ALKALI-FELDSPAR AS CATALYST FOR UPGRADING ENERGY GAS FROM BIOMASS GASIFICATION

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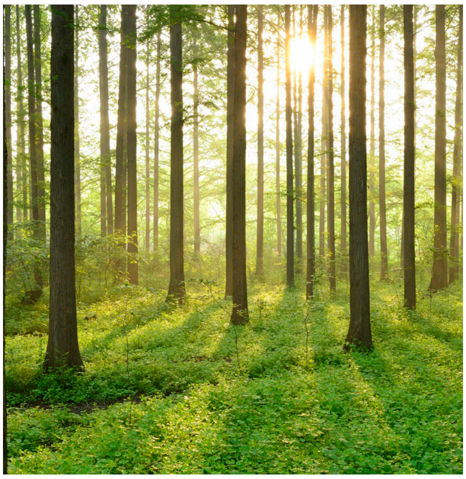

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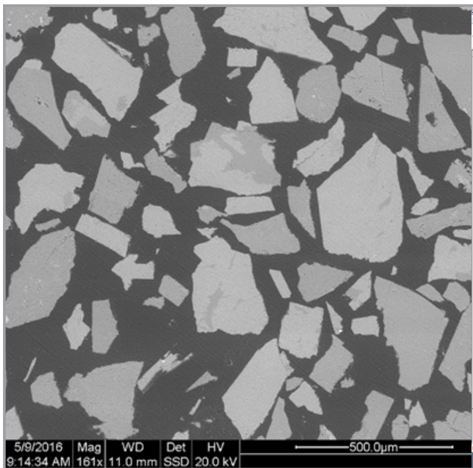

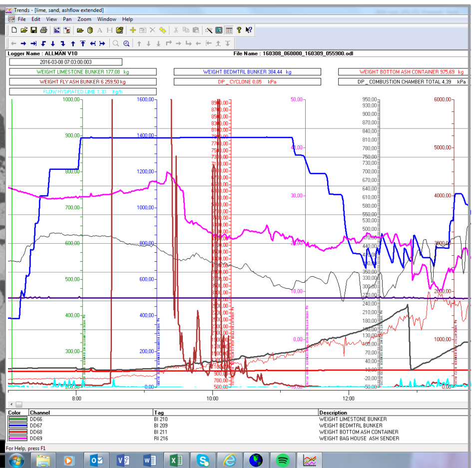

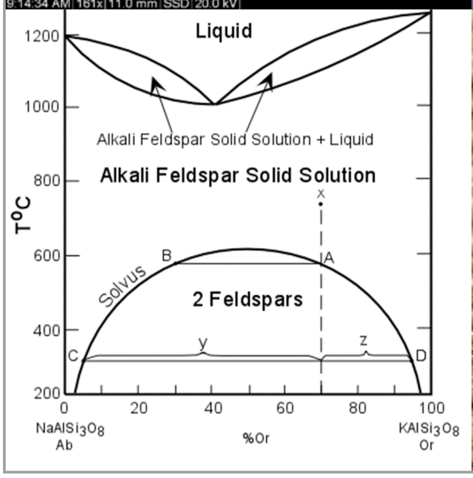

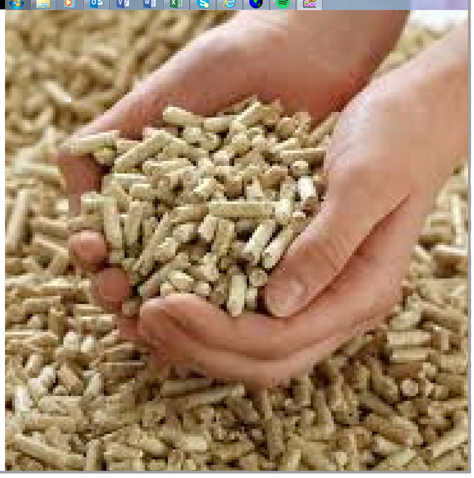

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Alkali-Feldspar as Catalyst for Upgrading Energy Gas from Biomass Gasification

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Authors' foreword

This project evaluated the use of an alkali-feldspar as alternative bed material in the production of energy gas through indirect gasification of biomass.

The report has been produced by Chalmers University of Technology and the authors are Nicolas Berguerand, Teresa Berdugo Vilches and Sebastien Pissot.

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We would also like to thank SIBELCO Nordic AB for in-kind delivery of the bed material used in the experiments and being our industrial partner in this project. This work was also made possible by financial support from the Swedish Gasification Centre (SFC). Operation of the gasifier was supported by Göteborg Energi, Valmet, Akademiska Hus, and the Swedish Energy Agency (Energimyndigheten).

The authors thank research engineer Johannes Öhlin for his help during experiments. Special thanks to research engineer Jessica Bohwalli for the assistance in analyzing the SPA samples for tar quantification and preparing the bed samples for SEM-EDX characterization.

Sammanfattning

Detta projekt bidrar till forskningen kring katalytiska bäddmaterial för gasrening i samband med indirekt förgasning av biomassa. Som adekvat katalysator till uppgradering av energigaser efterfrågar man ett billigt material som inte innehåller giftiga och miljöfarliga ämnen, som har en hög aktivitet för tjärnedbrytning, inte transporterar syre och lämpar sig till fluidbäddsförhållande. Här var idén att introducera en i detta sammanhang ny naturligt förekommande malm i form av en alkali-fältspat (K, Na) $AlSi_3O_8$; ett material som uppfyller ovanstående kriterier och har visat sig högst lovande i en förstudie. I projektet föreslogs att använda fältspat i den unika semi-industriella Chalmers förgasare som erbjuder möjligheten att i detalj och storskaligt utvärdera bäddmaterialets prestanda. Huvudmålen i projektet var att i) bevisa att man framgångsrikt kan använda alkali-fältspat som alternativt bäddmaterial till exempelvis olivin och följa upp effekten av bäddåldrande på gassammansättningen hos den producerade rågasen utan bäddregenerering ii) att undersöka påverkan av varierande driftparametrar på förgasarens prestanda och ge ledtråd om hur förgasningsprocessen kan optimeras.

Utifrån resultaten av den experimentella kampanjen kunde bevisas att fältspaten lämpar sig som bäddmaterial i en indirekt förgasare. Den tål alltså fluidbäddförhållande under höga temperaturer (upp till 900 °C) och växlande redox gasatmosfärer. Materialet har visat en stark aktivitet på vattengas-skiften och för reformering av kolväten, bl.a. tjära. Under de första 4 dagar bevittnades en ökande aktivitet gentemot dessa för att till slut nå höga halter av H_2 och lägre halter av CO och tjära. Generellt så blev gaskvalitén jämförbar med den hos aktiverad olivin eller bauxit undersökta i samma förgasare. En mycket trolig förklaring av aktiviteten hittades m.h.a. EDX analys av partiklar samlade under första veckan där ett askpåslag runt partiklarna hade bildats under tiden i loopen. Påslaget innehåller främst Ca, Mg, K and Na d.v.s. alkali-metaller/jordartsmetaller från biomassabränslet. Efter ytterligare tre dagar under panndrift och exponering för bränsleaskan hade fältspaten fått förmågan att transportera syre från pannan till förgasaren. EDX analysen pekar på att det kan vara relaterat till S och Fe som slagit på partiklarnas yta ovanpå det initiala inre skalet, även om de flesta ämnena i påslaget också kan bidra till syretransport, som oxider eller sulfater/sulfider. Denna aspekt visar att en rimlig/optimal nivå av bäddomsättning skulle kunna leda till gynnsamma förhållanden för förgasaren och en annan kan erhålla möjligheten att förbättra bränsleomvandlingen i pannan genom en utökad syretillgänglighet genom dess geometri.

Slutligen, variationer i driftparametrar hos förgasaren har visat att högre ration i ånga/bränsle och högre förgasartemperatur gynnar gaskvalitén, speciellt vätgasproduktionen, och reducerar tjärhalten i rågasen. Dock är denna uppnådda positiva effekt någorlunda begränsad i förhållande till de stora driftändringar som infördes. Regenerering av bäddmaterialet under dagen och förgasardrift resulterar i en lägre aktivitetsgrad hos fältspaten genom utspädning med färskt icke-aktivt material och motsvarar effekten bevittnad under nattregenerering då endast pannan är bränslematad.

Överlag har projektet etablerat alkali-fältspat som ett lämpligt bäddmaterial i indirekt förgasning av biomassa och alltså som ett intressant alternativ till referensmaterialet olivinsand i detta sammanhang.

Summary

The present project contributes to research on catalytic bed materials for gas cleaning in the context of biomass indirect gasification. Appropriate catalysts for gas upgrading should be cheap, have high mechanical stability, not contain hazardous compounds, present a high activity towards tars, not possess the ability to transport oxygen and should be resistant to fluidized bed conditions. Here, the idea was to introduce a new material in this application, namely a naturally occurring alkali-feldspar (K, Na) $AlSi_3O_8$. This ore fulfills the aforementioned properties and was proven as highly promising in a pre-study. In the project, this material was introduced as bed material in the unique semi-industrial Chalmers indirect gasifier, giving the possibility to thoroughly scrutinize its behavior in larger scale. The principal goals of the project were i) to show that one can successfully use the alkali-feldspar as an alternative to e.g. olivine and observe the time-on-stream effect of the bed material on the raw gas composition without regeneration ii) to investigate the influence of changes in operating conditions on the gasifier performance to provide guidance for process optimization.

From the results of the experimental campaign, one could prove that feldspar is an adequate bed material for use in indirect gasification of biomass. It could withstand longer fluidization durations under high temperature and alternating redox atmospheres. Experiments established its high potential for water-gas shift and for reforming of higher hydrocarbons, in particular tars. This activity was gained through time-on-stream in the loop and the gas composition shifted towards higher levels of H_2 and lower levels of CO and tars during the first 4 days without any bed regeneration. The yields for these species were comparable to those obtained with e.g. activated olivine or bauxite in the same unit. The main explanation to the increase of catalytic activity during the first 4 days of operation is related to the formation of active ash layers consisting of principally Ca, Mg, K and Na originating from the fuel ash. This was evidenced by EDX material characterization of collected bed samples. After an additional 3 days without regeneration but only under boiler operation, the feldspar showed a capacity to transport oxygen from the boiler to the gasifier. EDX mapping indicates this could be related to the presence of S and Fe that deposited on the particles surface on top of the initial inner layer, although most of the species present in the layer can to some extent induce oxygen transport, either as oxides or sulfates/sulfides. This aspect also opens up the possibility to improve fuel conversion in the boiler through an increased access and distribution of oxygen carried by the material over the boiler geometry.

Lastly, experiments involving changes in operating parameters for the gasifier confirmed that higher steam-to-fuel ratios and gasifier temperature induce better gas qualities, in particular higher yields of hydrogen and somewhat lower tars. However, the overall gains were rather limited compared to the amplitude in operation changes. Regeneration of bed material during day time lowers the total feldspar activity by diluting particles of different activity levels with fully inactive fresh material. The observed effect is close to that obtained when regenerating bed material night time when only the boiler is fueled.

Overall, this project has shown that the alkali-feldspar is a suitable bed material in indirect gasification of biomass and thus an interesting alternative to e.g. olivine sand in this application.

