The mechanism of bed material coating in dual fluidized bed biomass steam gasification plants and its impact on plant optimization

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The bed material and especially its catalytic activity plays an important role in biomass steam gasification in dual fluidized bed gasifiers. The bed material is modified by interaction with biomass ash during operation of the gasification plant forming layers at the particles which are induced by the biomass ash. Optimization of dual fluidized biomass steam gasification will have significant influence on the process variables such as temperatures, inorganic composition and product gas composition. The influence of these changes on layer formation is still unknown. This paper summarizes results of investigations about bed material characteristics taken from the industrial-scale biomass steam gasification plant in Güssing where woody biomass is used as fuel. Analyses of the surface and the crystal structures of the bed material particles treated in gasification and combustion atmospheres were carried out. The thermal behavior of used olivine and fresh olivine in different atmospheres was analyzed. A suggestion for the mechanism of formation of the layers is presented and the influence of possible optimization measures is discussed. A change in the elemental composition of the surface was not detectable but a slight change in the crystal structure. Thermal investigations show a weak endothermic weight loss with used olivine in a CO2-rich atmosphere which could not be determined with fresh olivine. The formation of layers at the olivine particles is considered to be caused by the intensive contact with burning char particles in the combustion reactor.

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1. Introduction

The utilization of biomass for energy generation seems to be indispensable for the supply of energy from renewable energy sources. A well proven technology for the generation of electrical energy and heat is biomass steam gasification in a dual fluidized bed (DFB) gasifier in connection with gas engines [1–6]. Biomass steam gasification in DFB plants is carried out in two fluidized beds. In a gasification reactor that is operated in bubbling bed mode, mainly endothermic gasification reactions take place. The bed is fluidized with steam. A part of the fuel is transported via the bed material in a chute to the combustion reactor where it is combusted and the bed material is heated up. The combustion reactor is operated in a fast fluidized bed regime. Due to circulation of the bed material between the combustion reactor and the gasification reactor, heat is transferred from the combustion reactor to the gasification reactor. The product gas is cooled down and filtered to remove inorganic particles and char. Tars are removed in a scrubber that is operated with rapeseed oil methyl ester (RME). The cleaned product gas is utilized in a gas engine to generate electricity and heat. The flue gas from the combustion reactor is cooled down, and fly ash is separated in a fabric filter and the clean flue gas is released into the atmosphere via a chimney. Detailed descriptions of the process can be found in the literature [1–6]. A flow sheet of the gasification process is shown in Fig. 1.

This technology is developed to industrial-scale size in various plants in operation in Europe [7–9]. The development of different technologies for alternative utilization of the product gas from the dual fluidized steam gasification such as Fischer–Tropsch synthesis, synthesis of synthetic natural gas (BioSNG), and mixed alcohols is ongoing and each type of synthesis has different requirements regarding the composition of the product gas [10–14]. The most efficient way to influence the composition of the product gas is to change the parameters directly in the gasification process rather than the downstream application of upgrading steps, for example, a steam reformer.

On the other hand, the economic pressure which is caused on the one hand by increasing wood prices and on the other hand a constant feed-in tariff for electricity creates demand for a further optimization of the gasification process in terms of economic and technological efficiency. This can be achieved by increasing the product flexibility by generating not only electricity and heat but also synthetic fuels or chemicals. Higher fuel flexibility can have similar positive effects on the economic efficiency due to lower prices of alternative fuels. Woody biomass, which is used in industrial scale biomass steam
gasification plants nowadays, has a high softening as well as melting temperature of the ash compared to other biomass, which has an impact on the agglomeration behavior [15–17]. Other biogenous fuels such as energy crops or biogenous waste from agriculture such as straw, corn cobs, and others have even a worse melting behavior of the ash and often causes problems in biomass combustion plants [18–22].

A promising way to increase the technological and economic efficiency is to decrease the gasification temperature. A reduced gasification temperature brings advantages in the technical efficiency of the plant [23,24] and reduces the risk of ash related problems such as bed material agglomeration, fouling, and slagging [25,26].

