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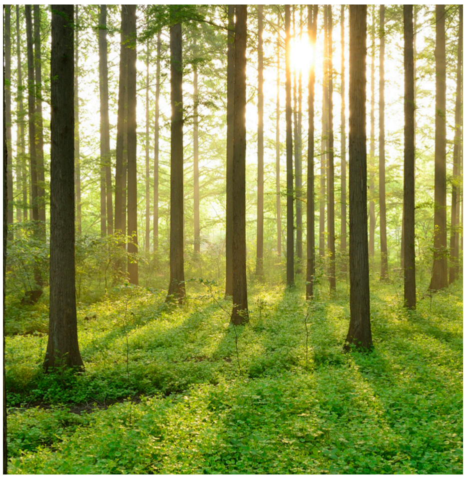

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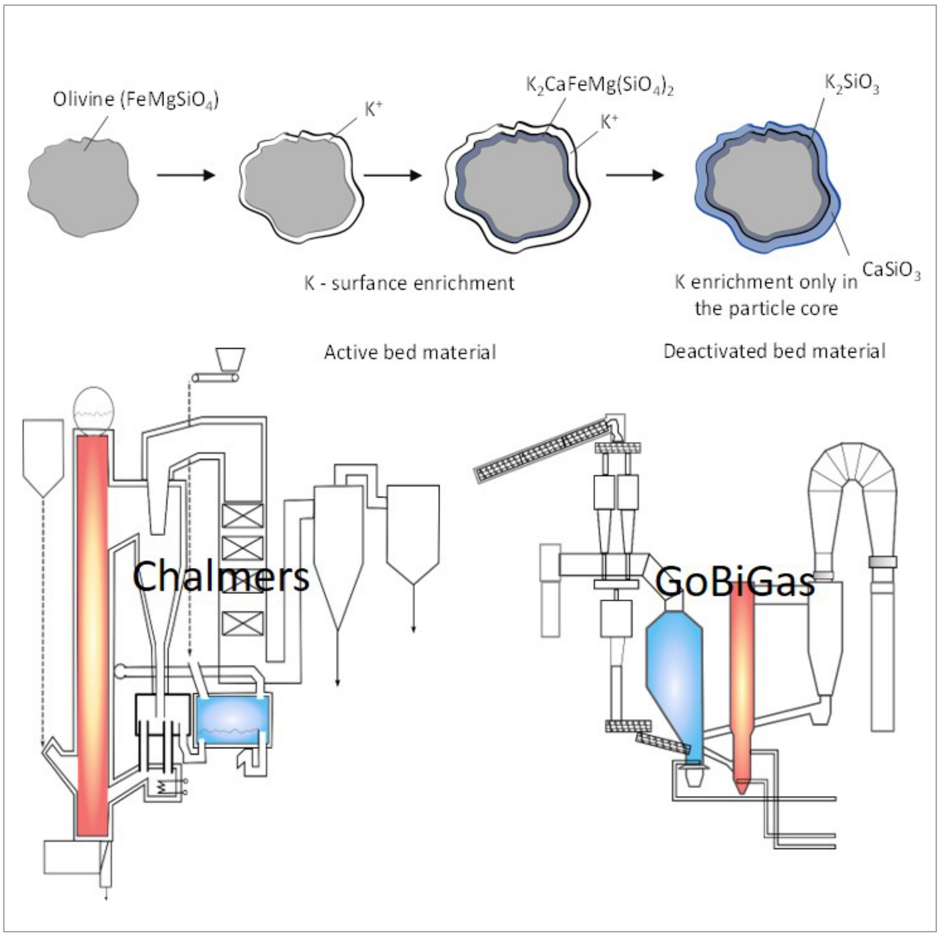

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Choice of Suitable Additives and Design of Activation Procedure for Olivine

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Authors Foreword

This project brings new knowledge on how to make the production of biofuels more efficient by simplifying the activation process of olivine. A lower tar content in the produced syngas reduces the need for gas cleaning and thereby increases the efficiency and lowers the cost of the process. The results from the project will contribute to increased knowledge regarding the catalytic activity of bed material in dual-bed gasification.

The report has been produced by Chalmers University of Technology, as a collaboration between the departments of Energy and Materials and Energy and Environment, Valmet AB, and Göteborg Energi AB. The authors are Pavleta Knuttson (Energy and Materials), Martin Seemann and Jelena Marinkovic (Energy and environment).

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The study had a reference/working group with the following members: Ingemar Gunnarsson (Göteborg Energi AB), Claes Breitholtz (Valmet AB), Anna-Karin Jannasch (Rise) and Anton Fagerström (Energiforsk).

Sammanfattning

Under biomassförgasning omvandlas biomassa till produktgas som kan användas vidare som drivmedel i transportsektorn, till produktion av värme och elektricitet eller som råvara till kemisk syntes. Bland komponenterna av den producerade produktgasen ingår oönskade komponenter såsom askkomponenter och tjäror. Tjäror definieras ofta som tyngre kolväten som kan orsaka oplanerade men representerar också förlust av energi från producerade gasen.

Användandet av katalytiskt bäddmaterial anses vara ett effektivt sätt att minska tjärinnehållet i produktgasen. Olivin är den mest använda katalytiska bäddmaterial inom förgasning. Det har observerats att genom modifikationer av olivin som till exempel värmebehandling eller genom tillsats av olika komponenter kan effektiviteten av olivin som katalytiskt material förstärkas. Även om det finns många studier om förbehandling av olivin och dess effekt på den producerade gasen så saknas tidigare studier som visar vilka parametrar som skulle ingå i en aktiveringsprocedur eller hur en sådan procedur skulle se ut.

Nuvarande studien utfördes i två anläggningar – Chalmersförgasaren samt GoBiGas-anläggningen där parametrarna varierades och deras effekt på både material men också gasinnehåll studerades. Bäddmaterial från båda anläggningar tagna under utvalda driftsvillkor karaktäriserades för dess innehåll med hjälp av total elementanalys och urlakning, men också morfologiskt och med hjälp av SEM-EDS och XRD.

Resultaten visade att alkali-salter tillsätta till bäddmaterialet i form av naturligt förekommande askkomponent eller som artificiella tillsatser kan öka den katalytiska effektiviteten av bäddmaterialet. Tillsats av K_2CO_3 kan resultera i direkt aktivering av bäddmaterialet.

Summary

During biomass gasification, along with the produced syngas, unwanted components such as tars and ash are also generated. Tars is the common name used for a group of heavy hydrocarbons that represent both a loss of efficiency for the process because of the energy they contain but also a challenge as upon condensation they can cause fouling and blockage of equipment.

Olivine, $FeMgSiO_4$, has been traditionally used as a catalytic bed material for tar cracking in biomass gasification. Different modifications of olivine have been shown to enhance its catalytic performance, such as heat pretreatment and additives in form of metallic compounds naturally existing in olivine or foreign to olivine compounds. A clearer choice of additives and procedure for activation of olivine is necessary for the improvement of the process efficiency in industrial applications. The goal of this project was therefore through a series of experimental campaigns on both laboratory and plant scale, to identify the necessary additives and actions needed for achieving the maximum catalytic performance of olivine.

The experiments described in the present report were performed at two different units – Chalmers 4MW gasifier and the 20MW GoBiGas plant. Bed materials have been sampled and characterized on compositional level through total elemental analysis and on structural level through SEM-EDS and XRD. The activity of the material has been followed through gas analysis and tar measurements. The results show that addition of K_2CO_3 to the process can provoke immediate response and improve the gas quality.

List of content

1 Backgroud

During biomass gasification, biomass is converted to a product gas that can be further used as fuel for the transport sector, for heat and electricity production or as resource for chemical synthesis. Along with the aimed product gas constituents (CO, CO_2, H_2 and H_2O) there are also undesired by-products such as tars. Commonly tars are defined as higher hydrocarbons (mostly aromatic) that are produced during gasification and that can condense on available surfaces within the process and thereby cause clogs in the system (Milne, Abatzoglou et al. 1999). Apart of being an undesired component in the product gas, tars contain chemically bound energy that can be up to 5% of the energy content of the fuel (Tunå, Svensson et al. 2010). Tar cracking is therefore regarded as a process that have a double positive effect as it decreases the operational costs connected with gas cleaning as well as increases the quality of the final product.

There are two main approaches that are usually used within the gasification step for tar cracking – catalytic or thermal (Han and Kim 2008, Anis and Zainal 2011). Tar cracking through catalytically active bed materials is a more effective alternative as it does not need additional input of energy in terms of higher temperature. Different bed materials have been investigated (Dayton 2002, Zwart 2009) and tar cracking of more than 90% has been reported previously at temperatures of 450-900 °C (Dayton 2002). The common parameters used to explain the bed catalytic activity of the bed materials can be summarized as: the surface area, the pore size and the content of active components such as Fe, Mg/Ca and alkali elements (Wen 1983, Wen and Cain 1984, Simell, Leppälahti et al. 1992, Seshadri and Shamsi 1998). Olivine, $FeMgSiO_4$, is the most common choice for catalytic bed material in use in gasification plants (Rapagnà, Jand et al. 2000, Courson, Udron et al. 2002, Devi, Ptasinski et al. 2003). Different activation pretreatments in terms of additives and/or heat treatment have been recommended in multiple studies (Courson, Udron et al. 2002, Rauch, Pfeifer et al. 2004, Devi, Ptasinski et al. 2005). Even though the material is run at several gasification plants, the parameters used for activation differ significantly between the different units and the changes that the activation process brings to the bed material remain unclear.

Some of the published results state that (Fe(III)) which is a naturally occurring compound in olivine has the main role for the activation of the material and the decrease of tars. Iron migration is therefore named as the parameter with most important role in the activation (Orío, Corella et al. 1997, Courson, Udron et al. 2002, Devi, Ptasinski et al. 2005). In several other studies the interaction between the material and the surrounding gas resulting in changes in the morphological and chemical structure of the material are instead stated to be of most importance(Grootjes, Meljden et al., Kirnbauer and Hofbauer 2013, Knutsson, Seemann et al. 2017).

