in the raw gas. From the increase in the H_2S level in the raw gas it can be concluded that sulfur was transported from the boiler to the gasifier. According to thermodynamic calculations, in the boiler environment, the sulfur reacts with potassium to form K_2SO_4 (see Table 6). Therefore, sulfur addition contributes positively to the amount of available potassium in the gasifier.
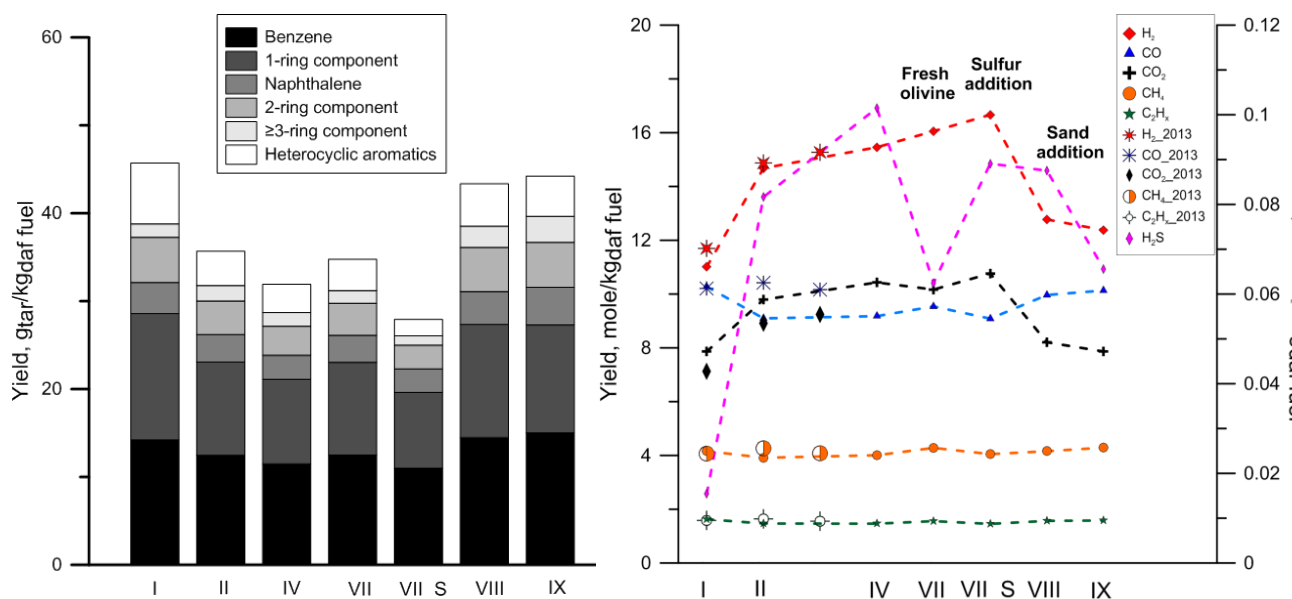
Figure 17. (a) Levels of tar components in the raw gas, presented as yields of specific tar groups (in gtar/kg daf fuel) versus time. *VII_S stands for an experiment in which sulfur was added to the system; (b) composition of the dry raw gas obtained during the experiment (given in mol/kg daf fuel)