The utilization of catalytic bed material is state of the art for the biomass steam gasification in DFB plants. The natural mineral olivine, which is a magnesium iron silicate, (Mg, Fe) SiO₂, is used in these plants, because it showed good results in laboratory-scale experiments concerning tar reduction in the product gas [27–34].

Olivine which is most frequently used as bed material in the DFB gasification plants interacts with the biomass ash during its utilization [4,35]. The long-term interaction with woody biomass in an industrial scale plant in Güssing was documented in an earlier study [4]. Two different calcium-rich layers are built at the surface of the bed material particles. The inner layer is homogenous and consists mainly of calcium and silicate. The outer layer has a similar composition to the fly ash of the plant.

This calcium-rich layer at the surface of the bed material influences the gasification properties significantly [5,36]. The water-gas shift reaction is enhanced, leading to higher hydrogen and CO₂ content in the product gas and to lower carbon monoxide content and lower content of higher hydrocarbons. The decomposition of primary tars is enhanced and formation of secondary tars is reduced, leading to lower total tar concentrations in the product gas. The enhancement of the water-gas shift reaction was confirmed by Kern et al. [37] in laboratory scale examinations of the bed material.

The high amount of calcium at the surface of the bed material particles can make CO₂ adsorption and transport with the bed material possible. The CO₂ transport with the bed material is desired in the sorption-enhanced reforming (SER) process, where calcium-rich bed material such as calcite is used. The adsorption of CO₂ in the gasification reactor at lower temperatures and the desorption of CO₂ in the combustion reactor at higher temperatures transports CO₂ from the gasification reactor to the combustion reactor, bringing higher hydrogen contents in the product gas from around 55–70 vol. % depending on the bed material and process conditions. Details about the SER process (also called adsorption enhanced reforming, AER) can be found in the literature [3,38–44].

A new, optimized reactor design for a DFB gasifier presented by Schmied et al. [45] proposes significant changes in the reactor design, ash loops, and operating conditions of the process.

A wide range of desired process variations are possible, such as plant optimization by temperature reduction and the utilization of different fuels in industrial plants or overall optimization for the production of second generation biofuel plants via gasification and Fischer–Tropsch synthesis, BioSNG, or production of hydrogen rich gas by selective CO₂ transport. The bed material in a DFB gasifier can play an important role for directing the gas composition of the

Fig. 1. Basic flow sheet of the DFB gasification in Güssing.
syngas to the desired composition according to its application. However, detailed knowledge about the fundamentals of the formation of the calcium rich layer and the influence of the operating conditions of DFB plants would be necessary. Details about the mechanism of the layer formation have not been published and the location in the gasification plant where the layer formation takes place is still matter of speculations.

This paper summarizes recent research activities and analyses of bed material modification in DFB plants and describes the mechanism of formation of the layers. Qualitative statements are made about the thermal behavior of the bed material. The formation mechanism is discussed in the context of different possibilities for optimizing the operation of DFB biomass steam gasification plants. This study aimed on clarifying conditions for lab scale tests and for further investigations of bed material catalysts.

2. Fundamentals

Olivine the bed material in DFB plants is a natural mineral that has its origin in basaltic magma. It is a magnesium iron silicate and the first or an early crystallization phase from basalts [46]. Various authors from different disciplines have published examinations of the crystal structure and properties of olivine. Calcium diffusion in olivine is of interest in mineralogy for determining the cooling rate of samples from meteorites. These studies also show interesting results regarding the utilization of olivine in DFB gasifiers, its modification during long-term utilization, and the interaction with biomass ash.