Alkali salts released as a result of biomass gasification are usually also considered as unwanted constituent of the product gas as they can cause two main problems; 1) they can readily condense in the gas flue channel and cause corrosion; (Hansen, Nielsen et al. 2000) 2) they can interact with the bed material particles and form sticky deposits that can act as further surfaces for particle deposition and thereby cause bed material agglomeration (Bryers 1996, T. 1999). However, it has been proven that the presence of alkali content in the fed fuel increases the rate of the gasification process by enhancing the carbon conversion (Yuh and Wolf 1983, Hansen, Nielsen et al. 2000, Fahmi, Bridgwater et al. 2007, Zhang, Gong et al. 2014). Furthermore K_2CO_3 has been shown to suppress the formation of tar species (Elliott and Baker 1986, Sutton, Kelleher et al. 2001). The triggering effect of adding alkalis as catalysts have already been described in the literature (Lizzio and Radovic 1991, Suzuki, Ohme et al. 1992, Lee, Nam et al. 2000, Padban 2000). Alkaline catalyst effect is more prominent when it comes to wood gasification where a difference of 70 kJ/mole in the activation energy was reported in the presence of K_2CO_3 (Li, Yan et al. 1996).

The interactions between alkali, alkaline components and the bed material results in a build-up of a layer around the bed material particles that is related to an increase in the catalytic ability of the bed material (Kirnbauer, Wilk et al. 2012, Kern, Pfeifer et al. 2013, Kuba 2015, Kuba, Havlik et al. 2016). The nature of the catalytic effect of alkali have been examined in several investigations previously. In some studies alkalis are considered to be promoters for unzipping the cellulose chains (Padban 2000) in others - as promoters for the formation of liquid-surface interface and thereby assuring better contacts between the tars and the surface through wetting (Lizzio and Radovic 1991) thus reducing tar levels at a very early stage of the process. In older studies the effect of alkalis is considered to be based on the formation of peroxide complexes on the surface that act as oxygen transport so that more oxidizing conditions are locally available for the tars (McKee and Chatterji 1975) though regarding alkalis as catalytic agents through the whole process. Alkalis are natural constituents of the formed ashes. This results in a double positive effect as- handling of ashes as waste is avoided and at the same time they can be used as catalysts or have a triggering catalytic role in bed materials.

Even though that gasification is gaining more and more popularity and several demonstration units are built within Europe (with the largest being set in Gothenburg), the preliminary results obtained from them are not consistent with each other and do not contribute to a breakthrough in understanding. Different parameters are pointed out as triggering the activation of the bed material but still a clear activation process has not been suggested. There is therefore a need for understanding of the mechanism of activation, the needed material modifications that would lead to a maximum tar cracking and the role of the ash constituents on the bed material activity /deactivation.

In the present study based on previous experience, K_2CO_3 was added to the combustor side of the dual bed gasifier with the aim to artificially trigger activation.

2 Experimental

2.1 CHALMERS GASIFIER

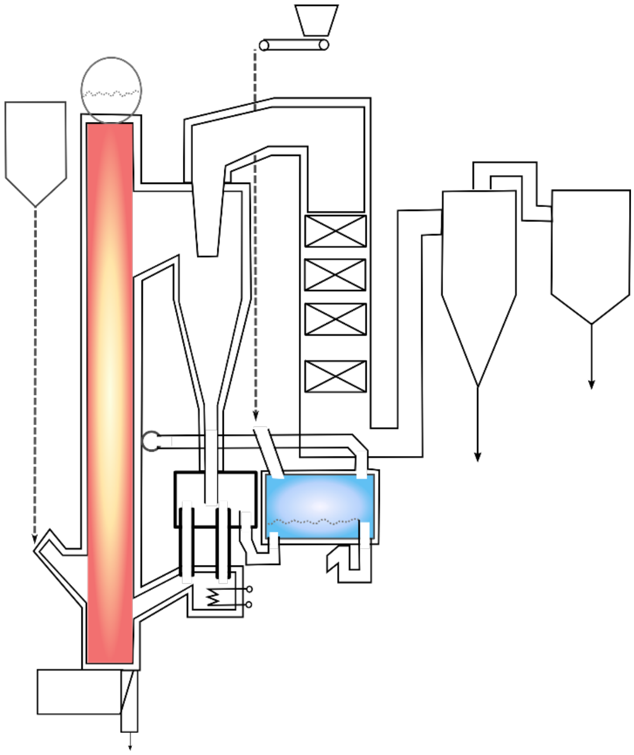

Figure 1 Schematic representation of the Chalmers unit with indicated gasifier (blue) and boiler (red) (Knutsson, Seemann et al. 2017).

The Chalmers dual fluidized bed (DFB) gasifier (Figure 1 ,also in references (Larsson, Seemann et al. 2013, Marinkovic, Seemann et al. 2016)) represents a 2-4 MW gasifier where steam is used as a fluidizing agent and the heat for the endothermic reaction is provided by a bed material that is circulated between the gasifier and a 12 MW boiler. Wood chips have been used as fuel for the combusting reactor and wood pellets as fuel for the gasifier. Two sampling points are used for bed material extraction, situated at the entrance of the gasifier and at its outlet accordingly.

2.2 GOBIGAS GASIFIER

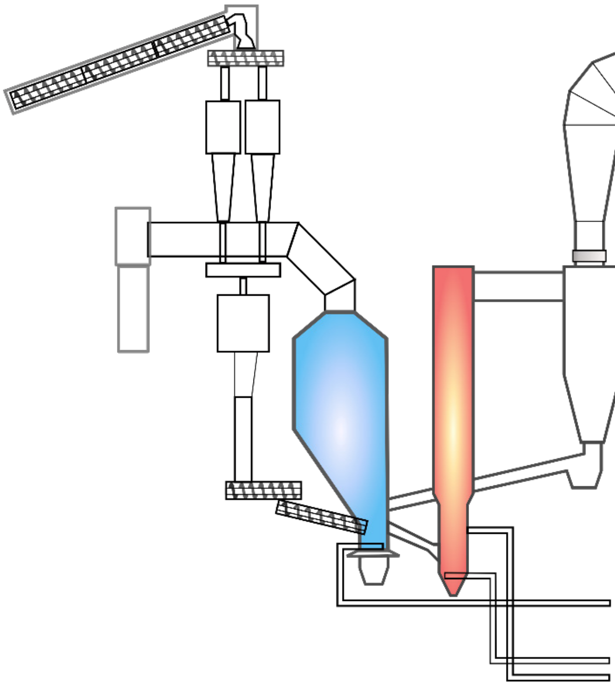

Figure 2. Schematic representation of the interconnected gasifier (indicated in blue) and boiler (indicated in red) of GoBiGas plant (Knutsson, Seemann et al. 2017).

The GoBiGas gasifier (Figure 2, also described in (Larsson, Seemann et al. 2013)) is a 20 MW dual fluidized bed (DFB) gasifier with two interconnected fluidized bed reactors – one for combustion and one for gasification. Heat is transported with a circulating bed material between the reactors. The fuel is fed to the gasifier, which is a bubbling bed fluidized with steam where the fuel is partially converted into a product gas. The product gas is cooled to recover heat and cleaned, before it is synthesized into methane. Part of the char formed during devolatilization of the fuel is not converted in the gasifier and instead transported with the bed material into the combustion reactor, where it burns to produce heat.

The two plants are operated under different preconditions. The GoBiGas plant is operated with the aim to have continuous and optimal operation for a maximized production of SNG where the product gas should meet the quality requirements of the downstream equipment. The Chalmers plant, in contrast, even though a production unit for heat, can be operated under more extreme conditions without the need to meet requirements for gas quality.

2.3 BED MATERIAL

Olivine is a silicate mineral with the general formula $(Mg^{2+}, Fe^{2+})_2SiO_4$. The magnesium and iron ions can freely substitute for each other and therefore the olivine is considered not a single mineral but instead a series of minerals in a larger group called the olivine group with Fayarite (iron-rich) and Forsterite (magnesium-rich) minerals as the extreme members (Lutgens and Tarbuck 2003).

In the present study two minerals from the olivine series have been used as bed materials with composition as listed in Table 1.

Table 1. Composition of the olivine used as bed materials in the Chalmers gasifier and GoBiGas

	Weight percentages	
	Calcinated serpentine magnolithe	Olivine NCM Incast LE 50
MgO	48.90	49.60
SiO_2	41.00	41.70
Fe_2O_3	9.50	7.40
Al_2O_3	0.30	0.46
CaO	0.13	0.15
Cr_2O_3	0.57	0.31
NiO	0.30	0.32
MnO	0.12	0.09
Na_2O	0.02	0.02
K_2O	0.01	0.03
L.O.I*.	0.00	0.56

**L.O.I – loss on ignition*

The used olivine in Chalmers was delivered by SIBELCO Nordic AB and is originally from Norway. The used olivine in GoBiGas is serpentine, a mineral from the olivine family, hat was calcined prior to use in Austria.

2.4 EXPERIMENTAL CONDITIONS

In the GoBiGas unit the bed material was circulated over a period of more than 3 months under which the operation was optimized based on findings from previous investigations and own operation experiences. During the activation campaign 5 l/h of 40wt% K_2CO_3 solution was added, on two occasions – 6-8 hours after addition of the K_2CO_3 and after a period of 6 days bed material, tar and gas was sampled.

Based on the results from the GoBiGas unit an activation campaign was executed at the Chalmers gasifier where 600 kg of bed material was regenerated during the first day and 400 kg the following days. 6 kg K_2CO_3 was added to the boiler.

The parameters of the runs in the GoBiGas and Chalmers gasifier can be found in Table 2.