3.3.   Ilmenite

The SEM/EDX images of the ilmenite extracted from the system after 1 h and 24 h of operation are shown in Figure 18 and Figure 19. At the start of the operation (Figure 18), potassium is detected as a thin layer on the bed material. However, with the aging of the ilmenite in the system, the potassium seems to diffuse into the core of the ilmenite particle (Figure 19). The particle core is enriched for Ti, while Fe is located at the surface of the particles. Ca is found to form two layers.
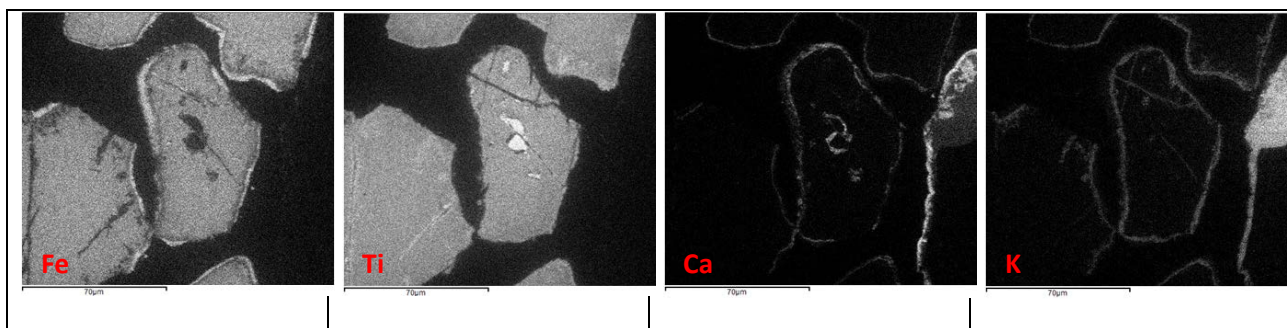
Figure 18. EDX maps of the distributions of iron, titanium, calcium, and potassium in the cross-section of an ilmenite particle from sample I.
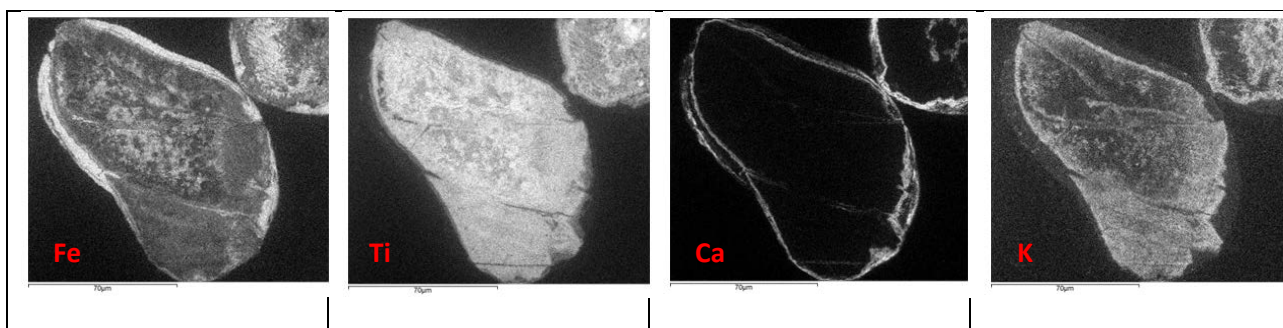

Figure 19. EDX maps of the distributions of iron, titanium, calcium, and potassium in the cross-section of an ilmenite particle from sample II.

To understand the interaction between potassium and ilmenite particles, leaching with deionized water was carried out on the particles extracted from the process. Thereafter, the particles were analyzed by SEM/EDX and the results are presented in Figure 20. As the elemental distribution within the particles remains the same and the analysis of the leachate shows that both K and Ca are leachable only to some extent, the conclusion is that the potassium is stored permanently inside the particle.
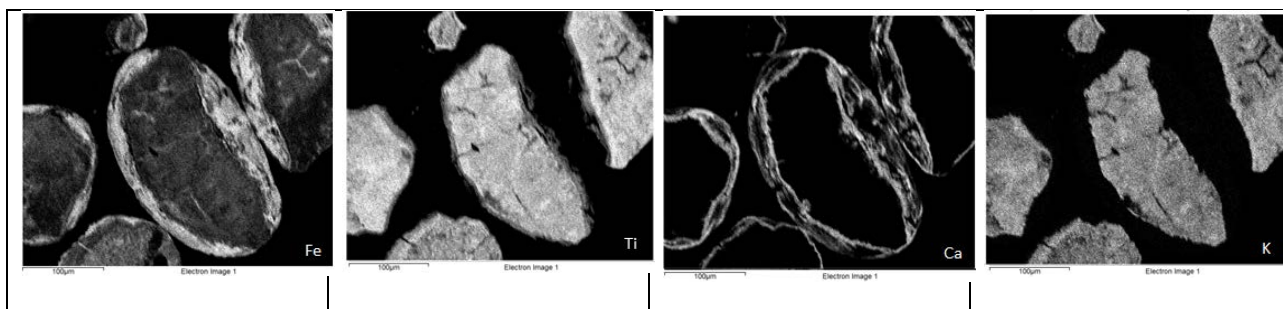

Figure 20. EDX maps of the distributions of iron, titanium, calcium, and potassium in the cross-section of an ilmenite particle from sample II that was leached for 72 hours.