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1 Background

1.1 BIOMASS GASIFICATION AND THE TAR PROBLEM

During the gasification of biomass, in addition to the valuable raw gas, undesired species are produced such as particulate matter, inorganics or tars. Tars are condensable organic compounds stretching from oxygenated products to heavy deoxygenated hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) and their occurrence in the raw gas is highly problematic [1]. Indeed, the largest species such as pyrene have due points around 400°C. This means that blockage of equipment after the gasifier due to tar condensation is not uncommon in industrial applications and is associated with process failure. The total tar yields and variation in species is dependent upon the gasifier design, the feedstock and the operating conditions (temperature, residence time, etc.). These should be designed to minimize the formation of tars but, inevitably, some amounts will be present in the raw gas. Generally, with increasing severity (temperature and residence time), the tar yield is shifted from lighter primary oxygenated tars towards heavier deoxygenated secondary and tertiary tars [2]. Different strategies have been investigated to eliminate or lower their levels in the product gas. Primary measures are based on the use of active bed materials inside the gasifier chamber where tars are converted into lighter and valuable molecules that do not condense downstream [3]. Though proven efficient in reducing the tar levels, these are often insufficient and require additional actions hence adding to cost and complexity. Secondary measures designate solutions for gas cleaning placed downstream the gasifier vessel. These can be purely physical such as scrubbing using an adequate solvent, thermal by inducing high temperatures (1100-1300°C) to break the larger hydrocarbons or catalytic using active materials in the same manner as in primary measures [1, 2, 4]. Catalytic processes are more energy efficient as they allow lower temperature operation (700-900°C) than the thermal approach and do not consume any costly solvent nor excessively cool down the producer gas [4, 5]. Subsequently, in a secondary measure, they enable the thermal integration of the gas upgrading step with the gasifier exit temperature [6]. Optimally, the use of active bed materials in primary measures - even not fully sufficient - should minimize the burden on and simplify the design of the secondary cleaning step. This report encompasses catalytic processes for gas upgrading in the context of indirect gasification of biomass.

1.2 INDIRECT GASIFICATION

The process of indirect gasification is schematized in Fig 1. It has been presented by other authors, e.g. in [7, 8].

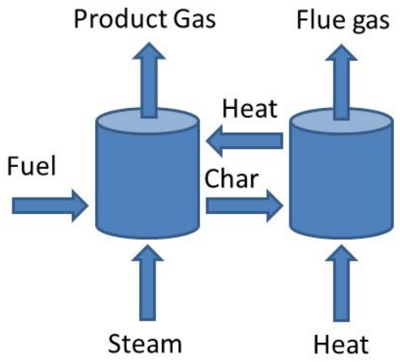


Figure 1: The indirect gasification process

To the left, the fuel is fed into the gasifier which is fluidized with steam, where the heat for the gasification is provided by the bed material. There, the biomass fuel devolatilizes and the char is partly gasified. As mentioned earlier, in primary tar measures, the bed material can also show catalytic properties towards e.g. reforming of tars in the producer gas. This gas exits the gasifier and is led further to the downstream gas conditioning and upgrading stages, e.g. scrubber, shift reactor, methanation reaction etc. Meanwhile, the bed material and the unreacted char enter the combustion reactor where the char is burned to heat up the bed material prior its recirculation to the gasifier. This loop-configuration also permits transport of important species such as K from the boiler to the gasifier where it enhances the reactions [9].

1.3 CATALYSTS

The key factor in the successful installation of any fluidized bed catalytic process is the appropriate choice of catalytic bed material. The material must be capable of handling the severe mechanical conditions during fluidization, as well as exposure to ash and noxious gas environments, e.g., sulfur, chlorine or phosphorus poisoning and deactivation by trace elements [10]. Inevitably, bed regeneration and catalyst replacement will be required. This means that the bed material must:

(i) be inexpensive;
(ii) be utilizable in a fluidized bed;
(iii) have a weak propensity to agglomerate;
(iv) provide sufficient catalytic activity; and
(v) not create hazardous waste.

Traditionally, to satisfy (i) and to some extent (v), naturally occurring and abundant ores have been preferred over manufactured particles. To fulfil (ii), the bed material must exhibit sufficient hardness to resist excessive attrition. Criterion (iii) is not solely reliant on the composition of the catalyst, but is also highly dependent upon the formation of an ash layer on the surface and the composition of the ash [11-13]. For (iv), the catalyst should have strong abilities to reform tars and possibly other potentially problematic hydrocarbons, such as paraffins, olefins, and alkynes, within the prevailing temperature range. These reactions should preferably not have any deleterious effects on any of the valuable permanent gas molecules. For criterion (v), one must ensure that the deposition of spent catalyst is not jeopardized by the presence of hazardous trace elements in the particle structure that could leach into the soil. These trace elements can be present in the virgin material and their mobility may be increased or they may accumulate during the time spent on-stream within the facility.

For both primary and secondary catalytic measures, most of the research has been dedicated to metal-based materials. Examples include oxides of iron, nickel, magnesium, aluminum and manganese [4, 14-16]. Olivine, an iron-magnesium silicate, is for instance the bed material chosen for the indirect gasifiers in Güssing and GoBiGas [17, 18]. It has been proposed that, through an efficient uptake and release of alkali from the fuel, olivine and bauxite have displayed a high capacity to reduce the tars in the producer gas [ref to Jelena's thesis].

The presence of alkali-salts in the biomass fuel or their addition to the bed inventory are also known to enhance the conversion of hydrocarbon and char [19, 20]. On the other hand, fuel potassium, especially, can be involved in chemical and physical mechanisms leading to corrosion issues (e.g. potassium chloride), deposition (potassium sulfate) on heat transfer surfaces or agglomeration of bed material due to ash melting (formation of potassium silicate in presence of silicon in the fuel) [9, 21].

Finally, the metal content of the aforementioned oxides is also synonym with a certain propensity to oxidize in the boiler or regeneration vessel to the gasifier or gas upgrading vessel where a fraction of the raw gas is combusted. Besides, olivine contains noxious species such as nickel in non-negligible amounts [11]. Oxygen transport was also observed with ilmenite, an iron-titanium oxide successful in reducing the tars but at the expense of the raw gas heating value produced from the Chalmers gasifier [6]. Contrarily, in another investigation, ilmenite showed appealing properties in enhancing fuel conversion in the boiler and minimizing emissions of e.g. NO_x and CO [22].

In all, from a gasifier point of view, it is crucial to search for alternative bed materials that exhibit a high activity in purifying a tarry fuel gas without transporting oxygen or containing health or environment unfriendly constituents. It is also important to follow the change in gasifier performance in terms of producer gas quality resulting from bed material exposure to ash-forming elements in the fuel and the possibility to release inorganics in the gas phase and enhance gas upgrading.

The present investigation pertains the use of an alkali-feldspar as a primary measure for gas upgrading and was inspired by the benefits observed from this material as a secondary measure in an earlier work by Berguerand et al. [23].

1.4 PRE-STUDY WITH ALKALI-FELDSPAR

Alkali-feldspars are tectosilicates with the general formula [(K, Na) $AlSi_3O_8$]. The quasi-absence of metals in the composition (that would lead to oxygen transport), the inherent load in K (and Na) usually promoting hydrocarbon decomposition and the fact this is a silicate as olivine or zeolites in Fluid Catalytic Cracking (FCC) made it an interesting candidate catalyst for raw gas upgrading. Experiments reported in [23] where conducted using a bubbling-bed of feldspar fluidized with a slip-stream of raw gas from the Chalmers gasifier, i.e. in a secondary measure. From this work, the following conclusions were drawn:

1. The alkali-feldspar has a strong potential to shift the gas composition to advantageous H_2/CO ratios for methanation (~ 3).
2. The methane levels in the reformed gas were unaffected.
3. Most of C_2H_2 and C_3H_6 were eliminated at the temperature of 800°C. This was complete at 900°C.
4. A strong selectivity on tar reforming was observed, yielding a reformed gas liberated from all branched tar species and containing pure ring molecules. The total tar reforming capacity was even higher than for fresh olivine in the same reactor.
5. The feldspar was able to withstand longer fluidization periods in harsh reducing conditions without any sign of agglomeration or deactivation.

Taken together, these results clearly suggested that the feldspar could also show some activity on the raw gas in a primary upgrading configuration. This formed the incentive of this project, the base of which consisted in the introduction of this material in the semi-industrial Chalmers indirect gasifier (2-4 MW) to thoroughly scrutinize its behavior in larger scale.

The specific goals of the present investigation were thus:

I. To follow the ageing process of the feldspar bed material in an indirect gasification loop and the consequences of time-on-stream on the bed characteristics and associated impact on raw gas quality

II. To assess the performance of this material under varying operating conditions such as gasifier temperature and fuel-to-steam ratio to give hints on process optimization

2 Experimental

2.1 CHALMERS INDIRECT GASIFIER

The Chalmers indirect gasifier is schematized in Fig. 2 and has been detailed elsewhere [24, 25]. "1" represents the 12 MW boiler designed as a CFB fluidized with air where wood chips are fed and the combustion reactions produce heat which is partly transferred to the circulating bed material that is further led to the 2-4 MW gasifier "11". This heat together with the steam used as fluidizing agent enable the wood pellets fed in the gasifier to devolatilize and the remaining char to some extent be gasified.

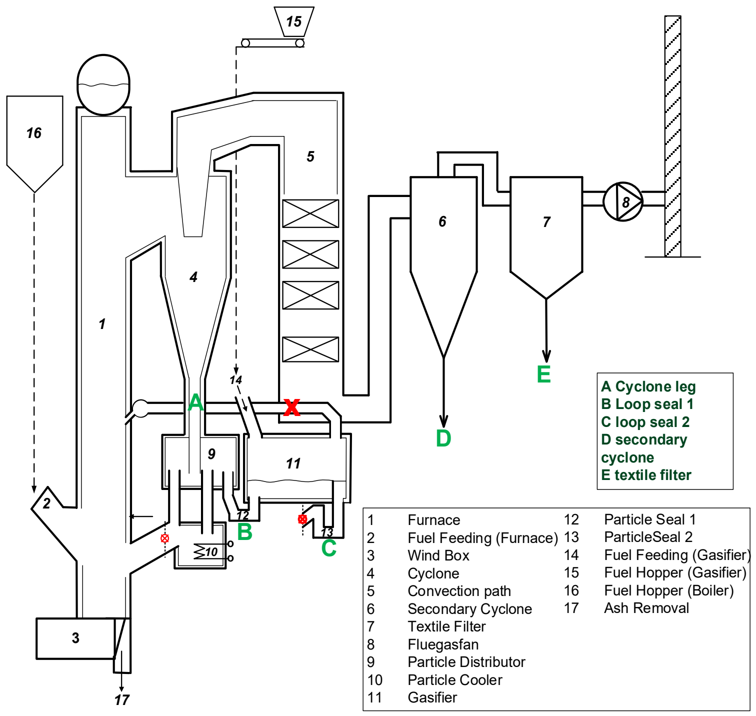


Figure 2. Schematic of the Chalmers Dual Fluidized Bed System. The red X corresponds to the sampling point, while the red circles represent connection points between Loop seal 2 and the down-comer to the boiler.