Table 2. Operational parameters used during activation tests run in GoBiGas and Chalmers gasifier

	Bed inventory	Temperature in the bed, gasifier [°C]	Fuel flow, [kg $_{daff}$ /h]	Fluidization level [kg$_{steam}$/h]	Temperature in the boiler, [°C]
Chalmers	Olivine	810	268	160	880
GoBiGas	Calcinated Serpentine	870	4600	2300	960

3 Methodology

During the activation period in the two units, gas and tar measurements were monitored. The activation state of the material was defined using an empirical correlation between the measured total tar yield and the CH_4 concentration (Figure 2) (Larsson, Hedenskog et al. 2015). Three main zones of activity could be distinguished: Non-activated (the fresh material before activation), Deactivated (material that has lost its activity after the run) and Activated (catalytically active bed material).

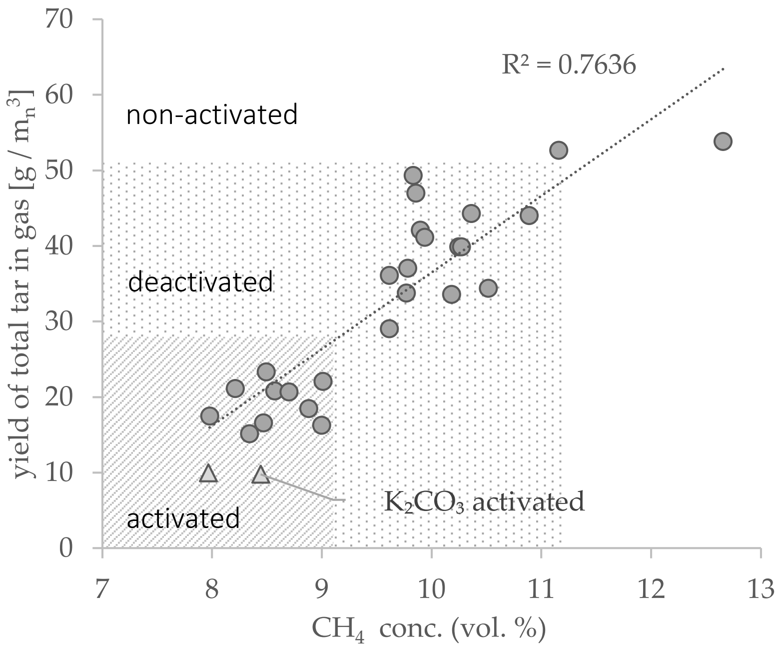

Figure 3. Correlation between the tar yield and CH_4 concentration used to define the bed materials activity and to determine sample occasions (Larsson, Hedenskog et al. 2015).

Based on Figure 3 samples were collected in their activated state as well as in deactivated state for the case of the GoBiGas plant. The sampled bed materials were characterized in terms of morphological and chemical changes. The results correlated to the gas and tar analysis were used to determine: 1) the mechanism of development of catalytic activity; and 2) the factors that could trigger activation in olivine during gasification.

3.1 ANALYSIS TECHNIQUES AND PROCEDURES

To follow the morphological changes that occur as a result of the applied activation, bed material particles were immobilized in epoxy resin, and grinded and polished so that a flat cross-section of the particles could be obtained. Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM-EDS) was used for the morphological evaluation of the material as well as for the elemental distribution within the particles. Tabletop Phenom ProX and Quanta 200FEG equipped with an Oxford EDS were the systems of choice for the evaluations. Both point analyses and intensity maps were used for the element distributions.

Leaching tests were performed to evaluate the stability of the substances formed under operation conditions. The leaching tests were performed at liquid to solid (L/S) ratio of 1/10 during three days under constant mixing conditions. The leachates were analysed by inductively coupled plasma-mass spectrometry (ICP-MS, Thermo Fischer).

The composition of the dried and cleaned product gas was measured online where the CO, CO_2 and CH_4 were measured with NDIR and H_2 was measured with a TCD. Additional measurements were conducted using a μGC to validate the online measurements and to measure the concentrations of C_2H_2, C_2H_4 and C_2H_6. Details on the GC-method and calibration have previously been presented (Milne, Abatzoglou et al. 1998).

Tars were sampled from the raw uncleaned product gas stream before the cooler using the Solid Phase Adsorption (SPA)-method, previously described in (Israelsson, Seemann et al. 2013). The pressure and temperature were measured at every sampling occasion and used to recalculate tar concentrations in g/m^3. The total tar here includes all components quantified with GC-FID using the SPA method, thus, including BTX-components as well as heavier components up to Coronene.

4 Results and discussion

The bed materials from Chalmers and GoBiGas have different origins and have been subject to different pre-treatment which makes it hard to draw conclusion from the comparison between the materials. The similar composition and crystal structure of the materials and the similarity in conditions that the materials are exposed to still allow to evaluate the factors affecting their catalytic ability.

4.1 NON-ACTIVATED BED MATERIALS

Figure 4 shows the materials in their non-activated state. There is increased porosity and cracks present in the material (visible at the overview and cross-section micrographs) at the GoBiGas olivine which can be attributed to the heat treatment in form of calcination that the material was subjected to prior to its use in the gasifier. Furthermore, with the difference from the olivine used as a bed material in the Chalmers gasifier iron segregation (observable in the elemental maps) is also noticeable.

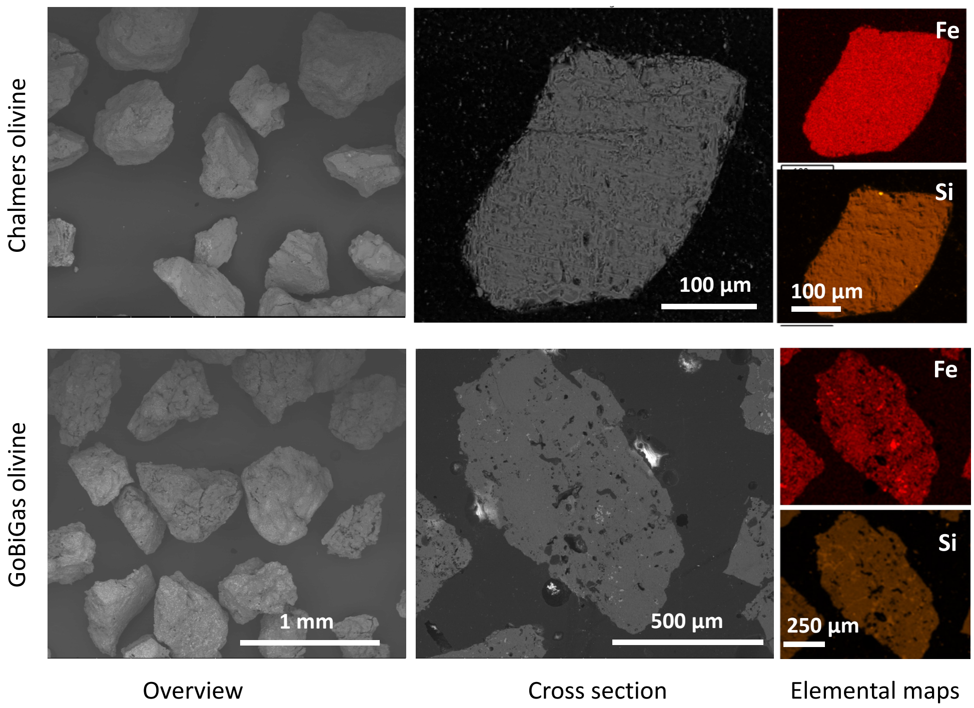

Figure 4. Electron micrographs showing the bed materials used in Chalmers gasifier (top) and GoBiGas (bottom) units, showing the overview structure of the bed material particles (left), cross-section of a representative particle (middle) and elemental distribution of Fe and Si (right)(Knutsson, Seemann et al. 2017).

Fe-segregation at high temperature to regions with high porosity has been previously observed in the case of ilmenite, $FeTiO_3$ (Knutsson and Linderholm 2015). Following the findings on ilmenite the iron migration in the present case can be explained with preferred migration of iron to locations with higher oxygen partial pressure such as larger pores or cracks. No iron migration to the surface of the particles or formation of iron layers around them could be observed on neither of the materials.

It should be also noted that as the materials differed in their crystalline phase content, with both containing forsterite as a main constituent. The comparison between the two materials is not the purpose of this study but rather the common factors that trigger activation in olivine sand used as bed material. For this purpose, the materials and the two gasifier cases will be discussed in parallel.

4.2 ACTIVATED BED MATERIALS

4.2.1 Chalmers case - gas and tar analysis

Tars in the raw gas were collected with SPA and analysed in the GC-FID. The results for the non-active and activated case can be seen on Figure 5 and in Table 3, where the tar yield of the species identified as benzene, 1-ring compounds, Naphtalene, 2-ring compounds, compounds with at least three rings and phenolic species are presented.

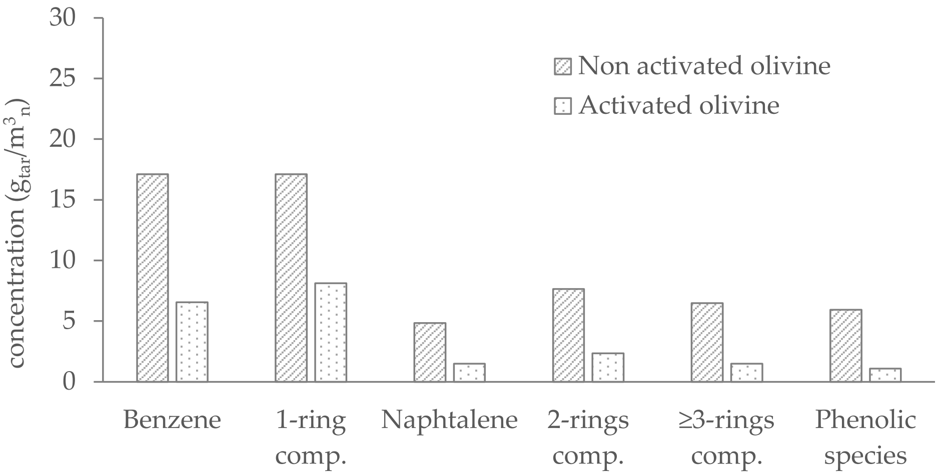

Figure 5. Concentration of collected tars for the Chalmers gasifier per tar species as collected before and after activation of bed material is performed (Knutsson, Seemann et al. 2017).