Olivine consists of two crystal structures: fayalite and forsterite. Fayalite is an iron-containing silicate, Fe2SiO4, and forsterite is the phase which is rich in magnesia, Mg2SiO4. The crystal structure of olivine is orthorhombic; it has two distinct metal sites (called M1-O and M2-O in literature) of the octahedrally coordinated cations, which can be Fe, Mg, Ni, Mn, or Ca. These two positions are interchangeable with different ions. At temperatures higher than 600 °C the angular distortion of the M1 and M2 octahedra increases and the exchange of ions at these positions is enabled [47]. With increasing temperature the distances at the M – O positions increase while the Si – O distances show zero or slightly negative expansions [47]. The behavior of fayalite is similar to forsterite with increasing temperature [47]. The position M2 is suggested to be preferred by calcium ions when exchanging Fe ions [47]. The Ca – Fe substitution in olivine is more extensive than Ca – Mg substitution because of the difference between the radii of Fe and Mg cations [48]. The diffusion rate of calcium into olivine is lower than the diffusion of iron or magnesium [48,49]. The diffusion rates along the different axes of the crystal structures show that diffusion occurs four to eight times faster along one axis compared to the other two axes [49]. The diffusion rates of calcium into the olivine structure increase with increasing oxygen fugacity because the partial oxidation of the Fe2+ ions to Fe3+ is charge balanced by the formation of these vacancies [49].

These findings seem to be relevant to the application of olivine in DFB gasification. They can help understanding the influence of the calcium rich woody biomass ash on layer formation, and its influence on the gasification properties. The modification of olivine due to the mobility of the iron ion at high temperatures is reported to have a positive influence on tar cracking in biomass gasification [28,30]. Fredriksson et al. [50] reported that unused olivine in a DFB gasifier is modified by the different atmospheres in the combustion reactor and the gasification reactor. In the combustion atmosphere, iron is mostly available as Fe2O3 and Fe3O4 or MgFe2O4, but it is reconverted under a reducing atmosphere to FeO and FeC and the formation of graphitic carbon can be detected [50]. The incorporation of calcium into the olivine structure takes place during long-term interaction with the calcium-rich biomass ash, resulting in a homogeneous inner layer of the particle [4].

Beside the diffusion of calcium into the olivine structure at the surface of bed material particles, a second, outer layer is built. This layer is composed mainly of biomass ash components [4].

The formation mechanism of the layers on the bed material particles is described by Öhman et al. [51] and was improved by Brus et al. [52], De Geyter [53], and Grimm et al. [54] for quartz as bed material. This mechanism is summarized by Grimm et al. [35] as follows: (a) Initiation by coating: ash components are melted and sintered onto the surface of the particle. This is initiated by potassium silicate melting accompanied by the diffusion or dissolution of calcium into the melt. This mechanism is suggested to be typical for woody fuels with ash rich in calcium and potassium with small amounts of silicon and phosphor. (b) Potassium compounds in gaseous or aerosol phase react directly with the particle surface, forming potassium silicates at the surface followed by sintering and agglomeration. This mechanism is suggested to be typical for fuels with high alkali content and relatively low silicon and phosphor contents. (c1) Direct adhesion of melted potassium silicate particles or droplets: this mechanism is typical for fuels with high potassium content and high content of organically bound silicon. (c2) Direct adhesion by partly molten potassium-calcium phosphates or magnesium phosphates: this is typical for biomass rich in phosphor, potassium, and calcium or magnesium.

Scala et al. [55] described the formation of agglomerates around burning particles where the temperatures are locally even higher than in the rest of the fluidized bed. Phosphor is described in literature to have significant influence on the agglomeration behavior which from interest with alternative fuels [35,54,56]. The influence of phosphor on the adhesion of potassium and its influence on the layer formation are considered to be low because of low phosphor concentrations in the fuel ash and in the particles.

3. Experimental Section

The investigations were carried out with bed material from the 8 MW [thermal] gasification plant in Güssing/Austria. Bed material samples were taken during regular operation. These samples were analyzed and investigations were carried out in small-scale test rigs.

3.1. Sampling and Analyses

The bed material which is described as “fresh olivine” was taken after delivery to the plant before usage in the system. The bed material was already calcined by the supplier at a maximal temperature of 1600 °C before delivery. Bed material which is described as “used olivine” was taken from the bottom of the combustion zone during regular operation. Samples were taken after cooling under ambient conditions.