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In addition, the XRD analysis of the particles before and after the leaching test showed no differences in composition. In both cases, the sample contained KTi_8O_{16}. Considering the presented results, ilmenite offers great potential as an alkali getter material for the combustion process.

3.4. Quartz-sand

With the aim of studying the influence of biomass ash on the otherwise inert quartz-sand in the gasifier of the Chalmers DFB system, experiment where no exchange of the bed inventory over four consecutive days was done.

In Figure 21, the yields of permanent gases versus time of operation (days) in the aging experiment are presented. The right-hand y-axes correspond to the yields of the H_2S in the raw gas, while the yields of H_2, CO, CO_2, CH_4 and C_2H_X are shown on the left-hand y-axes. Aging of the sand in the system caused an increase in the H_2 and CO_2 yields (points I to IV in Figure 21). An increase in H_2S yield is apparent over the time of operation. After regeneration of the bed inventory (point V in Figure 21), the composition of the raw gas is similar to that detected on the first day of operation.
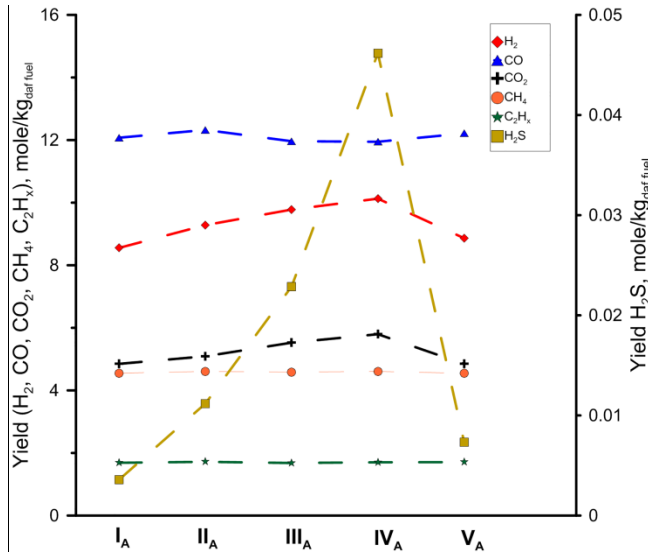

Figure 21. Composition of the dry raw gas obtained during the experiment (given in mol/kg daf fuel)

The influence of ash accumulation on the tar yields in the raw gas can be discussed in terms of the results of the SPA analysis (Figure 22). The tar yields are presented for specific groups of tar components: naphthalene, 2-ring component, 3-rings components and heavier hydrocarbons and phenolic components. Results are presented in $g/kg_{daf\ fuel}$. From Day I_A to Day IV_A, decreases in all the tar groups are observed. The greatest change occurs in the phenolic species, which decrease by 21%, and the total tar yield decreases by around 10%.
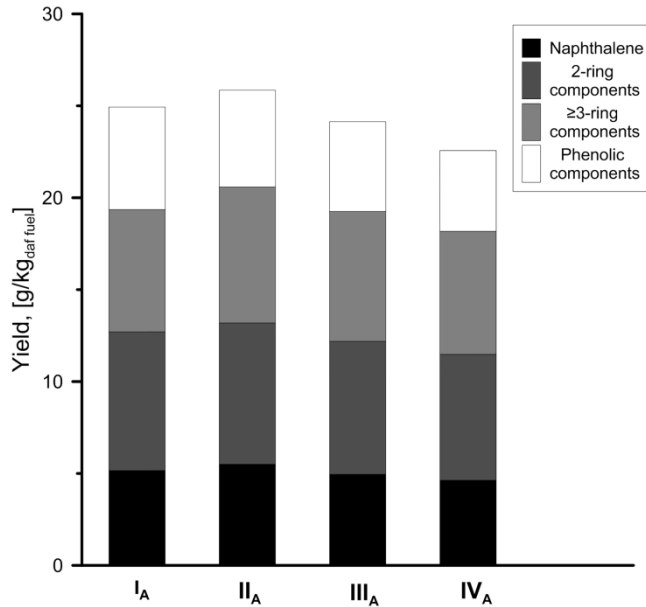