Table 3. Table showing permanent gas composition measured upon activation of bed material in Chalmers (Knutsson, Seemann et al. 2017)

	vol.%	
Gaseous components	non-activated	activated
H_2	31.5	40.99
CO	27.52	16.99
CO_2	20.41	28.65
CH_4	11.51	6.91
C_2Hx	4.3	2.34
C_3Hx	0.3	0.28
H_2S	0.18	0.24
N_2	4.28	3.6

It can be noted that benzene and compounds with one aromatic ring are the major tar constituents of the product gas in the Chalmers gasifier, with compounds containing two and more aromatic rings present at almost the same concentration (half of the concentration of benzene and 1-ring compounds). Upon activation of the material decrease in all the sampled tar can be noted. Similar decrease has been noted even in cases of olivine aging experiments (Berdugo Vilches, Marinkovic et al. 2016). From the presented tar groups the strongest effect of the alkali activation was reached in the case of phenolic species and compounds with two or more aromatic rings.

The effect of the activation of the bed material could also be followed by the content of the measured permanent gases (Figure 5, right). Because of the addition of K_2CO_3 an increase in H_2 and CO_2 coupled with a decrease in CO was observed which points on a governing influence of the Water Gas Shift reaction (WGS). This effect was expected and is in line with previous observations connected to an activation role of potassium on Water Gas Shift reaction (Amenomiya and Pleizier 1982). The ratio H_2/CO obtained through activation of the material increased from 1.14 to 2.4. The reached value was higher than the one obtained through aging (Marinkovic 2016) and was very close to the maximum ratio measured with olivine in the Chalmers unit - 2.6 (Berdugo Vilches, Marinkovic et al. 2016). CH_4 is the simplest representative of hydrocarbons. Changes in CH_4 levels can therefore be used as indicative for the occurrence of hydrocarbon reforming reactions. In the present case with olivine activation in the Chalmers gasifier, the decrease in the CH_4 content is observed pointing on the presence of hydrocarbon reforming reaction.

4.2.2 GoBiGas case– gas and tar analysis

The results for tar collected for the non-active and activated case can be seen on Figure 6 and Table 4.

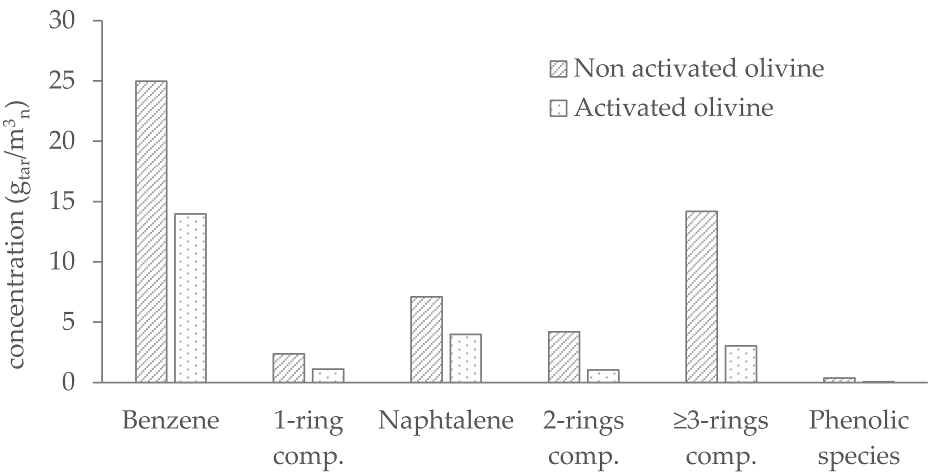

Figure 6. Concentration of collected tars for the Chalmers gasifier per tar species as collected before and after activation of bed material is performed (Knutsson, Seemann et al. 2017).

Table 4. Table showing permanent gas composition measured upon activation of bed material in GoBiGas (Knutsson, Seemann et al. 2017).

Gaseous components	vol.% activated
H_2	42.69
CO	24.76
CO_2	21.76
CH_4	8.51
C_2H_x	2.28
C_3H_x	0.00

It can be noted that from the measured tar groups, the ones of major concern for the GoBiGas plant are the benzene species together with the compounds containing three or more aromatic rings (close to double the amount measured in the product gas at the Chalmers gasifier). The yield of the phenolic and 1-ring compounds is almost negligible in comparison to the Chalmers gasifier. Upon activation of the bed material all the measured tar groups were affected by the alkali salt addition, where the relative decrease for each tar group was comparable to the decrease observed in the Chalmers case. In total, tar concentration decrease of 56 % was observed.

Like the case with the activated material in the Chalmers reactor, the effect of the activation of the bed material was also followed by the content of the measured permanent gases (Figure 6). Similar increase in H_2 and CO_2 coupled with a decrease in CO was observable pointing to the Water Gas Shift reaction (WGS). Unlike Chalmers reactor the levels of H_2 was lower in the case of activated material with higher CO levels and lower CO_2 levels. The H_2/CO obtained through activation was 1.72 (compared to 2.4 in the case of activated material in the Chalmers reactor). The levels of CH_4 was slightly higher leading also to the conclusion of lower level of tar conversion if compared to the one observed at Chalmers.

It should again be pointed out that the comparison between the different parameters is made just to understand the interplay between them and has a more comparative than defined value. The measurement of the permanent gases in all four cases were illustrated on a van-Kevelen diagram (Figure 7).

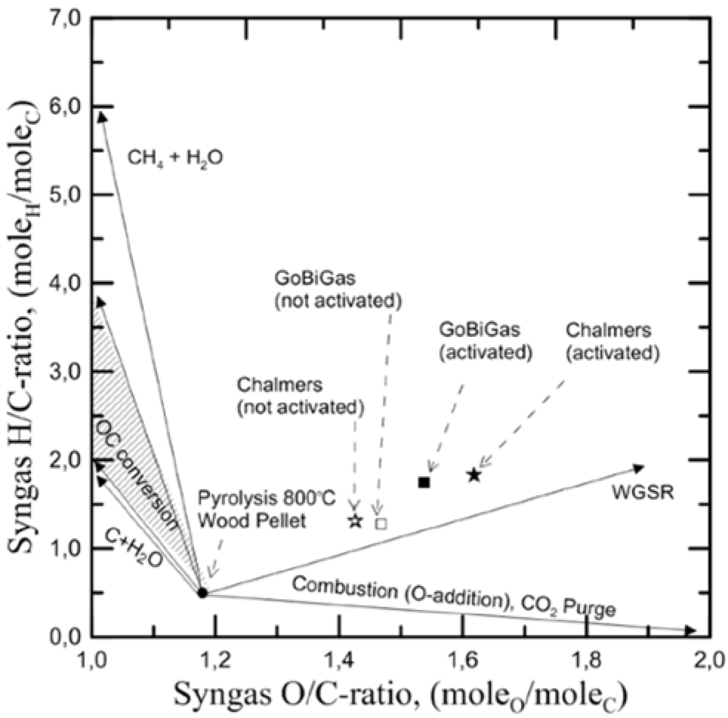

Figure 7. H/C ratio vs. O/C ratio with illustrated syngas composition from gasification exposures performed with and without activation at the Chalmers and GoBiGas (comparison with pyrolysis) (Larsson 2014).

From the diagram and the relative position of the composition of the product gas for the different experimental cases conclusions on the dominating reaction mechanism can be drawn. The position of the activated cases both in GoBiGas and Chalmers confirm the dominating influence of a combination of tar conversion and Water Gas Shift Reactions (WGSR). Furthermore, from the position of the experimental points over the WGSR vector a decrease in the loss-factor comparing to pyrolysis case (Larsson 2014) could be seen, where the materials can be ranged such as Chalmers (non-active) <GoBiGas(non-active) < GoBiGas(activated) < Chalmers (activated).

4.2.3 Chalmers case - bed material development

Figure 8 shows the cross-section micrographs of activated material sampled from the Chalmers gasifier.

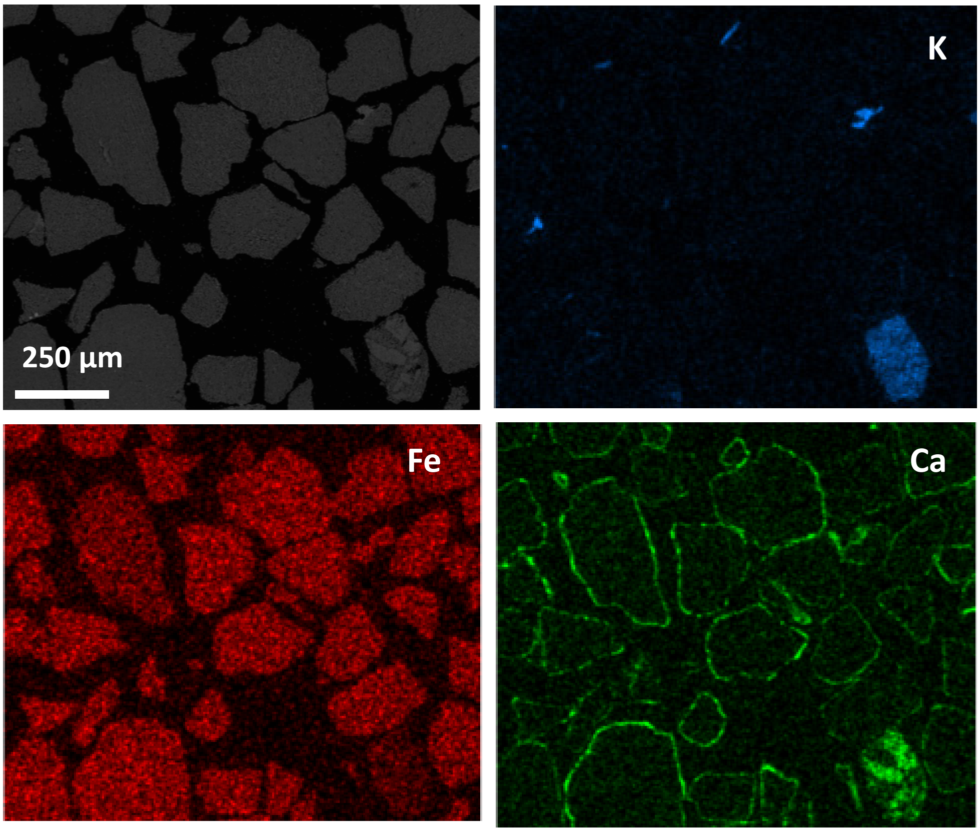

Figure 8. Cross-section of the activated material from Chalmers gasifier, cross-section micrograph (upper left), intensity elemental maps (down left and right) (Knutsson, Seemann et al. 2017).