The used bed material was taken after a period of regular production with wood residues as a fuel. A typical composition of the biomass ash is presented that represents the average composition of the ash.

Sieve analyses of fresh olivine and used olivine were carried out to determine the typical size distribution of the bed material.

The used bed material taken from the bottom of the combustion reactor of the Güssing plant was treated in a lab-scale fluidized reactor under a simulated gasification and combustion atmosphere. One sample was analyzed before treatment in the lab scale reactor as a reference, one sample was analyzed after treatment in gasification conditions, and one sample was analyzed after treatment under combustion conditions.

Used bed material samples after the exposing in combustion and gasification atmosphere were analyzed by X-ray diffraction measurements (XRD). X-ray diffraction measurements were performed with a PANalytical X’Pert PRO system. Refinements were carried out using the program package TOPAS 4.2. The preparation of the samples
was carried out in two ways: one analysis of the particles without further treatment and an analysis of grinded particles. Both samples showed similar trends, the sample without grinding will be presented because the trend is more pronounced.

The samples of particles which were exposed in gasification and combustion atmosphere were analyzed using a scanning electron microscope (SEM)–energy dispersive X-ray spectroscopy (EDX) analysis. The samples for analysis of the surface of the particles were fixed on a sample holder without further treatment. For the micrographs the samples were mounted in epoxy, sanded, and polished. Analyses were carried out on an FEI Philips model XL30 SEM combined with EDX. At least three spot analyses were carried out to determine the composition of the layers or surfaces on different particles and average compositions were calculated. The EDX-analysis indicates the elemental composition of the surface of the sample. The results were calculated without carbon or oxygen.

Thermo-gravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry analysis (DSC) of fresh and used bed material particles were carried out in a NETZSCH STA 449 C Jupiter System. The sample crucible is equipped with a thermocouple for direct measurement of the temperature. The mass is measured by an electromagnetically compensated microbalance with a resolution of 0.1 μg and a maximum capacity of 5 g. The furnace allows temperatures of up to 1650 °C with heating rates between 0.01 and 50 K/min. Heating rates of 10 K/min were chosen to ensure minor mass or heat transfer limitations. The signal-to-noise ratio of the DSC is 15 μW. The gas used to provide the desired atmosphere flows upwards and the desired gas composition is mixed out of gas bottles with the aid of mass flow controllers. Gas flows were set to 40 \( \times 10^{-6} \) m\(^3\)/min. The mass for each sample was chosen to be approximately 70 mg. The results of the TGA were related to the mass at 250 °C as a reference mass. Temperatures below 250 °C are not considered due to inaccurate temperature controlling of the oven and because temperatures lower than 250 °C are not from interest for this topic.

The thermal analyses were carried out once for each sample in three different atmospheres. These analyses were part of an optimization program in the DFB plant in Güssing where thermal analyses of various inorganic matter were carried out. Due to the good agreement with other results the quality of the analyses are considered as good to conclude on qualitative trends.

Typical conditions for the bed material in the DFB plant in Güssing are summarized in Table 1. The temperature in the combustion reactor is depending on the fuel water content and is varying. The set of parameters is shown in the following table.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature in combustion reactor</td>
<td>°C</td>
<td>940–1050 °C</td>
</tr>
<tr>
<td>Temperature in gasification reactor</td>
<td>°C</td>
<td>830–870 °C</td>
</tr>
<tr>
<td>Average retention time</td>
<td>h</td>
<td>35–70</td>
</tr>
</tbody>
</table>

![Fig. 2. Flow sheet of the 5 kW lab-scale reactor.](image-url)
point for the temperature of the gasification reactor is 850 °C, due to variations in the fuel water content, this temperature can vary between the limits shown in Table 1. The retention time of the bed material in the system is depending on the performance of the cyclone between combustion reactor and gasification reactor. The typical range of the retention time is given in Table 1.