The boiler is fueled day and night while the gasifier only during day time when research is conducted and staff operating the boiler (Akademiska Hus) is available (between 6 am to 6 pm). Note that the gasifier keeps its temperature since the solids circulation still passes through the gasifier vessel during night time. A particle distributor "9" located downstream the cyclone "4" allows to direct circulation of the inventory to the gasifier or back to the boiler. Up- and downstream the gasifier, two steam-fluidized loop seals are present to ensure keeping different gas atmospheres between these vessels. Fig. 3 is a close up on the gasifier island [25].

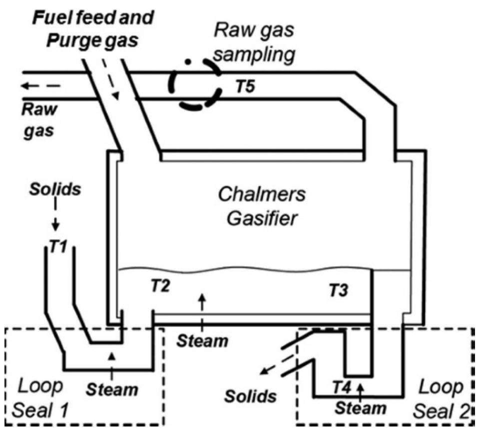


Figure 3. Close up on the Chalmers gasifier and loop seals [25].

“Loop seal 1” is located at the entrance of the gasifier while “loop seal 2” corresponds to the outlet of the gasifier, in the duct leading back the solids to the boiler, see Fig. 3. In the Chalmers indirect gasifier, the raw gas is not intended as a commercial product and is solely used to assess the process performance. This is why the raw gas duct leads to the boiler in Fig. 2 where the gas is combusted. In particular, the inorganic compounds are directly retrieved by the boiler whereas in a real system, their transport is achieved via secondary systems. The “x” in Fig. 2 indicates where a slip-stream of raw gas is extracted for analysis and/or as fluidizing medium for the secondary cleaning reactor in e.g. [16, 26, 27]

2.2 ALKALI-FELDSPAR

The material used was the same alkali-feldspar as in [23]. 30 ton of quality FFF K8 500 were delivered to the Chalmers Power Central by SIBELCO Nordic as in-kind contribution within the scope of this project. 5.6 tons were filled into the indirect gasifier loop during the first day (07/03). The specific gravity of the material is 2.6 g/cm^3 and the bulk density 1.4 ton/m^3. Table 1 shows the Particle Size Distribution (PSD) of the feldspar.

Table 1: Particle size distribution of the alkali-feldspar used in the experiments

Sieve (mm)	Retention (%)
1,000	100.0
0,710	99.9
0,500	98.8
0,255	89.5
0,250	70.0
0,180	47.8
0,125	29.8
0,090	17.0
0,063	7.7

The mean diameter is 200 μm and is thus noticeably smaller than that of the silica sand class SS36 or other materials used as heat carriers and/or active inventories in the Chalmers gasifier [25] [11, 28]. This means that special care to the boiler fluidization criteria (ratio between primary and secondary air) was taken during the start-up sequence. Also featured in Table 1 is the high proportion of fine material (<90 μm), nearly a fifth of the total inventory, meaning that one could expect a high initial loss of fines to the secondary cyclone "6" in Fig.1.

The feldspar delivered is a mixture of mainly K-feldspar and Na-feldspar in the proportions given by Table 2.

Table 2: Mineralogical composition of the alkali-feldspar

Mineralogical Composition	Weight (%)
Potash Feldspar	48
Sodium Feldspar	40
Calcium Feldspar	6
Quartz	6

Table 3 displays the chemical composition of the feldspar and evidences the important fractions of alkalis K and Na in the feldspar structure. It also shows the low contents of metals such as Fe, Mg or Mn. Interestingly, the material shows no trace of the health hazardous Ni, in contrast to olivine.

Table 3: Chemical composition of the alkali-feldspar, shown in the form of oxides

Chemical Composition	Weight (%)
SiO_2	67.5
Al_2O_3	18.8
K_2O	8.4
Fe_2O_3	0.11
CaO	1.2
Na_2O	4.3
TiO_2	0.01
P_2O_5	0.08
MgO	0.04
MnO	<0.0078

2.3 BIOMASS FUELS PROPERTIES

The boiler fuel consists of wood chips and the gasifier fuel of wood pellets with the ultimate analyses in Table 4. HHV is the higher heating value and LHV the lower heating value.

Table 4: Ultimate analyses of wood chips and pellets used as fuels (dry fuel basis, weight %)

	Wood chips	Wood pellets
Ash	0.5	0.4
Cl	<0.01	<0.01
S	<0.01	<0.02
C	50.2	50.8
H	6.2	6.3
N	0.12	0.05

	Wood chips	Wood pellets
O	43	43
HHV (MJ/kg)	19.95	20.34
LLV, (MJ/kg)	18.60	18.98

For the two weeks campaign, the moisture contents of the wood chips varied between 37.6% and 46.4% and that of the wood pellets between 7.5 and 8.5%.

Table 5 displays the main ash-forming elements in the fuels.

Table 5: Fuel characteristics of the main ash-forming elements (dry fuel basis, weight %)

	Wood chips	Wood pellets
Al	0.002	0.004
Si	0.008	0.016
Fe	0.002	0.004
Ti	<0.001	<0.001
Mn	0.006	0.012
Mg	0.022	0.017
Ca	0.13	0.10
Ba	0.001	0.001
Na	0.005	0.003
K	0.082	0.04
P	0.010	0.007

Among the elements in Table 5, the most reactive are K, Ca, Si, S and Cl [ref?]. In particular, special attention to the fate and influence of potassium on the operation and the interactions with the bed material need to be taken. Finally, the wood chips are rather silicon-lean which suggests that the formation of K and Ca-sulfates should be promoted on the combustion side as sulfur is retained in the ash [29].

2.4 EXPERIMENTAL MATRIX AND CONDITIONS

The experiments were designed as a two weeks campaign (weeks 10-11 in March 2016) in which the first one was dedicated to following ageing of the bed material and the second to process assessment and optimization through variations in the operating conditions prevailing in the gasifier.

Testing was initiated by filling feldspar to the boiler and heating up through oil burners. From a boiler temperature of 500°C, wood chips are fed and when 700°C is reached, the burners are shut down. Gradually, the circulation from the boiler to the particle distributor is established, see Fig. 2. To satisfy the heat requirements, wood pellets can momentarily be introduced to complement the flow of wood chips to the boiler. Once a suitable boiler temperature (800°C) is attained, the circulation is led to the gasifier, at this point fluidized with recirculated flue gases, which progressively are heated up. When the temperature in the gasifier exit duct is above 600°C, fluidization is switched to steam and gasifier fuel (pellets) is introduced. After approximately 30 min, the gasifier temperature is stable and the experiment can be started. In total, 5.6 ton of feldspar were fed to the indirect gasifier, out of which ca 600 kg were elutriated during the first day of operation and collected by the secondary cyclone. After that, no noticeable loss of fines was measured meaning this must have corresponded to the finer fraction of feldspar in the original batch, see Table 1.

Table 6 lists the days of operation for the boiler and gasifier and the intention with the experiments.

Table 6: Summary of the experiments. Regeneration refers to the bed material

Day	Boiler	Gasifier	Regeneration	Experiment
0				Start-up
1	x	x		Start-up/Ageing
2	x	x		Ageing
3	x	x		Ageing
4	x	x		Ageing
5	x			Ageing
6	x			Ageing
7	x	x		Oxygen transport
8	x	x	x	Steam/fuel ratio
9	x	x	x	Gasifier temperature
10	x	x	x	Day-time regeneration

During the first week, no bed material turnover was conducted and the material displayed a clear activity on the raw gas composition, with an increasingly favorable raw gas composition. At the beginning of the second week (Day 7), it was evident that during the ageing process, the properties of the virgin feldspar particles had been altered so the material exhibited a capacity to transport oxygen from the boiler to the gasifier (Note: only the boiler was in operation during the weekend). From this observation, the project plan was slightly modified so the corresponding Monday (Day 7) was dedicated to verify and quantify the oxygen transport by changing the solids circulation. Three increasing levels of circulation were tested and the corresponding runs are denoted Day 7-1, Day 7-2 and Day 7-3 in the Results section. To retrieve the bed properties witnessed the first week and favorable for the raw gas, regenerations of bed material (10-20% of the total inventory) were performed during the following nights. Day 8, the goal was to evaluate the influence of the steam/fuel ratio on the raw gas quality. The temperature, particle circulation and level of steam fluidization to the gasifier were kept constant while three levels of fuel feed were tested: 200, 300 and 400 kg/h pellets. Day 9, three levels of gasifier temperature were tested (770, 800 and 830°C) at constant fuel, steam levels and particle circulation. Finally, to phase out the campaign, Day 10, the aim was to investigate the effect of day-time regeneration of bed material - totalizing 20% of the inventory, in two steps - on the raw gas quality and gasifier performance.

Table 7 details the principal operating conditions for the gasifier during the experiments in Table 6.

The solids circulation is calculated through defluidization of loop seal 2 in Figs. 2-3, achieved by considerably decreasing the steam flow to this seal. This discontinues the overall particle circulation and as the bed material from the gasifier does not flow back to the boiler, this latter is gradually depleted from its inventory. Following the decrease in pressure drop over the boiler bed as a function of time - typically one allows a decrease of 1 kPa after which loop seal fluidization is restarted – it is possible to derive a bed flow in ton/h corresponding to the solid circulation.

Table 7: Experimental conditions

Experiment	Temperature in the gasifier [°C]	Solid circulation [t/h]	Fuel flow [kg/h]	Fluidization level [kg_{steam}/h]
Ageing	815-820	10.2-15.4	300	160
Oxygen transport	815-820	13.6 15.2 15.8	300	160
Steam/Fuel ratio	815-820	11.3	300 400 200	160
Gasifier temperature	770 800 830	11	300	160
Day-time regeneration	815-820	11.7	300	160

2.5 METHODOLOGY AND DATA ANALYSIS

To assess the process performance, different types of sampling and analysis are conducted during experiment. These have been thoroughly described elsewhere [24, 25]. The extracted slip-stream of raw gas is led to a gas conditioning system where steam is condensed and tars dissolved in isopropanol [25] so the permanent gases in the raw gas can be analyzed by a micro-GC (Gas Chromatograph, model Varian 4900). Prior to the conditioning, a port for Solid Phase Adsorption (SPA) is available to sample tar using amine columns on which these adsorb (dual-layer solid phase extraction columns with Supelclean ENVI-Carb/NH_2 SPE tubes from Sigma–Aldrich). Further tar analysis is performed by eluting the samples with a solvent and characterizing the tar species in a GC-FID (i.e. a GC with a Flame Ionization Detector). The SPA methodology is detailed in e.g. [30].

To quantify the total amounts of condensable species, the full elemental determination of C, N, O and H can be achieved using a High Temperature Reactor (HTR) operated at 1700°C where all gas constituents in the raw gas are converted to CO, CO_2, H_2 and H_2O [31, 32]. By comparison with the SPA-tars, the unknown condensable species (UCS) can be quantified. The high temperature reactor also allows gives the possibility to quantify the oxygen transport in case such occurs [32]. Results from the HTR are not included in this report. During gasifier operation, a known flow of He is added to the fluidization steam and is used to calculate the tar yields in g/kg dry ash-free fuel (DAF) and the molar yields of permanent gases in mol/kg daf fuel. This way, the yields relate to the actual fuel conversion and remove any gas dilution effect. Tars and permanent gas yields are the key criteria to diagnose the gasifier performance and to identify optimal operating conditions.