From the intensity maps, an even Ca-layer can be observed around the bed material particles. Enrichments of K can also be seen in the images at locations with pure silica sand particles that have no relevance for the present study. No Fe-rich layer or Fe-enrichments are present.

Electron micrographs at higher magnifications, on the for the sample bed representative material particles, (Figure 9) confirm the build-up of a uniform layer around the particles. K-enrichments within the formed Ca-layer can be also detected in the EDS intensity maps.

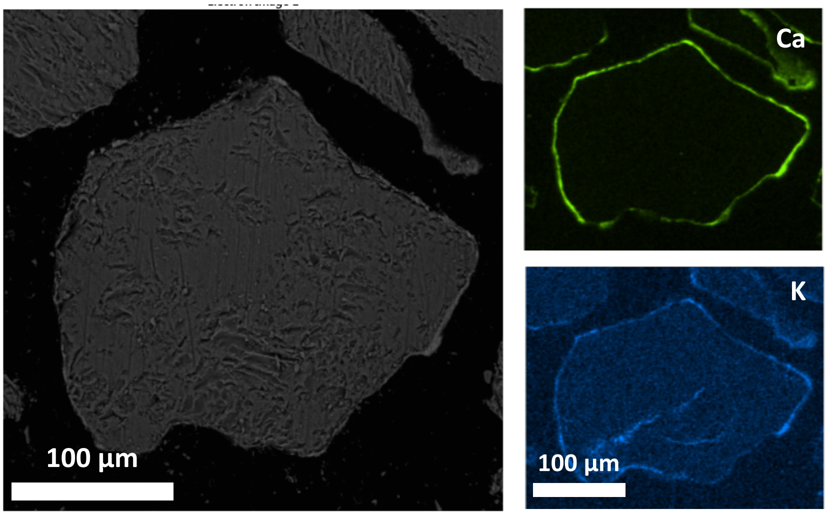

Figure 9. SEM micrographs of a cross-section of representative particle for the activated material in the Chalmers gasifier (left) and elemental intensity maps (right) (Knutsson, Seemann et al. 2017).

With the difference from the previously described cases of layer formation (Kirnbauer, Wilk et al. 2012, Kirnbauer and Hofbauer 2013) the formed Ca and K-enrichments were in the present case in the form of mixed layer rather than found in separate layers. EDS linescan confirmed that the concentration peaks of the two elements are situated at the same locations within the layer with Ca/K ratio of more than 10 (see Figure 10).

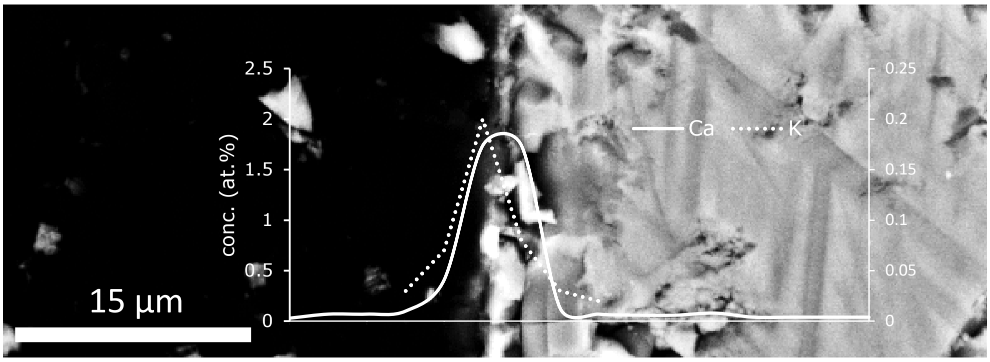

Figure 10. EDS linescan and a micrograph over a cross-section of an olivine showing Ca (left axis) and K (right axis) concentration (at. %) particle exposed to Chalmers gasifier (Knutsson, Seemann et al. 2017).

The layer formed upon activation is significantly thinner than those reported in the literature previously. The formed K, Ca – enrichments were under the detection limit (<5 wt. %) to be detected by an X-ray diffraction. However, on the taken diffractograms a similarity in crystal structure could be observed between the triggered activity observed in the Chalmers material and the unexposed material used in GoBiGas plant.

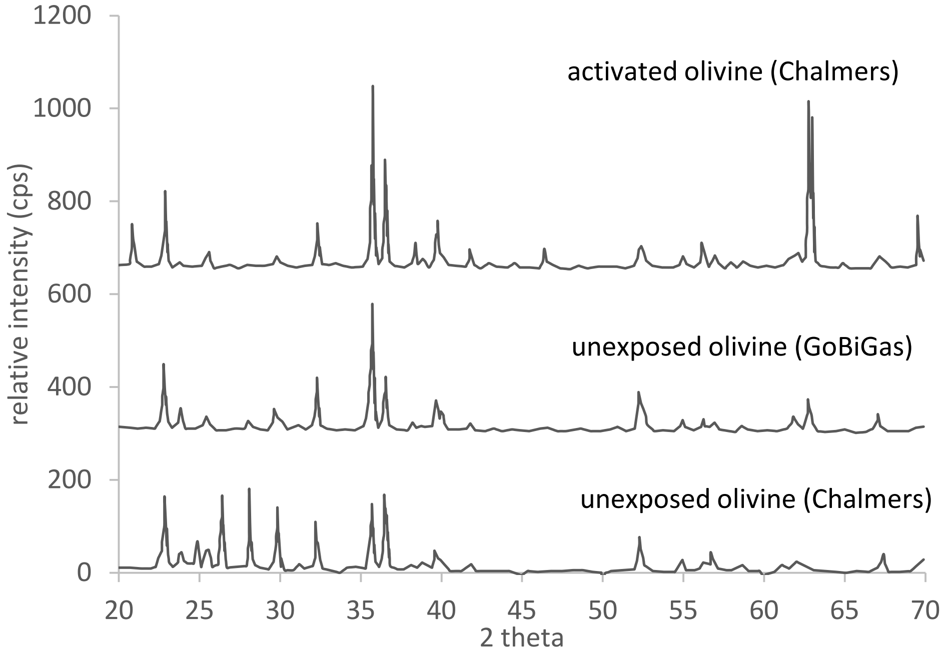

Figure 11. X-ray diffractograms of the unexposed olivine used in GoBiGas plant and Chalmers gasifier and the activated sample from Chalmers gasifier. Similar crystal structure between the exposed in the Chalmers gasifier sample and the calcined material used for GoBiGas (Knutsson, Seemann et al. 2017).

The observed comparability can be explained by similar changes in the olivine structures because of the exposure to high temperature conditions similar to the ones used for calcination. Furthermore, this observation suggests that upon continuous introduction of alkaline salt or other additives triggering catalytic activity similar effect could be expected.

4.2.4 GoBiGas case - bed material development

Figure 12 shows the cross-section micrographs of activated material sampled from GoBiGas.

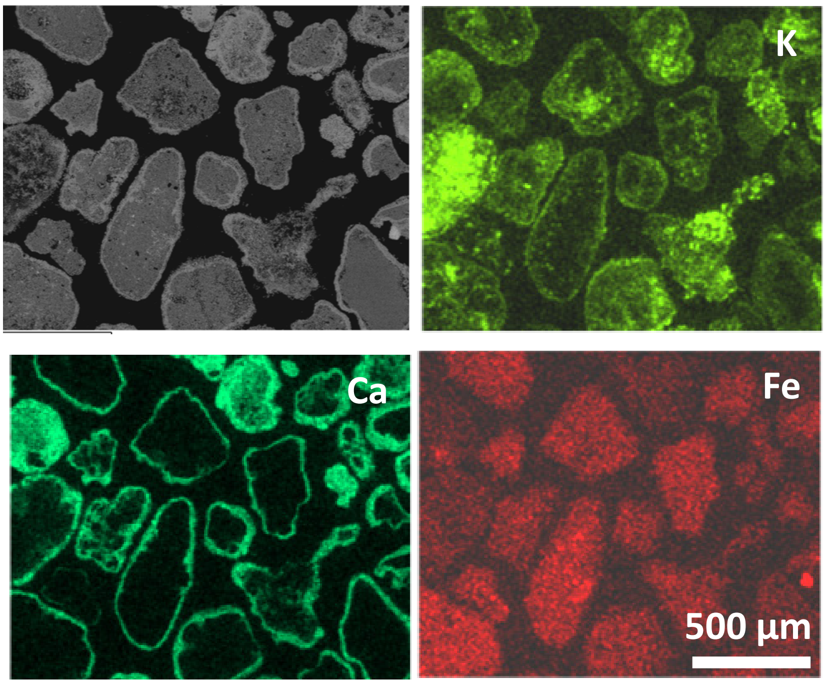

Figure 12. Cross-section of the activated material from GoBiGas, cross-section micrograph (upper left) and Fe, K, and Ca intensity elemental maps (down left and right) (Knutsson, Seemann et al. 2017)

Thicker layer is formed on the GoBiGas samples in comparison with the Chalmers gasifier case which can be seen in the micrographs of the particles cross-sections. Coating of Ca-layer around the particles is built. K-enrichments within the layer, but also in the particles can be detected. With the difference form the Chalmers case, Fe-rich locations can also be observed at several of the particles but no Fe-enrichments are present at any of the particles within the formed coating.