### 3.2. Lab-scale Fluidized Bed Experiments

A bench-scale fluidized bed reactor was used to evaluate the influence of the surrounding gas atmosphere on the crystal structure of the particles to obtain a better knowledge of whether the incorporation of calcium takes place in the gasification or the combustion reactor of the DFB system. The test rig consists of a reactor, a gas-supplying system, a solid-fuel-dosing system, and off gas handling (heat exchanger, cyclone, and filter). The off gas leaving the reactor and cooling section at gasification operation conditions has to be finally burnt before releasing to the environment. A flow sheet of the test rig is shown in Fig. 2.

The bench-scale reactor is made of stainless steel (1.4841) with a total height of 1.85 m, inner diameter of 65 mm, and wall thickness of 3 mm in the bed section. The reactor consists of two fluidized beds (FB1, FB2). Two perforated stainless steel plates are used as distributors. The lower fluidized bed serves for pre-heating the gas and the upper fluidized bed is used for the reaction and investigations. The lower fluidized bed has a height of 550 mm between the two distributors and the lower bed itself has a height of 100 mm; the upper fluidized bed is 1200 mm in height from the distributor to the gas exit. At the beginning of the experiments bed material is fed in to obtain a bed height of 100 mm.

The gas composition and flow rate are controlled by mass flow controllers. An electrically heated steam generator is used for supplying steam at atmospheric pressure. A bin with a screw-dosing system can be used for adding material into the fluidized bed. The conveying screw is speed-controlled by a frequency converter.

Before leaving the flue gas to the atmosphere, the gas is cooled down in a tube heat exchanger and cleaned in a cyclone and filter, and at operation in gasification conditions it has to be burnt before it is released into the atmosphere.

To heat the fluidized bed and keep the temperature constant, the reactor is equipped with electrical wall-heating elements which are regulated with proportional controllers. One heating shell is used for heating the lower fluidized bed (heating shell 1). The upper fluidized bed is heated with three heating elements.

<table>
<thead>
<tr>
<th>Component</th>
<th>Unit</th>
<th>Gasification atmosphere</th>
<th>Combustion atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>%db</td>
<td>42</td>
<td>-</td>
</tr>
<tr>
<td>CO</td>
<td>%db</td>
<td>-20</td>
<td>-</td>
</tr>
<tr>
<td>CO₂</td>
<td>%db</td>
<td>-23</td>
<td>-9</td>
</tr>
<tr>
<td>CH₄</td>
<td>%db</td>
<td>9</td>
<td>-</td>
</tr>
<tr>
<td>O₂</td>
<td>%db</td>
<td>0.2</td>
<td>8.5</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>%db</td>
<td>1.5</td>
<td>Rest</td>
</tr>
<tr>
<td>Higher hydro-carbons</td>
<td>4.3</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>%</td>
<td>40</td>
<td>19</td>
</tr>
</tbody>
</table>

The temperature is measured with one thermocouple at the lower fluidized bed and with three thermocouples at the upper fluidized bed and freeboard sections. All thermocouples are of type K with a measuring range of up to 1050 °C.

To generate similar gasification and combustion conditions compared to the industrial-scale DFB gasification plant, similar fuels are used. The gasification atmosphere is generated by using product gas from the Güssing plant for fluidization as the test rig was located in a laboratory just beside the Güssing plant. Since the tapping point of the product gas in the industrial-scale plant is located after the product gas cleaning (filter and scrubber), the gas is mixed with steam to generate a water content similar to that in the gasifier. The test conditions used in the test rig are summarized in Table 2. The product gas composition of the main components is shown in Table 3. The detailed gas composition is described elsewhere [1,13]. The combustion conditions were generated by combustion of product gas and char from the industrial-scale plant. To ensure a similar steam content in the combustion atmosphere, steam is added. The gas atmospheres of the gasification and combustion conditions are summarized in Table 3.

### 4. Results

The typical composition of the ash of the woody biomass which is utilized as a fuel in the gasification plant in Güssing is shown in Table 4. The composition is typical for woody biomass with a high amount of calcium oxide, silicon oxide, potassium oxide and other elements.