During a test, several sets of bed material samples are extracted from the process in the loop seals (Fig. 3) through two dedicated ports, using a water-cooled probe. More precisely, feldspar samples at different stages of activation were analyzed, i.e. a reference sample of unused material, low-activity feldspar on Day 1, catalytically active material on Day 4, and a sample of the feldspar with oxygen transport capability on Day 7. The aim of the bed material analysis was to observe the occurrence of an ash coat (one or several layers) formed on the particles and its composition. To do so, SEM/EDX, i.e. Scanning Electron Microscope with Energy-Dispersive X-ray Spectroscopy, of particles in the bed samples was achieved with a FEI Quanta 200 Field Emission Gun ESEM equipped with an Oxford Inca EDX system for chemical analysis (e.g. mapping of the dominant species).

3 Results

3.1 AGEING OF BED MATERIAL

This campaign corresponds to the first 8 days and was characterized with the absence of exchange in the bed inventory. Table 8 reports the cumulated hours of time-on-stream for the material when boiler respectively gasifier were operated.

Table 8: Total time-on-streams with boiler and gasifier fuel operations.

Day	0	1	2	3	4	5	6	7
Boiler (h)	0	16	40	64	88	112	136	150
Gasifier (h)	0	2	10	18	27	27	27	36
Total (h)	0	18	50	82	115	139	163	186

Day 0 was spent to fill in the 30 ton of feldspar from the delivery truck to the bed material silo and transfer approximately 1.2 ton to the so-called "day-silo" during which important adjustments were necessary. The particles of Day 0 are thus in their virgin state. Day 1 corresponds to the startup. From that point, the boiler was continuously fueled for the whole campaign. In the afternoon of Day 1, the circulation to the gasifier was established and wood pellets were fed to the gasifier. Slightly more than 2 h of operation could be reached that day. Each following day, around 8 h of gasifier operation were achieved except during the weekend (Days 5 and 6).

In total, it was possible to operate under 186 h of fuel addition with the same bed inventory without any difficulty. In particular, no defluidization/agglomeration issue was experienced, which is a very positive indication.

3.1.1 Influence on tar yields

Tars in the raw gas were collected with SPA and analyzed in the GC-FID. The results for Days 1-4 and 7 are presented in Fig. 4 showing the total tar yields for identified species between benzene and coronene, gathered into six representative groups: benzene, 1-ring compounds, naphthalene, 2-ring compounds, compounds with at least three rings and phenolic compounds. From Fig. 4, one can clearly see a decrease in all tar yields from Day 3 compared to Day 1. The activity of the feldspar bed material towards tar seems to have increased through time-on-stream. The same trends have been observed in aging tests for olivine in the same gasifier and operating conditions though for feldspar the relative changes in yields are more pronounced [9, 11]. For olivine, at the peak of activation, a maximum of 30% tar reduction compared to the first operational day was attained. Here, a total tar reduction of 10%, 47% and 59% was obtained Day 3, Day 4 and Day 7 respectively in comparison to Day 1. Note that for Day 7, the case 7-1 for the lower particle circulation is presented here. If one excludes the BTX, the feldspar material showed a decrease in tar yields of 70% from fresh to activated material while bauxite used in the same system had a decrease of 40% under the activation phase [9]. One should also keep in mind that the PSD of feldspar is lower than that of the aforementioned tested materials, meaning that it offers a comparatively higher active surface, and presumably better gas-solid contact, which contribute to the better tar conversion rates.

For Day 2, an increase in benzene, naphthalene and more markedly species containing at least 3 rings is visible, most likely due to the decomposition of Undetected Condensable Species (UCS) into these measurable tar compounds. Indeed, in a previous study, a significant amount of UCS species was quantified by Israelsson et al. [32] using an inert silica sand bed material in the same unit and at similar operating conditions. The authors found that an increase of the severity of operation, for instance by higher temperature, results in higher yield of SPA-measurable tar. By means of an independent measurement, it was confirmed that the increase of SPA-measurable tar was indeed the result of the decomposition of condensable species (that fall out of the SPA range) into more mature tar, which can be measured by the SPA method. A significant amount of UCS species are also expected in Day 1 of operation with feldspar, as the activity of the material at that stage is similar to that of the silica sand in [32]. Therefore, the higher yield of tar in Day 2 is most likely the result of a more mature tar composition, in line with the increasing activity of the feldspar.

Overall, the total tar levels obtained with the feldspar are markedly lower than those obtained with quartz sand and in the same range or lower and comparable species distribution than other active materials used in the Chalmers gasifier such as olivine, bauxite or ilmenite; olivine being a given reference in biomass gasification [9].

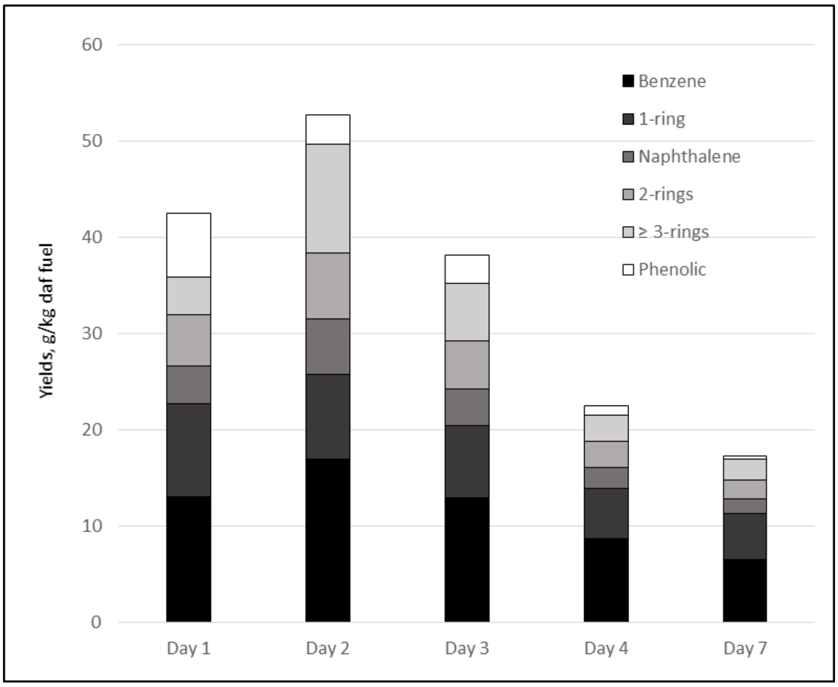


Fig. 4: Tar yields for Days 1-4 and 7

3.1.2 Influence on permanent gases

During the first 4 days of operation, the raw gas produced in the gasifier had an increasingly good quality as a function of time spent in the loop. Fig. 5 shows the evolution of the gas yields vs. day of operation for the four most important permanent gas species in the raw gas. Fig. 6 presents the yields of C_2H_2, C_2H_4, C_2H_6, C_3H_6 and C_3H_8.

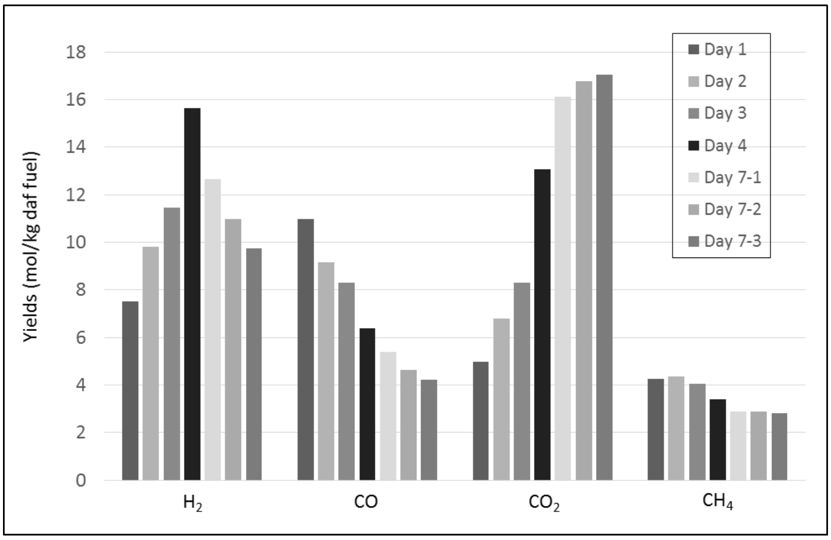


Fig. 5: Yields of the four most abundant permanent gas species in the raw gas as a function of operation day

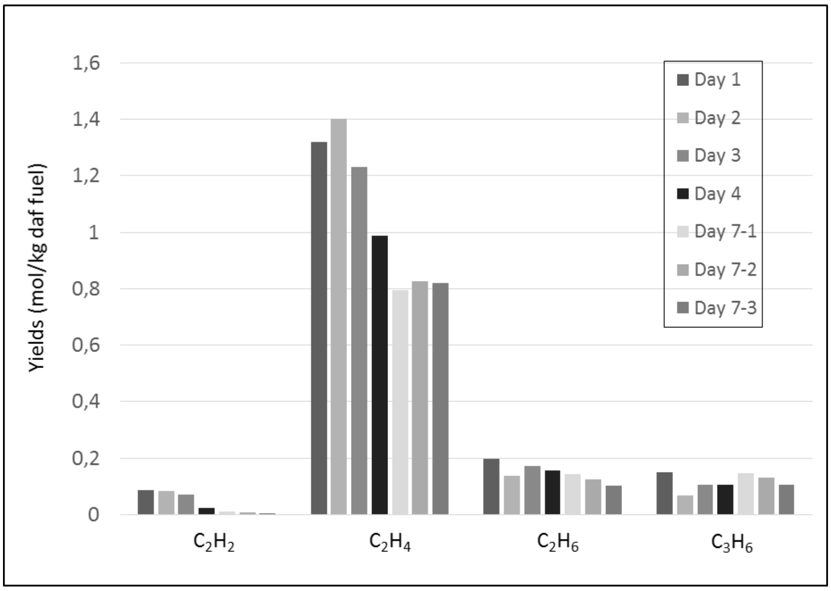


Fig. 6: Yields of C_2H_2, C_2H_4, C_2H_6 and C_3H_6 as a function of operation day

Between days 1 and 4, accordingly to the trends witnessed for the tars in the previous section, one can observe the consequences of an activation process. This is more particularly expressed by the yields of H_2 which increase to reach a maximum Day 4, here representing the bed in its activated state. Since CO_2 increases while CO decreases, the Water-Gas Shift (WGS) seems to play a key role in the resulting gas composition. However, the decrease in CO does not fully agree with the WGS stoichiometry as CO is also produced through steam reforming of tars. For Day 1, the overall permanent gas yields were similar to those obtained with quartz sand in the Chalmers gasifier. In contrast with quartz sand though, from Day 2, methane and C_2H_4 see there levels diminish while C_2H_2 and C_2H_6 steadily decrease from Day 1 [9]. Noteworthy, the consecutive yields of C_2H_4 (and methane) follow these of the total tars in Fig. 4; a trend that has also been seen in other studies [33, 34]. No clear trend is observed for and C_3H_6 during the first four days. The yields of H_2 and methane obtained Day 4 are comparable to these achieved with e.g. activated olivine and ash-activated bauxite in the Chalmers gasifier and at fairly similar operating conditions (fuel load, steam fluidization, gasifier temperature and solids circulation) though the particle size of feldspar is smaller, as said earlier [9]. Advantageously though, the activated feldspar presents a lower yield of CO compared with these materials which brings the H_2/CO to 2,5; higher than e.g. olivine used in ageing tests. For instance, a ratio of 3 corresponds to the stoichiometry for the methanation reaction. Finally, the yield of H_2 for the activated feldspar is actually close to the value obtained with this material at the same temperature but as a secondary upgrading measure in the pre-study [23]. In all, this material - at its activated state - appears as a highly interesting alternative to olivine in primary gas upgrading.