Figure 22. Compositions of the tar components in the raw gas , presented as yields of specific tar groups in gtar/kg daf fuel

Figure 23 shows the measured yields of sulfur in the produced raw gas (in the form of H_2S) in two different experiments: (i) a case with regeneration of the bed material, with the experiment being done in a separate study; and (ii) a case without regeneration of the bed material, performed within the study. In the regeneration case, the experiment lasted 7 days, with around 20 wt% of the bed inventory being exchanged on a daily basis. For this case, between points III_R and VII_R, only the boiler was in operation for 3 days. The results are expressed as mole $S/kg_{daf\ fuel}$ versus days of operation. Figure 23 also shows the amounts of sulfur that enter the system *via* the fuel feed to the gasifier and the total sulfur level (both in the boiler and gasifier fuel feed). Figure 23 clearly shows that sulfur is accumulated within the system and subsequently released into the gasifier. Already on the second day of operation the amount of sulfur in the gas exceeded the amount that originated from the fuel fed to the gasifier . On the third day the amount of sulfur in the gas exceeded the total amount of sulfur introduced into the system with all the fuel.

The SO_2 concentrations in the exit flue gas from the boiler were also monitored at the boiler exit point. Considering that the raw gas from the gasifier was re-directed back to the boiler where the

gas was burnt, a relatively high emission level of SO_2 should be expected in the boiler flue gas exhaust due to the oxidation of the H_2S. However, the concentration of SO_2 recorded during both experiments (bed regeneration and bed aging) in the boiler flue gases were <10 ppm for all days of the operation. This low level of SO_2 concentrations can be explained as resulting from recapturing the sulfur released during combustion of the raw gas by the circulating bed material in the boiler.
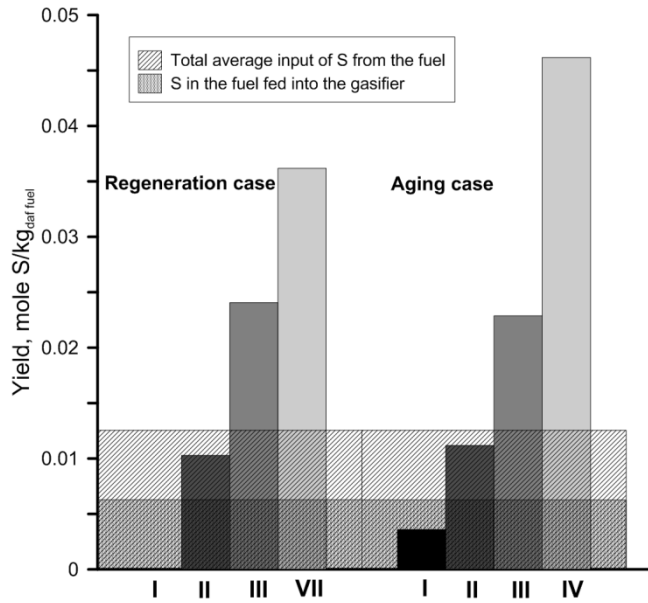

Figure 23. Measured levels of S emissions in the form of H_2S in the dry raw gas and the amounts of sulfur added to the system with the fuel; kg of S/h vs. days of operation of the gasifier.

With the intention of studying the changes in the bed material during the interaction with ash, XRF and SEM/EDX analyses were carried out on the solids extracted during the regeneration experiment. Thus, it was possible not only to observe both fresh and old particles in the system, but also to gain information about a suitable extent of regeneration of the material.

The results of the XRF analysis done for points II_R, III_R, and VII_R are shown in Figure 24a for the solids samples extracted from Loop seal 1. In Figure 24b, the differences between the elements in the samples extracted at Loop seal 1 and Loop seal 2 are presented. The analysis shows enrichment of the bed with ash components over time. This can be interpreted as reflecting ash layer formation on sand bed particles and less amount of unreacted quartz present. When Loop seal 1 is compared to Loop seal 2 (Figure 24b), decreases in all the ash components are noted. However, silicon increased in percentage. This indicates that attrition of the ash coat of the bed