Thick layer consisting of two sub-layers can be distinguished in the electron micrographs at higher magnifications (Figure 13). The morphology is very similar to the one observed on olivine particles exposed in the Gussing plant in Austria where the same bed material was used (Kirnbauer and Hofbauer 2013). In the GoBiGas case, the inner sublayer is dense in consistency while the outer one is 4-6 times thicker and porous. It should be mentioned that the sampled particles have been in operation even before activation so with difference from the Chalmers activation case in GoBiGas case speculations about initial layer build-up can only be suggested but are rather difficult to confirm. Furthermore, all the detected changes and transformation in the morphology and chemical content can be indicative for the influence of the introduced additive.

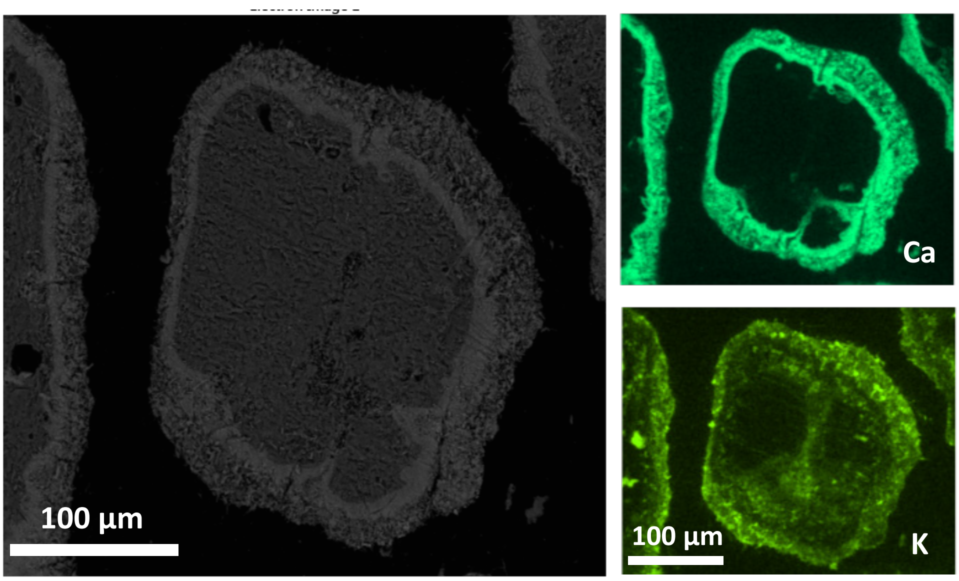

Figure 13. SEM micrographs of a cross-section of representative particle for the activated in GoBiGas material (left) and elemental intensity maps (right).

From the intensity maps, like the Chalmers case Ca and K are found in the coating formed around the particle. In the GoBiGas activated material, the formed K-enriched layer is not continuous as in the case of Chalmers gasifier. K-signal can be found predominantly in the outer layer but even within the core of the particle. The presence within the particle suggest an inward migration of K from the outer layer. Inward migration of K has been observed previously on ilmenite with a growth rate of 2 um/hour during the first 100 hours (Corcoran, Lind et al. 2017) . Ca-enrichments are found only on the outer side of the layer. Similar layer morphology has already been discussed when studying particles from Gussing, a plant with similar operation to GoBiGas (Kirnbauer and Hofbauer 2013, Kuba, Kirnbauer et al. 2017).

EDS linescan along the formed layer (Figure 14) indicates a Ca and K-enriched layer, with Ca/K ratio close to 5 which is half of the ratio observed in the case of the Chalmers activated bed material. From the performed EDS point analysis, it was found that the inner dense part of the layer was enriched in Ca which is in line with the observations of the initial formation of a $CaSiO_3$ layer on the particles (Kuba, Kirnbauer et al. 2017).

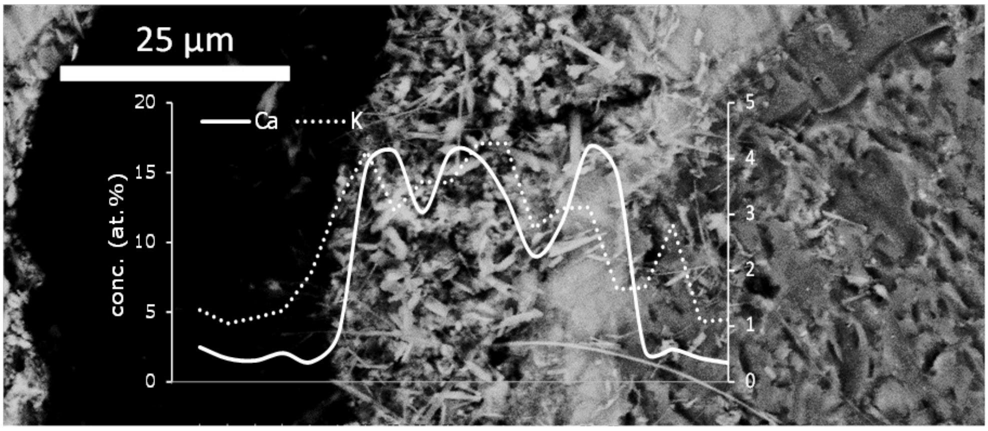

Figure 14. EDS line scan and a micrograph over a cross-section of an olivine particle exposed at GoBiGas (Knutsson, Seemann et al. 2017).

4.3 DEACTIVATED BED MATERIALS

Figure 15 shows the cross-section micrographs of bed materials from GoBiGas defined as deactivated based on Figure 3.

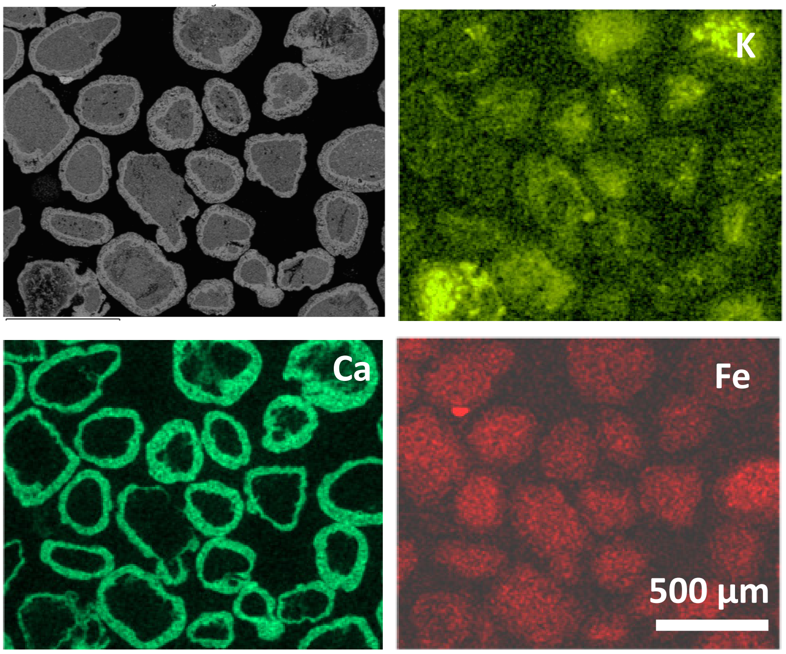

Figure 15. Cross-section of the deactivated material from GoBiGas, cross-section micrograph (upper left), intensity elemental maps of K ,Fe and Ca (down left and right) (Knutsson, Seemann et al. 2017)

Similar morphology as observed in the case of activated material from GoBiGas formed around the bed particle. The difference from the activated material was that the formed Ca-layer was thicker and the K was distributed in the core of the particle rather than in the layer. No Fe-segregations was detected on the particles.

The two distinct sublayers observed even in the case of activated material can be distinguished even more clear on micrographs at higher magnification (Figure 16).

It can be seen that the thickness of the formed coating was double as thick as the one present in the case of the activated material.

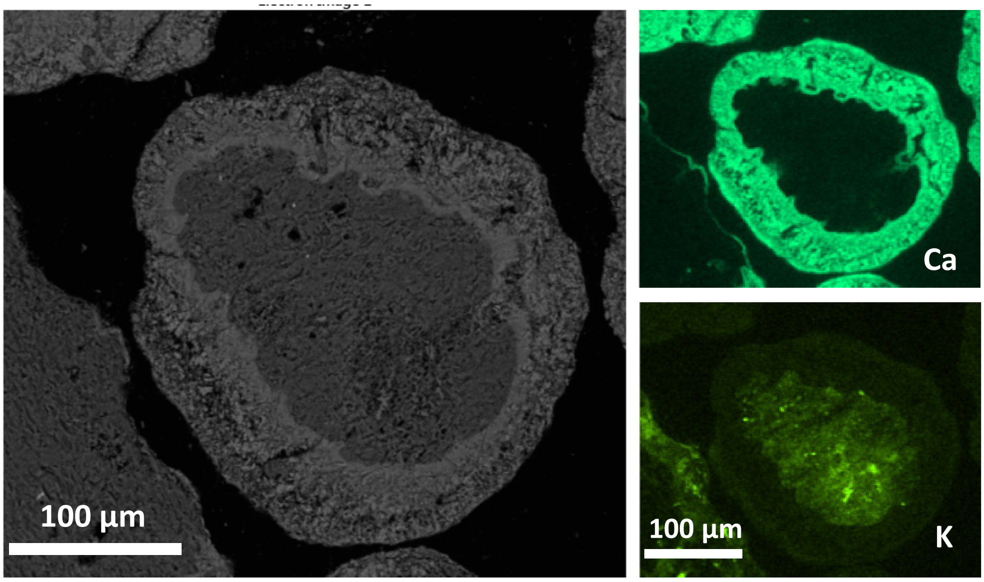

Figure 16. SEM micrographs of a cross-section of representative particle for the material deactivated in GoBiGas (left) and elemental intensity maps of Ca and K (right) (Knutsson, Seemann et al. 2017).