Day 4 seems to represent the onset of an oxygen transport phenomenon. From this day, the H_2 and CO yields decrease through combustion via transported oxygen and CO_2 increases. The ability for the material to transport oxygen Day 7 is corroborated by the three experimental cases (7-1, 7-2 and 7-3). Indeed, the increase in CO_2 is exactly proportional to the increase in solids circulation (values in Table 7). At this stage, the authors presumed that the oxygen carrying capacity results from the properties and composition of the ash layer formed on the particles during the ageing process, as the feldspar contains very low amounts of metals (e.g. Fe). The oxygen transport can explain some of the decrease in tar yields on Day 7, as seen in Fig. 3, though enhanced catalytic reforming is most likely also involved. This also means that the optimum of activity from a gas upgrading point of view was probably achieved Day 4.

Fig. 7 summarizes the yields of H_2S versus day of operation. S fed with the pellets to the gasifier represents 0.006 mol S/kg daf fuel (counted as H_2S). The values in Fig. 7, largely surpassing that figure already during the first day of operation, mean that sulfur must be transported from the boiler to the gasifier with the bed material flux. This feature has been observed for merely all bed materials investigated in the Chalmers gasifier [9]. Owing to the particular configuration of the gasifier where the raw gas duct leads to the boiler and the raw gas is combusted (Fig. 2), one could expect high levels of SO_2 in the boiler flue gas. However, monitored measurements indicate extremely low values, <10 ppm. This agrees with sulfur reacting in the boiler and being transported to the gasifier. Further, each time the gasifier is shut down in the early evening, CO in the boiler flue gases increases, as it also has been witnessed with e.g. olivine [9]. In [9], Marinkovic et al. explain this phenomenon with the fuel-originating alkali, and particularly potassium, known to prevent CO oxidation. Thus, removing potassium from the boiler would benefit the conversion of CO. In the oxygen-rich boiler, potassium and sulfur react to form potassium sulfate that condense on the bed material and is transported to the gasifier where it decomposes under reducing environment. Positively, the decomposition can produce KOH and K_2S that are available for conversion of hydrocarbon in the gasifier but also H_2S, as confirmed by the high levels of sulfur in Fig. 7 [9].

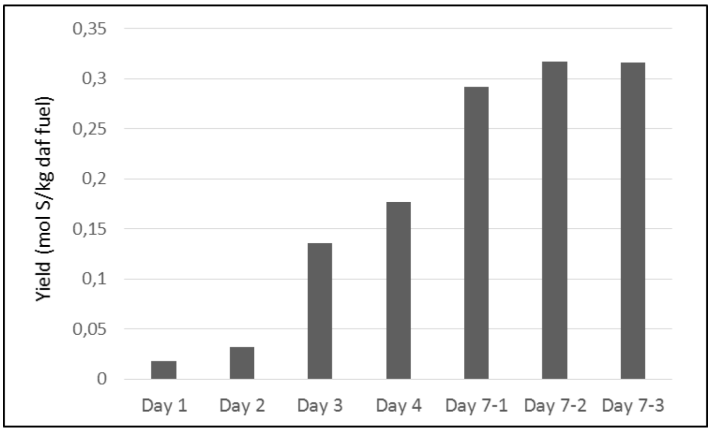


Fig. 7: Yield of Sulfur in the raw gas versus day of operation

Another consequence of this alkali-sulfur interaction is that during the time-on-stream, sulfur is clearly accumulating in the system, see Fig. 7. It is important to remind that no bed regeneration was conducted during these days.

Finally, the CO increase after shutting down the gasifier where much lower (at mostly < 50 ppm with a short peak at ~100 ppm on Day 3) than those obtained with olivine (peaks > 1200 ppm), which represents a strong advantage for the feldspar compared to olivine [11].

3.1.3 SEM/EDX analysis

The bed activation described above can be related to the inventory exposure to ash-forming elements in the fuel that gradually form an active layer around the bed particles. To support this possibility, the bed samples extracted from loop-seal 1 on a daily basis were analyzed with SEM/EDX. The results for day 0, day 1, day 2, day 4 and day 7 are in focus in the following. Day 0, the bed material was still in its virgin state, i.e. “unused”.

Fig. 8 shows a SEM picture of the fresh feldspar. The overall shape of the particles is rather edgy as expected from mined ores.

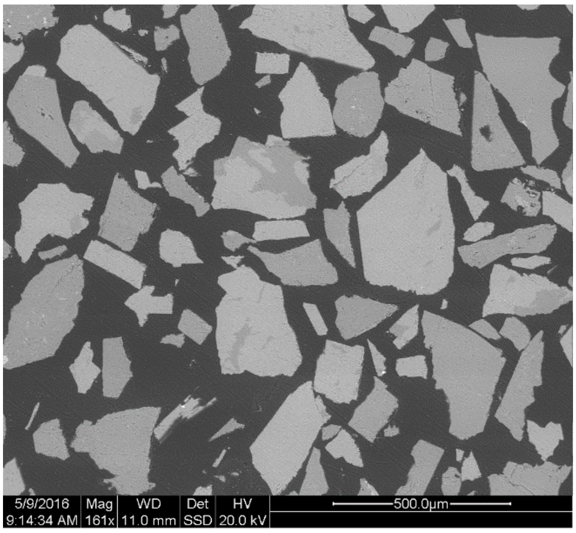


Fig. 8: SEM image of the fresh feldspar (Day 0)

A magnification of the central part of Fig. 8 is shown in Fig. 9 together with the EDX mapping for the five elements detected in the fresh feldspar.

In Figs. 8 and 9, one can distinguish different shades of grey between and within some of the particles. In particular, one can see that the darker regions/particles in Fig. 9 are those where Na-feldspar dominates while the lighter are the K-feldspars.

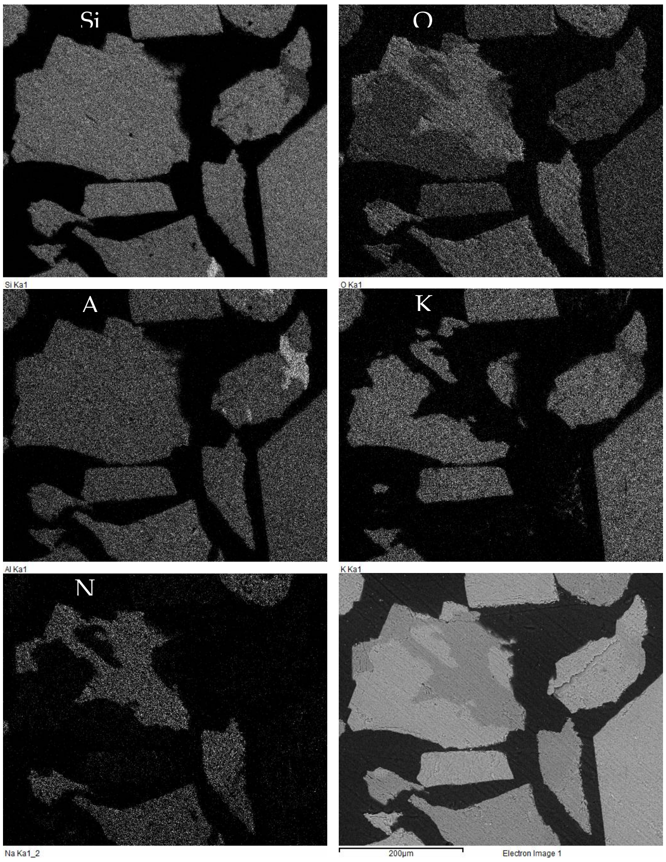


Fig. 9: SEM and EDX mapping for the unused feldspar (day 0)

After a whole day of operation, Day 1 the particles collected had merely the same shape as the fresh material and from particle screening, even the same PSD. Fig. 10 shows the SEM image and EDX mapping of some representative particles from this day. One can observe that the Na-feldspar particles had a thin layer of potassium formed on their surface. This may be interpreted as potassium deposing and then diffusing inside the particles; however, it is difficult to distinguish between the diffused potassium and the original intrusions of K-feldspar into the Na-feldspar which can be found in the unused material. A pure silica sand particle was found on the left hand side of the pictures (6% of the inventory is quartz sand, see Table 2). It also seems to have captured potassium, which is not unexpected owing to the special affinity of Si for potassium, see e.g. [9, 35].

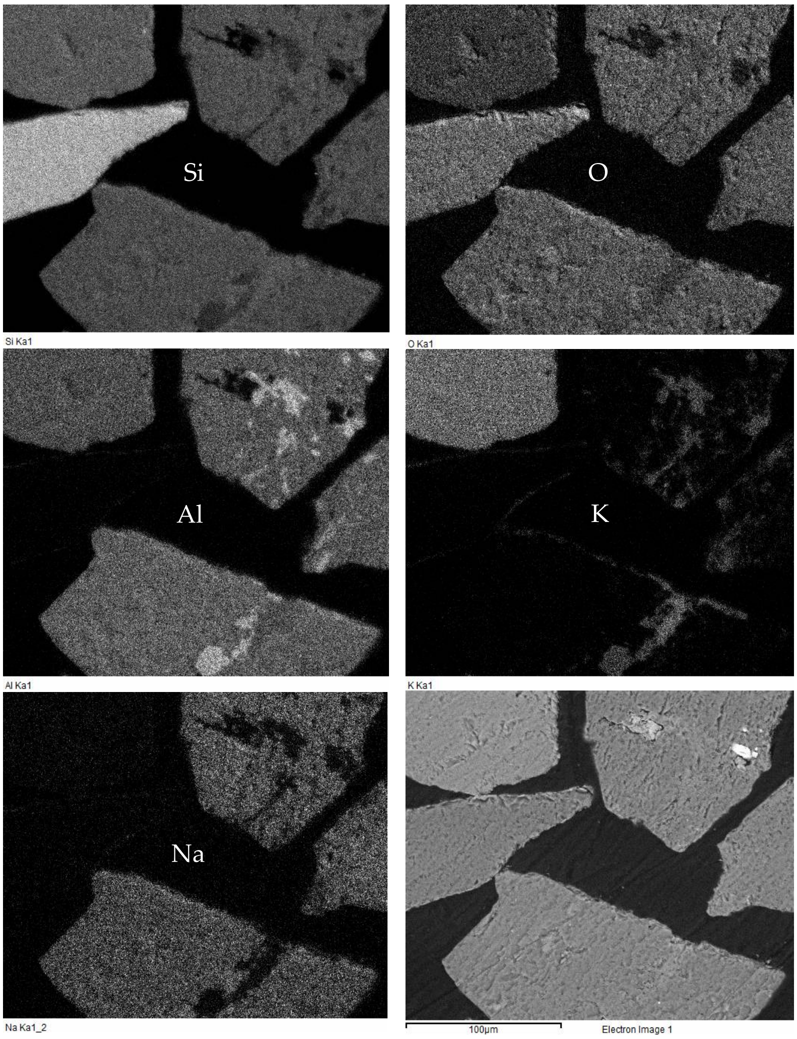


Fig. 10: SEM and EDX mapping for Day 1

Day 2, the layer formation has continued and is more distinct, as revealed by the SEM/EDX analysis results from this day in Fig. 11. At this stage, K, Na, Ca and Mg are detected on the surface of all particle types. In Fig. 8, one can again see that potassium has a particularly high affinity with pure silica sand particles. Overall, the activation process seems to have proceeded and accordingly, the high level of