particles is occurring in the gasifier. Discussing solely sulfur, the elevated concentration of H_2S measured in the raw gas (Figure 23), together with the trend observed in the XRF analysis, lead to the conclusion that the decrease in the sulfur content of the bottom bed material is due to both attrition and its release to the gas phase.
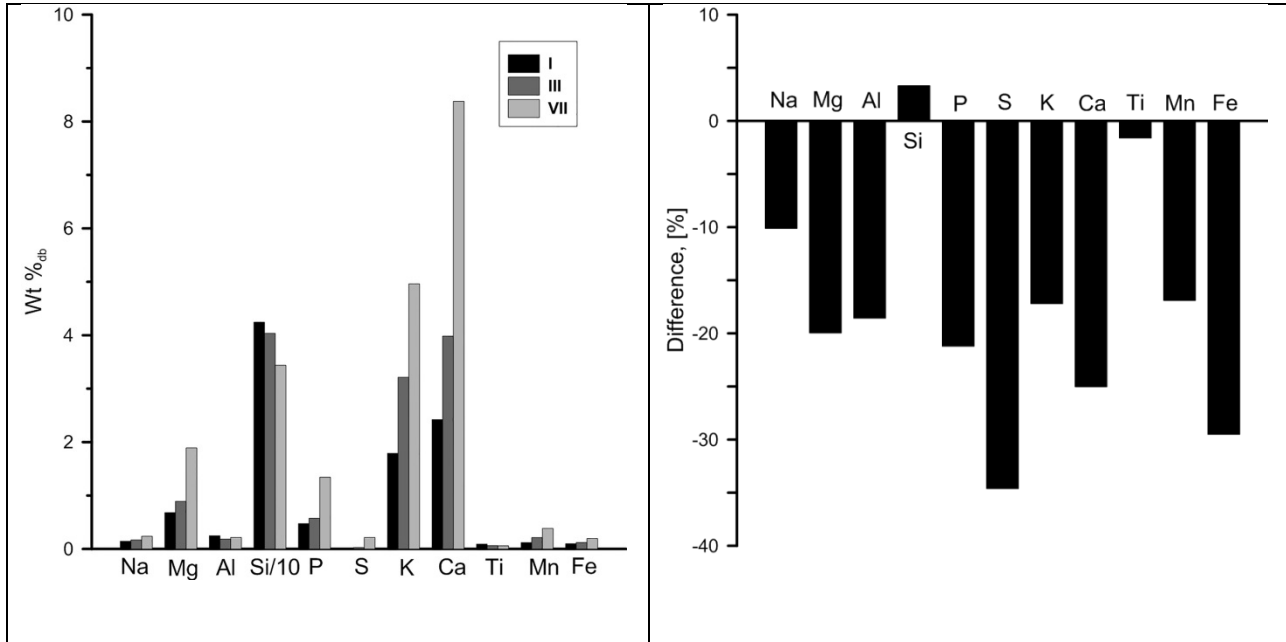

Figure 24. Results of the XRF analysis. (a) Elemental compositions of the bed material samples collected on Days II, III, and VII in the regeneration case (left panel); (b) Percentage differences in elemental composition between Loop seal 1 and Loop seal 2 for sample III.