The particle size distribution of the fresh and used olivine which is utilized in the plant in Güssing is shown in Fig. 3. Used olivine has a slightly higher content of fine particles due to abrasion. Earlier studies only showed micrographs of the particles [4] without recognizing their impact on the gasification performance. But later the influence of the bed material and especially the modification of the particles on the gasification properties became known [5,36]. A detailed examination of the surface of the olivine particle is of interest. A picture of the surface of one particle is shown in Fig. 4. A non-porous surface can be seen, with small dimples as the suggested origin of abrasion in the fluidized bed or elsewhere in the plant. A detailed picture of the surface is shown in Fig. 5, revealing small cracks in the surface, which is mainly smooth. The formation of the two layers outside on the particles is shown in Figs. 6 and 7 in detail. The inner layer could be explained by the diffusion of calcium into the crystal structure of the olivine while the outer layer is similar to the fly ash composition and is considered to grow outward from the particle (see Kirnbauer et al. [4]).
A comparison of the elemental composition of the surface of the particle is shown in Fig. 8. Both the outer layer and also the analysis of the surface showed that calcium had the highest concentration, followed by magnesium and silicon. The concentration of silicon is lower at the surface of the particle than in the outer layer, while the concentrations of potassium and phosphor are higher. The other elements are in the same range in both pictures. In general the composition in the surface of the particle is similar to that in the outer layer in the micrograph.

An analysis of the surface of the particle at different gas atmospheres simulating the atmospheres in the gasifier and the combustion reactor is shown in Fig. 9. No significant change in the composition of the surface between the reference case and the treatment under gasification conditions and combustion conditions can be observed. Gasification conditions showed slight increases in iron, chrome, and nickel, which are considered to come from the stainless steel reactor walls of the test rig. The composition of the stainless steel wall is removed in the fourth column of Fig. 9 by calculation and shows a similar composition compared to the reference case and the combustion atmosphere.

The examination of the crystal structure by XRD analysis under gasification and combustion conditions is shown in Fig. 10. The main crystal structure is forsterite, which is the main component of olivine; periclase, calcium silicates such as larnite, and iron oxides such as magnetite and hematite could be detected. Small amounts of potassium silicates were also detectable.

A comparison of the samples under gasification conditions and combustion conditions showed an increase of monticellite, which is a calcium-magnesium silicate, in the combustion atmosphere. Larnite could be detected in a slightly higher amount under combustion conditions compared to gasification conditions. The amount of magnetite decreased under combustion conditions compared to gasification conditions. A slightly weaker signal of forsterite could be detected under combustion conditions.

Figs. 11 and 12 show a comparison of the thermal behavior of fresh and used olivine particles, respectively, in different atmospheres.

A TGA of the bed materials shows moderate weight losses for fresh olivine in air, inert gas (nitrogen) and carbon dioxide gas (mixed with nitrogen) at different temperatures. The only exemption is air, where an increase in weight can be seen at temperatures higher than 900 °C. The weight loss is around 0.05% up to 0.1% of the total mass. The DSC signals shows a plateau between 250 and 450 °C with an endothermic weight loss and a change of thermal properties over the whole temperature range but no characteristic peak with a weight loss at temperatures above 450 °C.

Used olivine shows weight losses of around 0.1% (up to 0.2%) of the mass in the TGA. In nitrogen and air atmosphere, the weight loss occurs at temperatures of around 550 to 600 °C. In a mixture of 15% carbon dioxide and 85% nitrogen by volume a weight loss can be seen at around 800 °C. In a carbon-dioxide-rich atmosphere, the
DSC signals only indicate a significant endothermic peak at 800 °C, where the weight loss occurs. At higher temperature (>850 °C) a slight decrease in mass can be observed which amounts about 0.2% above 2100 °C.

In an air atmosphere, both the fresh and the used olivine showed significant increases in weight at temperatures higher than 850 °C.