SPA tars measured Day 2 most likely results from an exacerbated conversion of UCS into these molecules, as explained by Israelsson et al.[32]

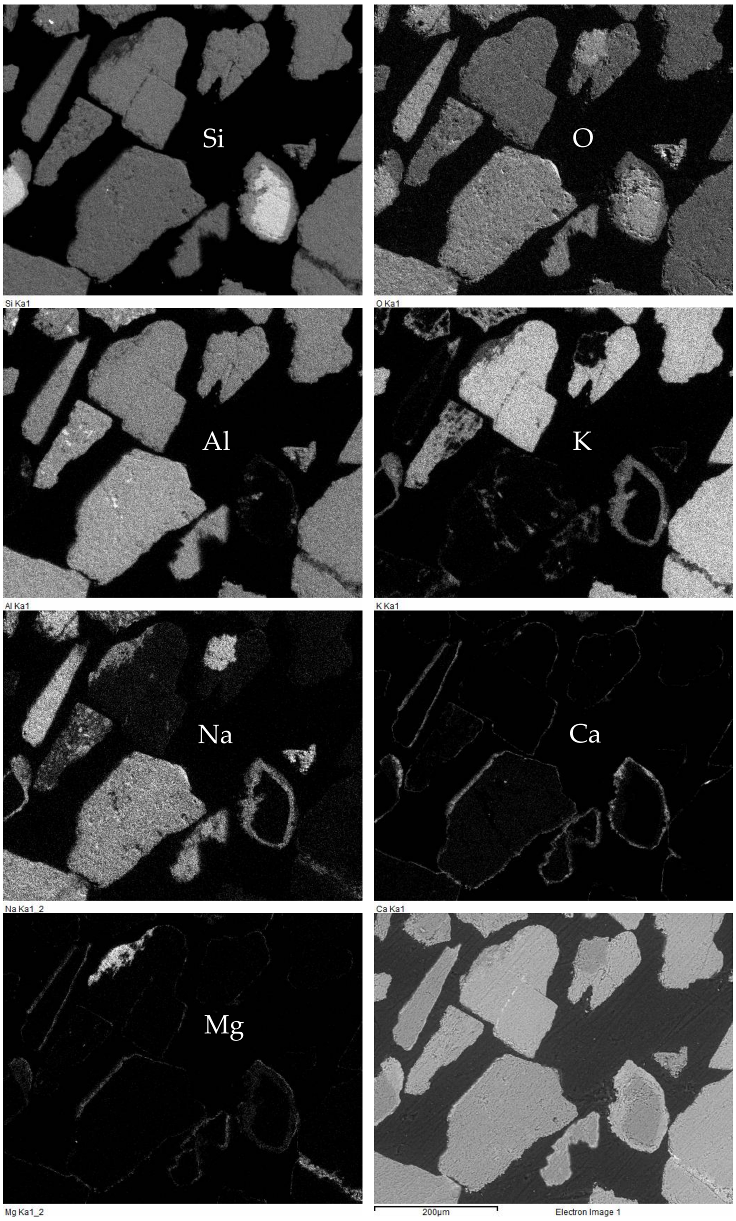


Fig. 11: SEM and EDX mapping for Day 2

As seen in 3.1.2, after four days of operation, the gas for Day 4 had the best quality in terms of tar yields and permanent gases. Fig. 12 shows an SEM picture of the corresponding batch together with the identified species from EDX mapping. Via time-on-stream erosion, the particles shape has turned smoother; the sharp edges have disappeared.

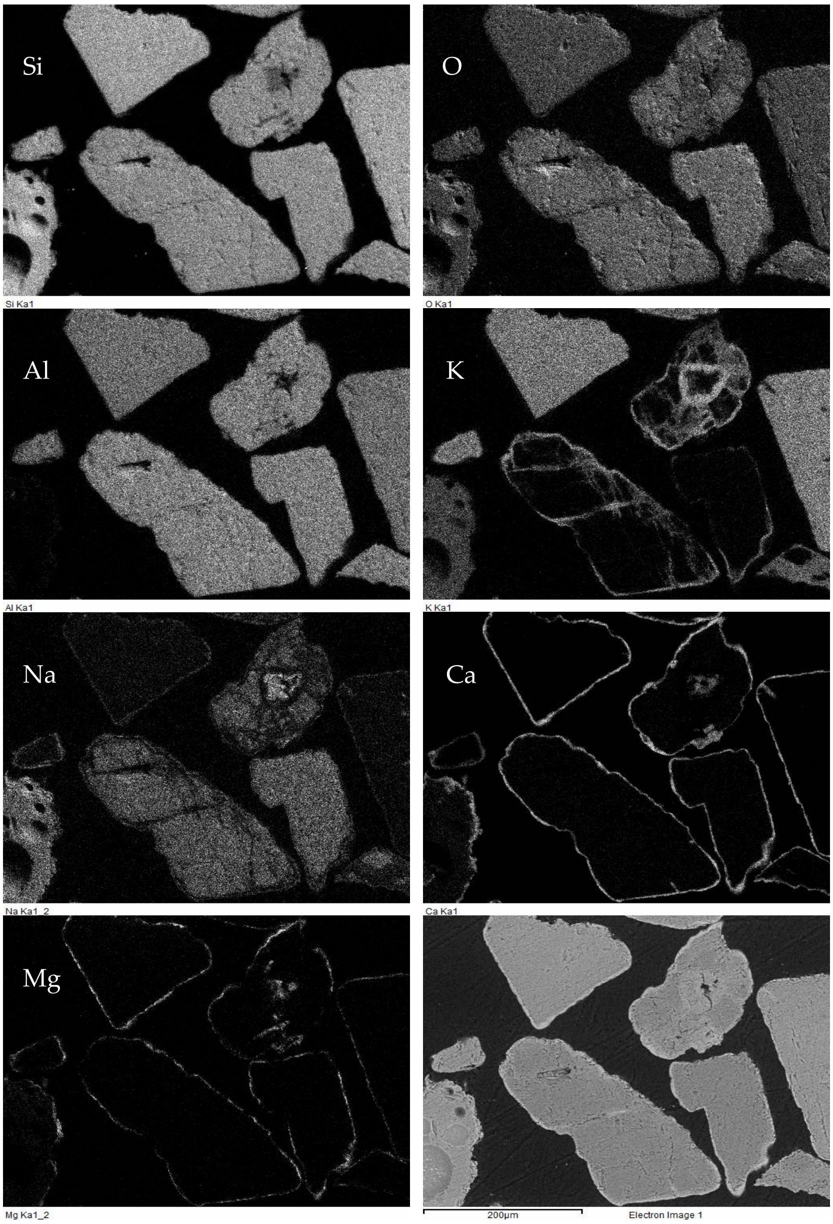


Fig. 12: SEM and EDX mapping for Day 4

The layer formation has also continued during this prolonged operation and both its thickness and distribution in constituents has increased. Day 4, all particles have a layer consisting of - in decreasing importance - Ca, Mg, K and Na. Though these elements are already present in the fresh feldspar at various extents, considering their location in Fig. 12, it seems reasonable that they originate from the fuel. The improved activity of the feldspar material after these 4 days of operation is likely a result from the active elements accumulated in this layer. In the same experimental context and with other bed materials, this has been reported as well by Marinkovic et al. in e.g. [9]. Mg-based materials such as olivine and dolomite have a proven activity on tar reduction and contribute to the conversion of tars witnessed in Fig. 4 [11, 17, 18, 36, 37]. The layer of Ca can prevent the formation of K-silicate and instead allow potassium to be transported in its releasable salt form - e.g combined with the transported sulfur detailed earlier - thereby promoting tar reduction and char conversion in the gasifier [38]. This supports the tar and gas trends in Figs 4 and 5. Besides, the Ca layer seems to have built up above the thin layer of K (and Na), as phenomenon also observed in combustion research [39]. In line with this, it is important to remind that the fresh material is already loaded in K which may have prevented fuel-K to form large amounts of potassium silicates, precursor to bed agglomeration [9]. This combination of factors can also explain why no potassium diffusion into the feldspar has been observed, even prior to the Ca-layer formation, contrarily to e.g. ilmenite or bauxite used in the Chalmers gasifier. Further, the Ca layer itself contributes to the tar reduction observed Day 4 compared to the previous days [9]. Calcium sulfate, in addition to its contribution to the sulfur transport, can even induce a certain transport of oxygen and thus yield tar oxidation [40]. Finally, species such as Ca and K are both known to play an active role in the WGS [41, 42]. Altogether, the constituents of the layer formed around the feldspar and their interaction with the raw gas support the observations on the gradual tar reduction and shift in the permanent gas composition described in the previous sections.

As mentioned above, Day 7 the feldspar displayed a pronounced oxygen transport capacity. Fig. 13 features the SEM and EDX mapping for the batch collected Day 7 (case 7-1). The transport of sulfur from the boiler has increased (Fig. 7) and is now visible in Fig. 13. Apart from K, Na, Ca and Mg which are now present in larger quantities in the layer, compared to Day 4, even present traces of Mn and Fe are present. Fig. 13 shows that an initial layer of K is formed on which Na, Ca and additional K deposit and onto which Mn, Mg, Fe and S themselves accumulate. He et al. have also witnessed a superposition of Ca-rich layer on an initial K-rich thinner layer using quartz sand in a CFB boiler [39]. Due to its location, Fe probably originates from the fuel-feed tough non-negligible amount of Fe are present in the virgin feldspar (0.11% Fe_2O_3). Fig. 13 and a line scan across the coats of K- resp. Na-feldspar (not included here) suggest that S is likely bound to the outer layer of K, e.g. in the form of sulfate, meaning that K can be released in the gasifier. Further, all species in the coat can at various extents contribute to the observed oxygen transport, either as oxides or sulfates/sulfides. This is for instance the case of Ca and Na as reported in [40]. That oxygen is present in the coat is now visible in Fig. 13. Finally, these observations means that a trade-off in accumulated amounts of these species in the coat is necessary to favor gas upgrading (tar conversion, WGS) instead of oxygen transport.