To conclude regarding the association of the sulfur within the material, an elemental analysis of the particle cross-section was performed using SEM/EDX. The results of the line scan for the particle extracted from Loop seal 1 are shown in Figure 25 and for the particle extracted from Loop seal 2 in Figure 26. Analyzed were particles collected on Day III_r. Sulfur is detected in the outer layer of the ash coat. Potassium, as anticipated from previous research [20, 47], diffuses into the core of the quartz particle. Calcium is present as a small fraction in the inner layer, but as a larger fraction in the outer layer. Analysis of the solids extracted from Loop seal 2 shows the same elemental distribution within the ash layer as was observed for the particles from Loop seal 1. Potassium is in the core associated with silicon, forming potassium-silicate. The majority of the calcium is in the outer layer.
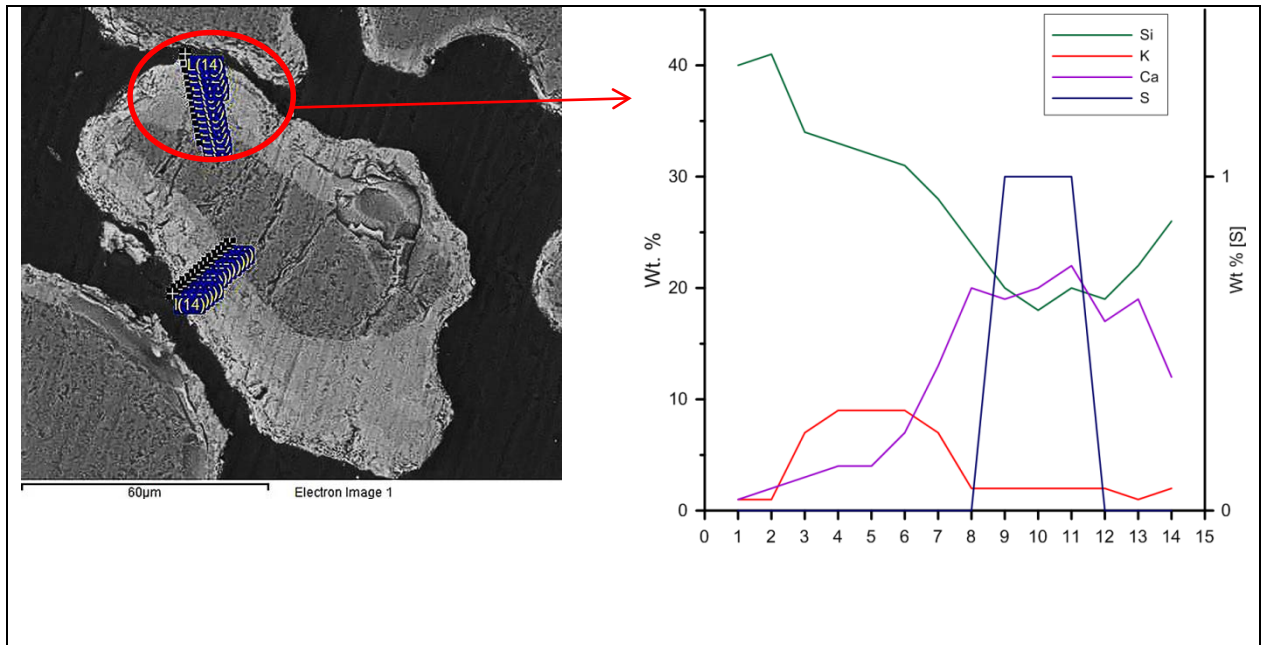
Figure 25. Line scan over an ash-coated particle obtained from Loop Seal 1 and the element concentrations in wt%. On the *x*-axis, the value of 1 represents the location near the interface of the quartz particle-ash layer, while the value of 14 represents the outer surface of the ash layer.

Figure 26. Line scan of an ash-coated particle collected from Loop Seal 2, and the elemental compositions (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 15 represents the outer surface of the ash layer.
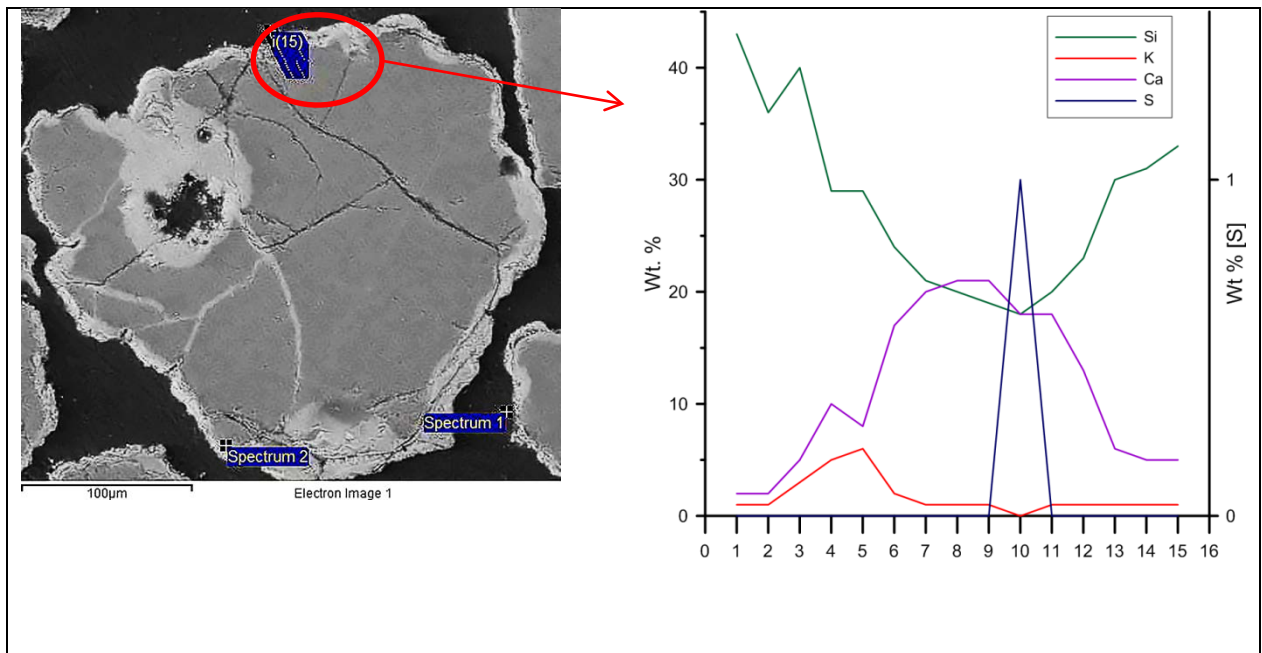
As sulfur is located in the part of the ash layer that is rich in calcium, its association with calcium can be proposed (see Figures 25 and 26). To determine the phase in which sulfur originates in the sample, an XRD analysis was done. However, due to the low level of sulfur (lower then confidence level of the equipment), these results cannot be used for the discussion.