From the intensity elemental maps, it could be seen that K enrichments were absent at the outer layer and K-signal could be detected predominantly in the core of the particle. The observed increase in the thickness of the layer based on the maps taken could be almost entirely appointed to Ca-enrichments.

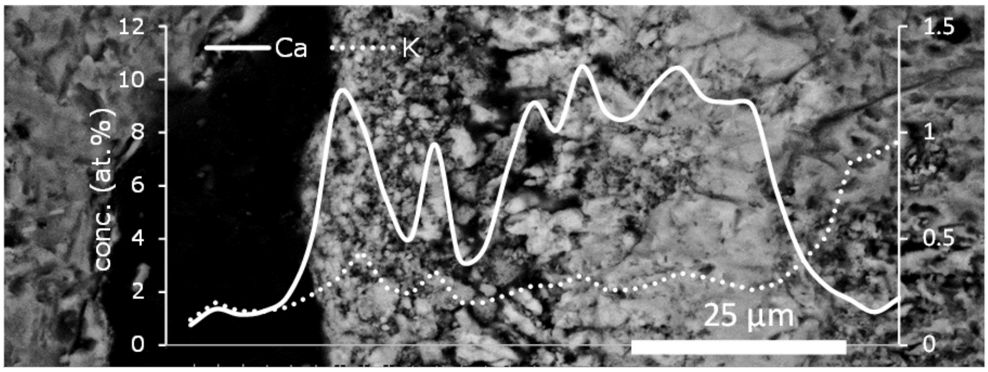

Figure 17. EDS linescan and a micrograph over a cross-section of deactivated olivine particle from GoBiGas showing Ca (left axis) and K (right axis) (Knutsson, Seemann et al. 2017).

The performed line-scan supported this hypothesis, where K was found only on the outermost part of the layer at a Ca/K ratio of 20 and diffused in the core of the particle (Figure 17). The low detected concentration of K in the formed layer can be explained with loss of K due to mechanical attrition or to the loss of K to the gasifier environment.

No crystal phases containing K could be found by XRD, which was expected if the K in the material is less than 5 wt. %. (Figure 18).

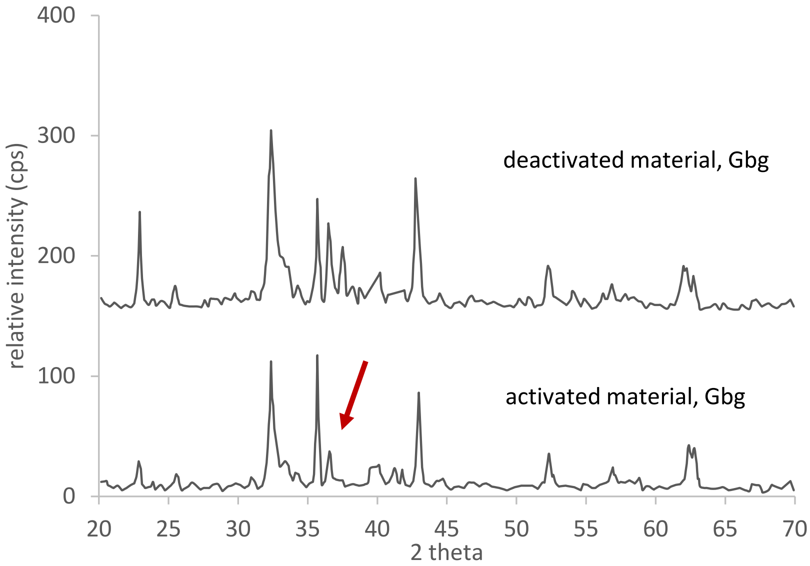

Figure 18. XRD diffractogram of activated and deactivated olivine from GoBiGas. Arrow pointing on the enstatite ($Ca_{0.025}Mg_{0.78}Fe_{0.2}SiO_3$) phase found in the case of activated olivine (Knutsson, Seemann et al. 2017)

XRD results pointed on the formation of enstatite ($Ca_{0.025}Mg_{0.78}Fe_{0.2}SiO_3$) along with calcium iron oxide ($CaFe_2O_4$) in the case of activated olivine but not in the case of deactivated material. Enstatite is a phase where Ca has partially substituted for Mg in the olivine structure.

Based on the additive used (K_2CO_3) and the observed activation because of it, K-species rather than Ca are expected to be responsible for the activation. In order to find in which form within the material K is active, the total amount of K along with its leachable fraction were followed (Figure 19).

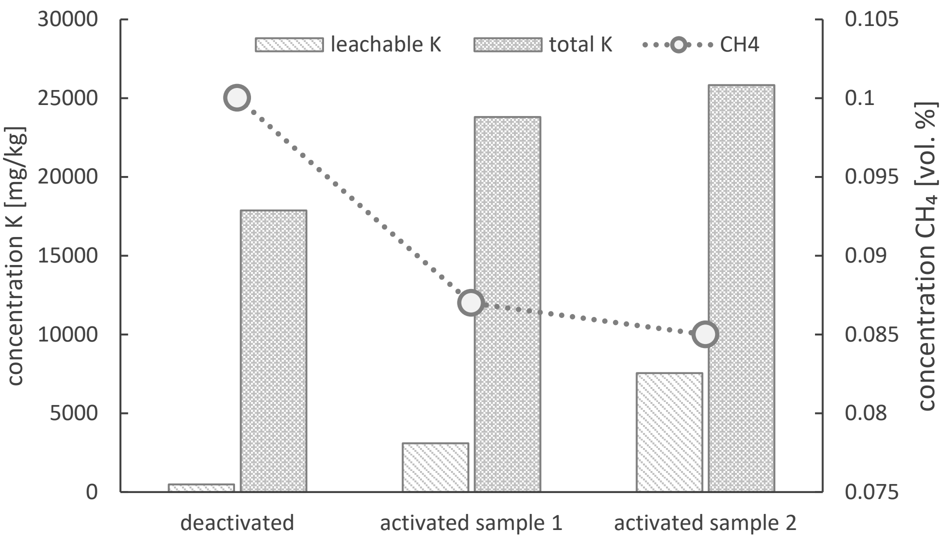

Figure 19. K concentration measured in activated and deactivated bed materials from GoBiGas – in form of total amount in the sample and leachable fraction. CH_4 concentration is used as indicative for activity (Knutsson, Seemann et al. 2017).

5 Conclusions

5.1 SUMMARY OF FINDINGS

Based on the findings from GoBiGas and the Chalmers gasifier it can be concluded that

- Fresh olivine can be activated of the alkali constituents of biomass upon exposure in the gasifier and can reach similar crystal structure as pre-calcined material
- The activation of material leads to an increase of the H2/CO ratio, where a ratio of up to 2.4 was reached with activated olivine. Introduced K-species are catalytic for the Water Gas Shift reaction and for the tar reforming.
- K-species are catalytically active only if they are near the particle/gas interface. In all the active materials K and Ca-enriched layers were formed. Deactivation of material was observed at K/Ca ratio of 20, which needs to be further investigated
- The leachable phase of K, rather than the total accumulated amount of K is responsible for material activation

5.2 POSSIBLE MECHANISM

Based on the findings from both units, the following mechanism can be indicated for forced activation of olivine (Figure 20).

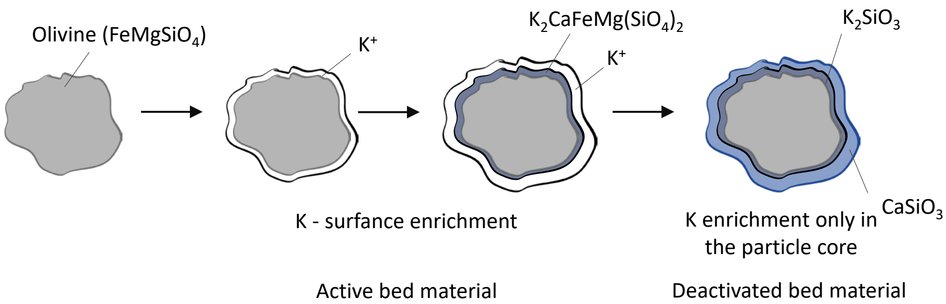

Figure 20. Mechanism of activation of olivine when K_2CO_3 is introduced as additives in the system (Knutsson, Seemann et al. 2017).

Upon addition of K_2CO_3, K, most probably as ions, are partially available in the gas phase where they are active for tar cracking and partially are deposited and interact with the bed material surface. The deposited K-containing species that are mobile - part of them can again participate in the gas phase and thus have catalytic role for tar reduction; part of the K-species interact with the bed material surface forming mixed silicates. The mobile fraction is represented by the leachable fraction of the bed material. With time, K diffuses inside the particle and is no longer available for the K-species (adsorbed) – K-species (gas) equilibrium reaction. With increased time of exposure and no new supply of K, K diffuses into the bulk of the particles and the bed material becomes deactivated.

6 References

Amenomiya, Y. and G. Pleizier (1982). "Alkali-promoted alumina catalysts." Journal of Catalysis **76**(2): 345-353.