In view of the results, this material clearly proved to be suitable for fluidized bed conditions. It could maintain its mechanical integrity, shown with the negligible production of fines during these prolonged tests and the ability to resist thermal degradation for operation up to 900°C (boiler). In particular, no signs of defluidization nor agglomeration were observed despite the high fuel-alkali levels in the system. From a chemical point of view, the alkali feldspar, initially rather inert, could benefit from the fuel-ash elements through the build-up of layers around the particles containing important alkali-metals, alkaline earth metals or metals that in turn induced a strong activity on the producer gas. This considerably improved the hydrogen yields while abating tars. Moreover, one should keep in mind that this is an ore available worldwide with a bulk price comparable to that of high quality silica sand thus definitely cheaper than other materials interesting in this application, e.g. olivine, bauxite or ilmenite [23]. It contains no hazardous species which makes disposal of spent inventory facile. These aspects imply that a larger frequency or bed exchange can be tolerated and without noticeably affecting the operational cost. From this present study, a bed turnover would in any case prove necessary as through longer time-on-stream, an ability to transport oxygen was yielded, with a negative impact the producer gas energy value. In any case, the alkali-feldspar tested appeared as a highly promising alternative bed material in indirect gasification of biomass both as a primary catalyst, as seen in the present work, and a secondary catalyst as proven in [23].

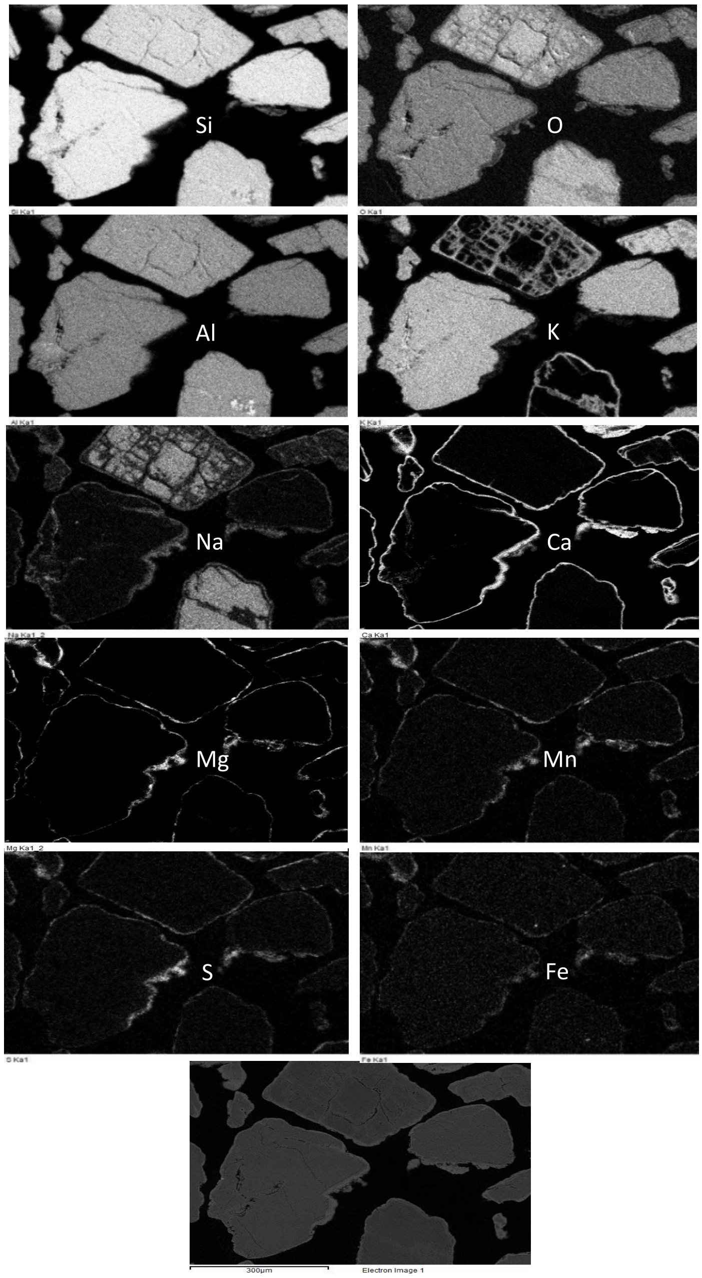


Fig. 13: SEM and EDX mapping for Day 7

3.2 OPERATION VARIATIONS AND PROCESS OPTIMIZATION

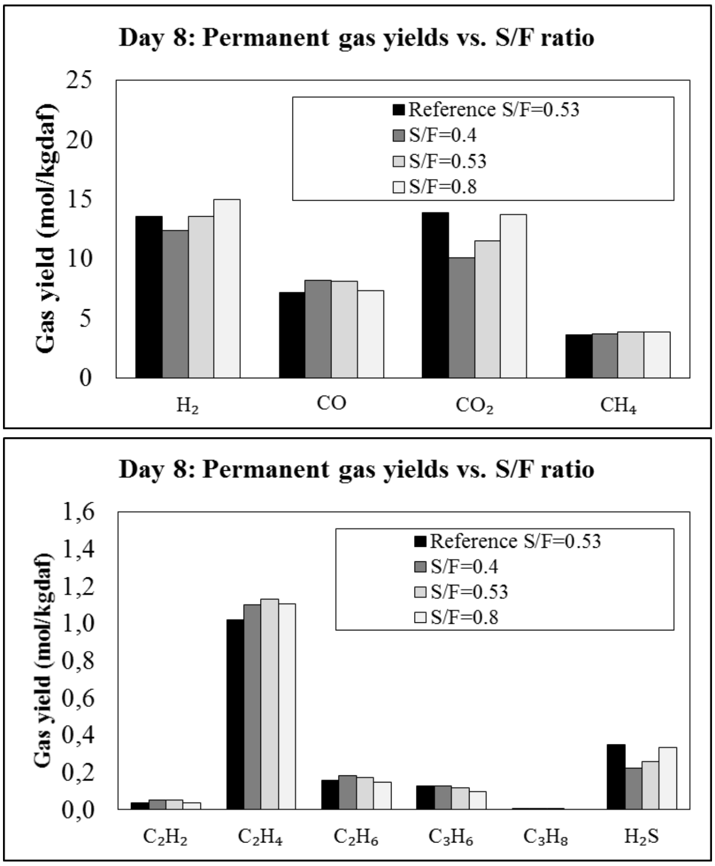
Finding optimal operation of the gasifier in terms of high raw gas quality is crucial for the process efficiency and was the object of dedicated investigations. Experiments involved changes in fuel load to the gasifier (3 levels, keeping circulation and temperatures constant) and changes in the gasifier temperature (three levels: 770-800-830°C). The campaign was concluded by monitoring the effect of bed regeneration on the raw gas composition (two levels of regeneration in terms of total mass of fresh material introduced were achieved for a total of 500 kg).

The indicators used to evaluate the impact of operating conditions on the process performance are: i) oxygen transport; ii) activity towards tar reforming; iii) activity towards CH_4 reforming; iv) activity towards carbon conversion; and v) activity towards the WGS reaction.

Note that no SEM/EDX analysis of sampled bed particles was performed for these tests, as the focus of these experiments is on operating conditions rather than on bed material properties.

3.2.1 Variation in steam-to-fuel ratio

During the night following Day 7, a certain fraction of the bed inventory was regenerated. Day 8, three steam-to-fuel ratios were obtained by changing the fuel load to the gasifier at constant steam fluidization. This enables the investigation of steam-to-fuel ratio without significant alteration of the level of fluidization of the gasifier. The experimental cases involved the following and consecutive fuel loads: the reference load of 300 kg/h, then 400 kg/h, then 300 kg/h again, then 200 kg/h. This corresponds to steam-to-fuel (S/F) ratios of resp. 0.53, 0.4, 0.53 and 0.8. The resulting yields of permanent gases are given by Figs. 14a and b.



Figs. 14a and b: Yields of the permanent gas species in the raw gas (Day 8)

The bed inventory at the beginning of Day 8 is a mixture of highly activated oxygen carrying feldspar and fresh inactive particles. This explains the quantitative gas yields in Figs. 14a and b as compared with those in Fig. 5, i.e. an average scenario between these two extreme cases and a somewhat lower gas quality (e.g. H_2 levels) compared to the case with the most active feldspar on Day 4. One can also notice that the reference case and the case repeat at 300 kg/h later on do not yield exactly the same gas compositions, despite involving nearly similar operating conditions.

Lowering the fuel feed means comparatively more steam available in the gasifier. This implies more favorable conditions for the WGS to occur. This is visible from Fig. 14a were a clear trend towards higher H_2 and CO_2 and lower CO yields is visible. The slight discrepancy in WGS for the CO trend can be explained by an improved steam gasification of the char and/or reforming of tar. The same general gas trends have been observed by e.g. Berdugo et al. using other bed materials in the same gasifier [28]. The yields of C_2H_2, C_2H_6 and C_3H_6 decrease with increasing steam-to-fuel ratios. The higher partial pressure of steam in the gasifier can enhance the hydrocarbon reforming reactions in presence of the partially active feldspar. Interestingly, methane seems rather unaffected by the changes in operation.

That steam reforming reactions were promoted by increasing steam-to-fuel ratios is somewhat visible from the total SPA tar trends in Fig. 15.

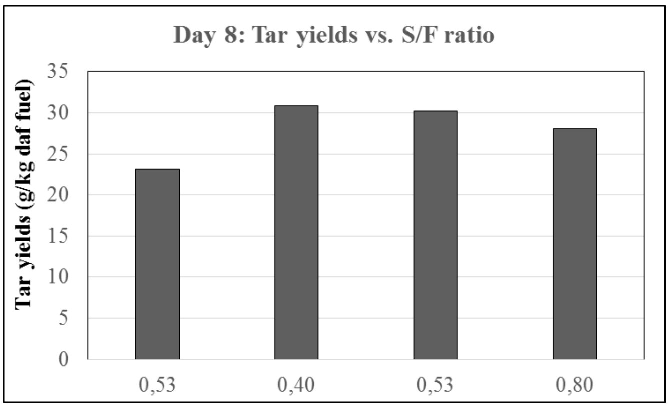


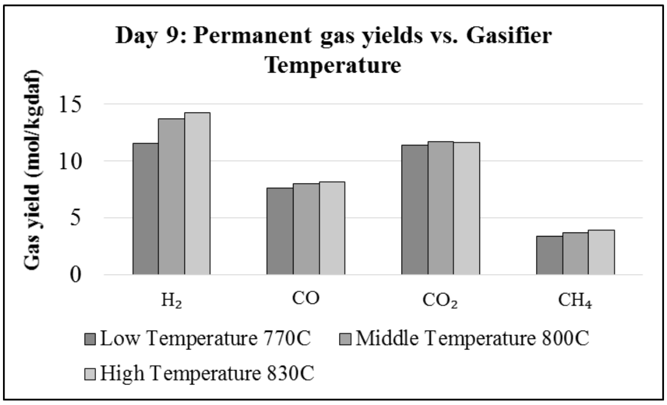
Fig. 15: Total tar yields in the raw gas (Day 8)

Indeed, when increasing the S/F ratio from 0.4 to 0.8 by decreasing the fuel feed, the total tar yields are reduced from 31 to 28 g/kg daf fuel. This variation, though moderate, is in the same order of magnitude than that witnessed for the permanent gases in Figs 14a and b.