5. Discussion

Investigations of the particle surface of used bed material particles and comparison with the outer layer using micrographs showed no significant differences in the elemental composition. Only small differences in the amount of potassium and phosphor can be seen, which might be explained by condensation reactions during the cooling process when the samples were taken. The difference could be also caused by the accuracy of the measurement, the results are average values from multiple samples which reduces the mistake. The relative error of for concentrations between 1 and 5 wt.% is given with 20% by the supplier of the EDX.

The elemental composition of the carbon- and oxygen-free particle surface of used olivine particles also seemed to be stable in different atmospheres during test runs under laboratory conditions. Only the concentration of potassium in the surface decreases compared to the reference in a combustion atmosphere and even more in a gasification atmosphere. This can be explained by the assumption that potassium is mainly available as KOH [35] in the gasification atmosphere and also in the combustion atmosphere and is released from the reactor with the gas phase (product gas and flue gas respectively). Also the high calcium content can be considered to enhance the potassium release in the gas phase [57–59]. In the industrial-scale plant, the conditions can be considered balanced, where a constant balance between incoming potassium that is fed into the gasifier with the biomass and a loss of potassium with the product gas flow leads to a constant potassium concentration in the gas atmosphere and within the bed material. A similar balance can be considered in the combustion reactor, where potassium is fed via ash loops to the combustion reactor and released with the flue gas.

Consideration of the crystal structures of used bed material particles in combustion and gasification atmosphere shows that an increase of monticellite is detected under combustion atmosphere, while forsterite is detected in lower amounts. This can be explained by the incorporation of calcium into the crystal structure of the olivine. The substitution of Fe with Ca is promoted compared to the substitution of Mg with Ca [48]. Nevertheless, a significant amount of MgO can be detected. The diffusion of Ca into the crystal structure of olivine is promoted at higher oxygen fugacities because the partial oxidation of Fe²⁺ to Fe³⁺ is charge-balanced to the formation of these vacancies [49]. In contrast to an earlier study [4], iron silicates are not detected in samples in this study. This might be due to changes in the solid loops (ash circulation and bed material circulation) of the gasification plant which were carried out between this study and the earlier study [4] with the aim of reducing bed material consumption, which leads to a longer retention time of the bed material in the system. Iron silicate structures are considered to be removed from the crystal structures of the olivine during plant operation [30,50].

The detection of crystal structures of potassium silicates in used bed material particles also contrasts with the findings of the earlier study and can be explained again by the change in the ash loops. K₂Si₆O₁₅ is a crystal of K₂O and SiO₂ at the ratio of 1:2 on a molar basis. Considering the binary phase diagram of potassium and silicon oxide [60], this structure crystallizes when cooling down a melt to
1036 °C, which is the maximum melting temperature of the binary phase in the concentration range between two eutectics points with a potassium oxide concentration of more than 30% on a molar basis. This crystal structure is a mixture of 57% potassium oxide and 43% silicon oxide by weight. Temperatures higher than 1036 °C are considered to be possible locally around burning char particles in the combustion reactor. Considering the mechanism of the layer formation summarized by Grimm et al. [35], described above, the potassium silicate can be considered to be incorporated in the outer layer according to mechanism (a), where melted ash components stick on the surface of the particle and calcium is diffused into the particle. The investigation of the particle surface (see Figs. 4 and 5) shows a smooth surface, which confirms the assumption that layer formation mechanism (a) occurs with a molten surface.

The thermal analysis showed a weight increase of both samples (used and unused bed material) in air at higher temperatures: This might be caused by the oxidation of magnetite [50] or by the decomposition of fayalite with the oxidation of iron. Since fayalite was not detected by analyses of the crystal structure it is evident that the iron of the bed material sample that was taken as a reference was neither oxidized to Fe₂O₃, nor were the samples treated in the combustion atmosphere or gasification atmosphere fully oxidized to Fe₂O₃.