Anis, S. and Z. A. Zainal (2011). "Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review." Renewable and Sustainable Energy Reviews **15**(5): 2355-2377.

Berdugo Vilches, T., et al. (2016). "Comparing Active Bed Materials in a Dual Fluidized Bed Biomass Gasifier: Olivine, Bauxite, Quartz-Sand, and Ilmenite." Energy and Fuels **30**(6): 4848-4857.

Bryers, R. W. (1996). "Fireside slagging, fouling, and high-temperature corrosion of heat-transfer surface due to impurities in steam-raising fuels." Progress in Energy and Combustion Science **22**(1): 29-120.

Corcoran, A., et al. (2017). "Mechanism for diffusion and layer growth of biomass ash elements on ilmenite used for oxygen carrier aided combustion."

Courson, C., et al. (2002). "Hydrogen production from biomass gasification on nickel catalysts: Tests for dry reforming of methane." Catalysis Today **76**(1): 75-86.

Dayton, D. (2002). Review of the Literature on Catalytic Biomass Tar Destruction: Milestone Completion Report. Other Information: PBD: 1 Dec 2002**:** Medium: ED; Size: 33 pages.

Devi, L., et al. (2003). "A review of the primary measures for tar elimination in biomass gasification processes." Biomass and Bioenergy **24**(2): 125-140.

Devi, L., et al. (2005). "Pretreated olivine as tar removal catalyst for biomass gasifiers: Investigation using naphthalene as model biomass tar." Fuel Processing Technology **86**(6): 707-730.

Devi, L., et al. (2005). "Catalytic decomposition of biomass tars: Use of dolomite and untreated olivine." Renewable Energy **30**(4): 565-587.

Elliott, D. C. and E. G. Baker (1986). "The effect of catalysis on wood-gasification tar composition." Biomass **9**(3): 195-203.

Fahmi, R., et al. (2007). "The effect of alkali metals on combustion and pyrolysis of Lolium and Festuca grasses, switchgrass and willow." Fuel **86**(10): 1560-1569.

Grootjes, A. J., et al. Improved Gasifier availability with bed material and additives C. a. E. R. ECN Biomass.

Han, J. and H. Kim (2008). "The reduction and control technology of tar during biomass gasification/pyrolysis: An overview." Renewable and Sustainable Energy Reviews **12**(2): 397-416.

Hansen, L. A., et al. (2000). "Influence of deposit formation on corrosion at a straw-fired boiler." Fuel Processing Technology **64**(1): 189-209.

Israelsson, M., et al. (2013). "Assessment of the solid-phase adsorption method for sampling biomass-derived tar in industrial environments." Energy & Fuels **27**(12): 7569-7578.

Kern, S., et al. (2013). "Reactivity tests of the water–gas shift reaction on fresh and used fluidized bed materials from industrial DFB biomass gasifiers." Biomass and Bioenergy **55**: 227-233.

Kirnbauer, F. and H. Hofbauer (2013). "The mechanism of bed material coating in dual fluidized bed biomass steam gasification plants and its impact on plant optimization." Powder Technology **245**(0): 94-104.

Kirnbauer, F., et al. (2012). "The positive effects of bed material coating on tar reduction in a dual fluidized bed gasifier." Fuel **95**: 553-562.

Knutsson, P. and C. Linderholm (2015). "Characterization of ilmenite used as oxygen carrier in a 100 kW chemical-looping combustor for solid fuels." Applied Energy **157**: 368-373.

Knutsson, P., et al. (2017). "Use of K_2CO_3 for the forced activation of Olivine." Fuel **Submitted**.

Kuba, M., et al. (2016). "Influence of bed material coatings on the water-gas-shift reaction and steam reforming of toluene as tar model compound of biomass gasification." Biomass and Bioenergy **89**: 40-49.

Kuba, M., Havlik, F., Kirnbauer, F., Hofbauer, H. (2015). Investigations on the Catalytic Activity of Bed Material Coating Regarding the Water-Gas-Shift Reaction and Steam Reforming of Model Compounds for Lighter and Heavier Hydrocarbons. 23rd European Biomass Conference and Exhibition. Vienna**:** 562 - 567.

Kuba, M., et al. (2017). "Influence of coated olivine on the conversion of intermediate products from decomposition of biomass tars during gasification." Biomass Conversion and Biorefinery **7**(1): 11-21.

Larsson, A. (2014). Fuel conversion in a dual fluidized bed gasifier, Chalmers University of Technology.

Larsson, A., et al. (2015). Monitoring the Bed Material Activation in the GoBiGas-Gasifier. Conference procedures Nordic Flame days.

Larsson, A., et al. (2013). "Evaluation of performance of industrial-scale dual fluidized bed gasifiers using the chalmers 2–4-MWth gasifier." Energy & Fuels **27**(11): 6665-6680.

Lee, S. W., et al. (2000). "The Effect of Na2CO3 on the Catalytic Gasification of Rice Straw over Nickel Catalysts Supported on Kieselguhr." Korean Journal of Chemical Engineering **17**(2): 174-178.

Li, T.-c., et al. (1996). "Study on gasification of peat and its kinetic behavior." Fuel Science and Technology International **14**(7): 879-896.

Lizzio, A. A. and L. R. Radovic (1991). "Transient kinetics study of catalytic char gasification in carbon dioxide." Industrial and Engineering Chemistry Research **30**(8): 1735-1744.

Lutgens, F. K. and E. J. Tarbuck (2003). Essentials of Geology, Prentice Hall.

Marinkovic, J. (2016). Choice of bed material: a critical parameter in the optimization of dual fluidized bed systems, Chalmers University of Technology.

Marinkovic, J., et al. (2016). "Impact of Biomass Ash–Bauxite Bed Interactions on an Indirect Biomass Gasifier." Energy & Fuels **30**(5): 4044-4052.

McKee, D. W. and D. Chatterji (1975). "The catalytic behavior of alkali metal carbonates and oxides in graphite oxidation reactions." Carbon **13**(5): 381-390.

Milne, T. A., et al. (1998). Biomass gasifier" tars": their nature, formation, and conversion, National Renewable Energy Laboratory Golden, CO.

Milne, T. A., et al. (1999). Biomass Gasifier "tars": Their Nature, Formation, and Conversion, National Renewable Energy Laboratory.

Orío, A., et al. (1997). "Performance of Different Dolomites on Hot Raw Gas Cleaning from Biomass Gasification with Air." Industrial and Engineering Chemistry Research **36**(9): 3800-3808.

Padban, N. (2000). PFB Air Gasification of Biomass, Investigation of Product Formation and Problematic Issues Related to Ammonia, Tar and Alkali.

Padban, N. (2000). PFB Air gasification of biomass, investigation of product formation and problematic issues related to ammonia, tar and alkali, Ingemar Odenbrand, Department of Chemical Engineering II, Lund University.

Rapagnà, S., et al. (2000). "Steam-gasification of biomass in a fluidised-bed of olivine particles." Biomass and Bioenergy **19**(3): 187-197.

Rauch, R., et al. (2004). "Comparison of different olivines for biomass steam gasification." Proc Conf Science in Thermal and Chemical Biomass Conversion, Victoria, Canada Conference.

Seshadri, K. S. and A. Shamsi (1998). "Effects of Temperature, Pressure, and Carrier Gas on the Cracking of Coal Tar over a Char−Dolomite Mixture and Calcined Dolomite in a Fixed-Bed Reactor." Industrial & Engineering Chemistry Research **37**(10): 3830-3837.

Simell, P. A., et al. (1992). "Catalytic purification of tarry fuel gas with carbonate rocks and ferrous materials." Fuel **71**(2): 211-218.

Sutton, D., et al. (2001). "Review of literature on catalysts for biomass gasification." Fuel Processing Technology **73**(3): 155-173.

Suzuki, T., et al. (1992). "Alkali metal catalyzed carbon dioxide gasification of carbon." Energy & Fuels **6**(4): 343-351.

T., L. (1999). Ash formation in circulating fluidised bed combustion of coal and solid biomass. VTT Research Centre of Finland.

Tunå, P., et al. (2010). Modeling of Reverse Flow Partial Oxidation Process for Gasifier Product Gas Upgrading. International Conference on Thermal Engineering:Theory and Applications 2010. Marrakesh, Morroco, International Conference on Thermal Engineering.

Energiforsk

Wen, W. Y. and E. Cain (1984). "Catalytic pyrolysis of a coal tar in a fixed-bed reactor." Industrial & Engineering Chemistry Process Design and Development **23**(4): 627-637.

Wen, Y.-W. (1983). Thermal and Catalytic Cracking of Tars and Tar Constituents from Coal Gasification Processes. DOE/MC/14385-1484. Massachusetts Clark University

Yuh, S. J. and E. Wolf (1983). "FTIR studies of potassium catalyst-treated gasified coal chars and carbons." Fuel **62**(2): 252-255.

Zhang, Y., et al. (2014). "Potassium catalytic hydrogen production in sorption enhanced gasification of biomass with steam." international journal of hydrogen energy **39**(9): 4234-4243.

Zwart, R. W. R. (2009). Gas cleaning downstream biomass gasification – status report 2009.

CHOICE OF SUITABLE ADDITIVES AND DESIGN OF ACTIVATION PROCEDURE FOR OLIVINE

During biomass gasification biomass is transformed into product gas that can be further used as fuel in the transport sector, for heat and electricity production or as a resource for chemical synthesis. The gasification process can be made more energy efficient if the procedure used for activation of the bed material (olivine) in the gasifier is simplified.

The present study was performed in two units – the Chalmers gasifier and the GoBiGas units. The effect of K_2CO_3, used as additive, was followed by measuring the tar levels and monitoring the gas content of the product gas. Bed material from both units was sampled under chosen conditions and characterized by leaching and SEM-EDS and XRD.

The results show that addition of K_2CO_3 to the process can provoke immediate response and improve the gas quality.