Overall, the direction for the trends in permanent gases and tar yields agree with the changes in operating conditions (S/F ratio) but the effect seems rather limited (Recall that the fuel feed was lowered by half between the two extreme cases). Note that the differences in gas and tar yields between the reference case and the repeat (i.e. S/F=0,53) are as significant as those induced by a double-fold of the fuel feed. It is suggested that the changes of the properties of the bed inventory during the day, e.g. ageing, influence the results. This hypothesis is supported by the different yields of H_2S when comparing the reference case and the repeat, which was conducted 4 hours later. The lower level of H_2S after several hours of operation can be interpreted as a net loss of sulfur-containing compounds from the bed inventory during gasifier operation. Further, the results evidence that higher partial pressure of steam enhances the release of H_2S from the bed, as a decrease of fuel feeding rate yields higher H_2S, despite the apparent loss of sulfur containing species over time.

3.2.2 Variation in gasifier temperature

Day 9, three levels of gasifier temperature were tested at a constant solids circulation, fuel and steam loads. Figs. 17a and b summarize the results for the permanent gas analysis from the raw gas. One can see appreciably modified gas yields as temperature is increased. Clear trends towards higher yields of lighter permanent gas species are witnessed. Indeed, higher temperature promotes both char gasification and decomposition of higher hydrocarbons. These feature explain the observed trends in Fig. 16a and b.



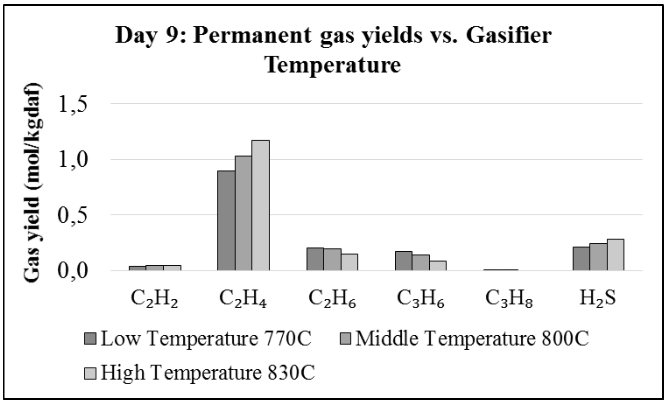


Fig. 16a and b: Yields of the permanent gas species in the raw gas (Day 9)

An interesting remark is that the gas yields for the highest temperature case are not significantly more advantageous than those obtained at the middle temperature case. Thus, the benefits from high temperature operation may not compensate the associate increase in energy consumption to reach this temperature.

Fig. 17 displays the total tar yields in the raw gas for the three temperature cases.

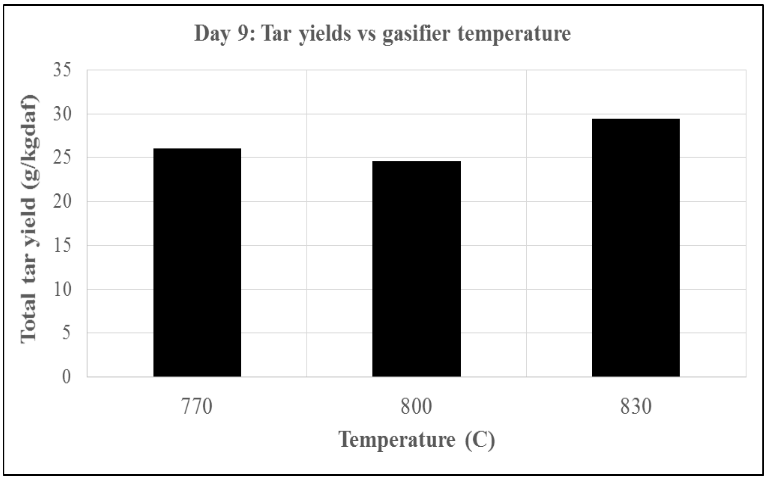


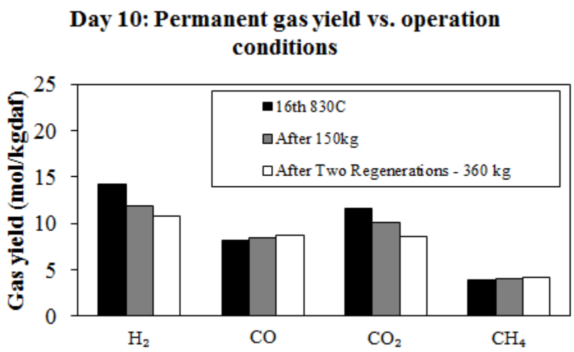
Fig. 17: Total tar yields in the raw gas (Day 9)

Between the low and middle temperature cases, there is only a slight variation in tar yields (slight decrease). However, at 830°C, the yield of SPA tars is highest. This is in agreement with the experience of Israelsson et al. using silica sand in the Chalmers gasifier, where increasing the severity in the gasifier (e.g. temperature and/or gas residence time) leads to an increase in more mature type of tar which can be measured by the SPA method [32]. However, it should be noted that an increase in SPA tars does not necessarily means an increase in total tars. Actually, Israelsson et al. showed that as the severity increases, the yield of undetected condensable species drops, most likely evolving into measurable SPA species, while the overall yield of tar decrease.

Overall, one can conclude from the gas and tar trends obtained in this test series that operating the gasifier at higher temperature is probably not worth the required increase in energy consumption.

3.2.3 Day-time bed regeneration

Figs. 18a and b show the permanent gas yields for the experiments involving day-time bed regeneration (total of 360 kg fresh material in two occasions). "16th 830C" (Day 9) corresponds to the high gasifier temperature case on the 16th of March and only serves for comparison.



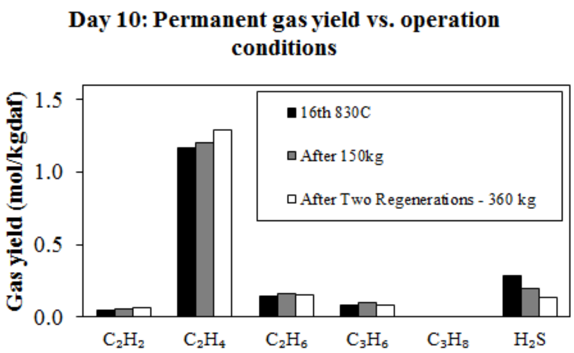


Fig. 18a and b: Yields of the permanent gas species in the raw gas (Day 10)

After partial regeneration of the bed material, through dilution of active material with fresh inactive particles, the gas quality is altered, see Figs. 18a and b. The permanent gas composition is shifted towards that observed the first days of the "ageing experiments", i.e. low quality with high tars, low H_2 and high CO, see section 3.1. Tars are presented in Fig. 19. Noticeably, ethylene yields increase after this bed regeneration. Accordingly, the total tar yields also augment [33, 34]. This is visible in Fig. 19.

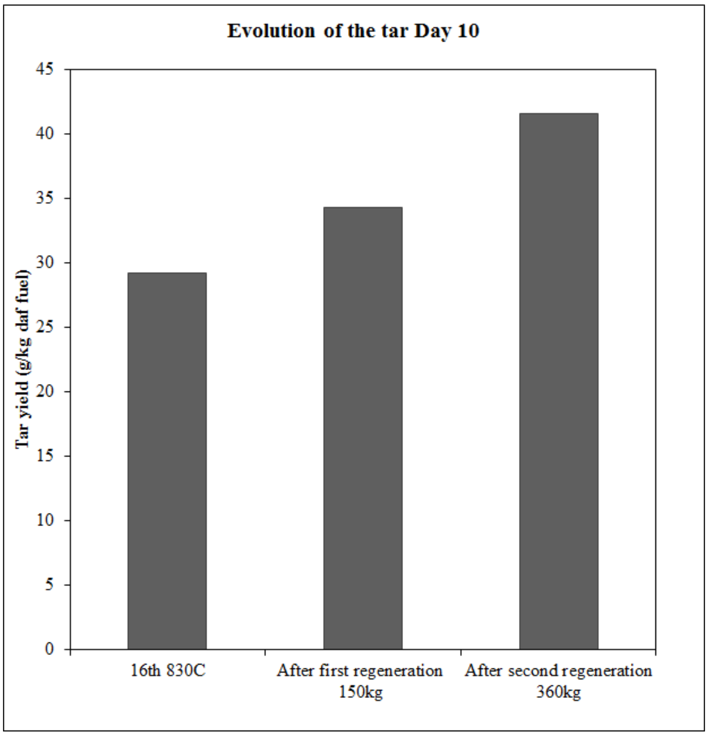


Fig. 19: Total tar yields in the raw gas (Day 10)

4 Conclusions

The goal of this project was to demonstrate the possibility to use an alkali-feldspar as bed material in an indirect gasifier and to assess its activity on the producer gas quality. The present investigation was based on experiments conducted in the Chalmers 2 MW indirect gasifier and the objectives were:

I. To follow the ageing process of the feldspar bed material in an indirect gasification loop and the consequences of time-on-stream on the bed characteristics and raw gas quality

II. To assess the performance of this material under varying operating conditions such as gasifier temperature and fuel-to-steam ratio to give hints on process optimization

In view of the results, the feldspar can clearly be employed as an alternative bed material to e.g. olivine or silica sand in indirect gasification of biomass. The material displayed a suitable behavior in longer-term fluidized bed conditions, e.g. low production of fines, and could keep its physical integrity under varying gas atmospheres. Its initial load in alkali seems to act as a protection against the combination of fuel-potassium with the material silica, a problem that occurs with silica sand. Thus, it minimizes agglomeration risk resulting from the formation of potassium silicates.

Due to exposure with fuel ashes, different layers of ash-elements formed around the particle, mainly Ca, K, Mg and Na, as revealed from SEM-EDX analysis. The material showed an ability to transport fuel-sulfur from the boiler to the gasifier. This can occur e.g. in combination with transport of potassium by the bed material as potassium sulfate, which brings more active potassium for reactions to the gasifier. The ash layer(s) around the feldspar particles induced a marked activity on the resulting raw gas composition; an effect which was more pronounced as time-on-stream increased. The tar levels were progressively reduced and the Water-Gas shift was enhanced, which resulted in higher yields of H_2. After a week without bed turnover, the feldspar had gained an oxygen-carrying capability that negatively impacted the raw gas composition by partial combustion of the valuable gases.

For the experiments focusing on change in gasifier operation, the main conclusions are that - not unexpectedly - higher steam-to-fuel ratios and gasifier temperature induce better gas qualities, in particular higher yields of hydrogen and lower tars. The slightly better gas yields at the highest temperature case in comparison to those for the middle temperature case do not seem to justify the additional energy consumption to operate at this temperature. Regeneration of bed material during day time lowers the total activity of the inventory by diluting particles with different levels of activity with fully inactive fresh material. The observed effect is close to that obtained when regenerating bed material night time when only the boiler is fueled.

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ALKALI-FELDSPAR AS CATALYST FOR UPGRADING ENERGY GAS FROM BIOMASS GASIFICATION

These results show that a safe operation, a drastic decrease in tar levels in the produced energy gas together with an advantageous shift in gas composition for methanation could be reached using an alkali-feldspar as bed material in an indirect gasifier of industry-relevant size.

The conditions created in the project imply that these experimental results are directly applicable and transferable to the industry at a low cost and risk. In the report, the possibility to readily and rapidly exchange the more expensive and health problematic olivine in existing indirect gasifiers was proven. This also means that a direct reduction in operational costs through a simpler gas cleaning step downstream and an easier disposal of spent material can be achieved.

For the industry, the use of this feldspar only corresponds to an operational adjustment in an existing infrastructure meanwhile giving the possibility to offer an extended portfolio of active bed materials.