The weight loss at 400 °C with fresh olivine might be caused by the decomposition of magnesium carbonates, which decompose at 400–600 °C [61]. The weight loss of used olivine at around 600 °C is suspected to be caused by the decomposition of calcium hydroxide, which can be built at the surface due to the humidity of the ambient air after sampling.

TGA in an atmosphere of 15% CO₂ in nitrogen shows a similar picture compared to the air and nitrogen atmosphere. The DSC signal of used olivine shows a small but clear endothermic peak at 800 °C during a weight loss of around 0.1 mass%. This peak is considered to be caused by the decomposition of calcium carbonates. The investigations of the
The surface of the particles showed a calcium content of 45 to 50%. As the crystal structures showed, at least a part of the calcium is incorporated into the calcium silicate structures but also a part seems to be reactive and can react with CO₂ forming CaCO₃ which is released at elevated temperatures. Pure calcium carbonate decomposes in an atmosphere of 15% CO₂ at temperatures of around 800 °C [40,62]. The thermal analysis showed that CO₂ transport of the used olivine is possible in conditions similar to the SER (Sorption Enhanced Reforming) process [3,38–44]. In regular conditions in DFB gasifiers with gasification temperatures of 850 °C and temperatures in the combustion reactor higher than 900 °C, CO₂ transfer between the gasification and combustion reactors is negligible. The surface investigations of the bed material showed a flat surface with a low specific surface of the particle, indicating a low capacity for the transport of CO₂. The weight loss in the CO₂-rich atmosphere is around 0.1%, which represents a far lower specific transport capacity of the bed material compared to bed materials that are typically used in the SER process [63].

Considering optimization potentials of the DFB biomass steam gasification, important results were obtained by this study.

(i) One option for optimization is the reduction of the gasification temperature which increases the electrical efficiency of the plant. By this measure the temperature in the combustion reactor is reduced accordingly. Since the layer formation is suggested to be dependent not only on the temperature of the fluidized bed but also on the combustion temperature of char particles, a lower temperature in the combustion reactor does not necessarily affect the layer formation. The combustion temperature of the char particles can be influenced by the oxygen excess in the combustion reactor.

(ii) The utilization of alternative fuels (other than woody biomass) will have an impact on the composition of inorganic matter in the plant and this will have an impact on the layer formation. According to Grimm et al. [35] the layer formation mechanism and the composition of the layer will change with different fuels, such as fuels rich in potassium or phosphorus. Since the elemental composition of the surface of the particle is similar to the ash composition (see Kirnbauer et al. [4]), a significant impact on the operation of the plant is expected by using different fuels with different ash compositions. Detailed investigations with different fuels and fuel blends are required to evaluate the influence of the different ash compositions on the gasification properties.

(iii) The synthesis of fuels and chemicals such as Fischer–Tropsch synthesis and synthesis of synthetic natural gas (BioSNG), mixed alcohols, or chemicals have different requirements regarding the product gas composition, for example the optimal H₂:CO ratio. A reduction of the gasification temperature will influence the product gas composition [36], and by choosing the correct temperatures of the gasification reactor and the combustion reactor, the transport of CO₂ from the gasification reactor to the combustion reactor is possible. The low CO₂ load capacity of the used bed material limits the influence on the product gas composition.

6. Conclusions

The following conclusions can be drawn from this work:

- The elemental composition at the surface of the used bed material particles is similar to the composition of the outer layer measured in micrographs and does not change significantly between the gasification and combustion atmospheres.
- The investigation of the crystal structure showed an increase of calcium-silicates in the combustion atmosphere, which is in accordance with theoretical considerations. Higher diffusion rates can be expected at higher temperatures and higher oxygen concentrations in the combustion reactor.
- An intensive contact of olivine particles and ash promotes the formation of the layers in the combustion reactor. Burning char particles promotes layer formation due to melt formation and random collisions of bed material with burning char particles.
- The calcium-rich surface of the used bed material particles allows the reaction with CO₂. At typical temperatures of DFB biomass steam gasification plants, CO₂ transport from the gasification to the combustion reactor is not expected.

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