Assuming that sulfur is linked with calcium, as being found in the very outer layer rich with calcium, in the oxidative environment, it should be present in the form of sulfate [68, 69]. This stable sulfate, carried by the bed material circulation, can be decomposed to calcium-sulfide and/or calcium-oxide in the reductive environment that prevails in the upper part of the gasifier, as described in previous studies [70, 71].

In the gasifier, part of the sulfur is released to the gas phase and part will be in the form of sulfide that circulates back to the boiler where it is re-oxidized. In the gas phase, sulfur is released in the form of H_2S, which is subsequently oxidized in the boiler.

4. Conclusions

Given that the bed is vital for the DFB gasification process, careful selection of the appropriate bed material is crucial for optimization of the 'biomass to biogas' route. A suitable bed material that has the required catalytic properties, resulting in 'cleaner' product gas from the gasification process would likely decrease the costs associated with the downstream process and might even decrease the number of operational units required for the production of gas of the desired composition.

However, if a secondary cleaning step needs to be introduced natural ores should be the materials of choice for the bed material. Careful selection of the material and operational conditions in the DFB system (CLR system) might entail simultaneous removal tar and H_2S, while the regeneration step would prolong the lifetime of the bed material.

Considering the bed material in a DFB gasification unit, two principal behaviors can be observed: the uptake and the release of inorganics from the fuel by the bed. The presence of inorganics may influence not only the operation of the process, but also the composition of the produced raw gas. Thus, a general conclusion is that it is vital to identify a suitable combination of fuel and bed material to be used in the system.

Given the environmental changes (oxidation/reduction) that the bed material is exposed to in the system, inorganics may be released from the ash coat to the gas phase. The focus in DFB systems is on heterogeneous reactions. However, the potential for the release of inorganics from the material to the gas phase highlights the importance of homogeneous reactions.

The presented work shows that to optimize the performance of olivine as a bed material in biomass gasification, it is necessary to understand fully the roles of the inorganics for its activation.

Other materials, such as ilmenite, tend instead to bond inorganics derived from the fuel, which is beneficial with respect to avoiding agglomeration in biomass- and waste-fired boilers. In the present study, it is shown that potassium diffuses into the core of the ilmenite particle. Potassium-titanium oxide, which is a compound that does not allow the release of potassium, is thereby formed. Consequently, ilmenite can be regarded as potassium getter material. Hence, used as an additive to a quartz bed, it can prevent agglomeration.

5. Future work

In the present work, the impacts of the bed material on the quality of the produced gas and on the operation of the overall process have been demonstrated. As discussed above, there is still a need for more appropriate materials that are catalytically active and environmentally friendly. In this context, natural ores are obviously favored.

Olivine is shown to be an attractive bed material, although the mechanism underlying its activation remains to be elucidated. By studying the influences of different salts on the material separately, deeper knowledge of this subject can be acquired.

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