Interactions of high temperature H_2S and HCl cleaning sorbents with biosyngas main components and testing in a pilot integrated biomass gasifier SOFC system

Cavalli, Alessandro; Chundru, Pradeep; Brunner, Thomas; Obernberger, Ingwald; Mirabelli, Ilaria; Makkus, Robert; Aravind, Purushothaman Vellayani

DOI
10.1016/j.renene.2021.08.114

Publication date
2021

Document Version
Final published version

Published in
Renewable Energy

Citation (APA)
Cavalli, A., Chundru, P., Brunner, T., Obernberger, I., Mirabelli, I., Makkus, R., & Aravind, P. V. (2021). Interactions of high temperature H_2S and HCl cleaning sorbents with biosyngas main components and testing in a pilot integrated biomass gasifier SOFC system. *Renewable Energy*, *180*, 673-682. https://doi.org/10.1016/j.renene.2021.08.114

Renewable Energy 180 (2021) 673–682

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Interactions of high temperature H_2S and HCl cleaning sorbents with biosyngas main components and testing in a pilot integrated biomass gasifier SOFC system

Alessandro Cavalli [a, *], Pradeep Chundru [a], Thomas Brunner [b], Ingwald Obernberger [b], Ilaria Mirabelli [c], Robert Makkus [c], Purushothaman Vellayani Aravind [a]

[a] *Process & Energy Department, 3me Faculty, Delft University of Technology, Leeghwaterstraat 39, 2628 CB, Delft, the Netherlands*
[b] *BIOS BIOENERGIESYSTEME GmbH, Hedwig-Katschinka-Straße 4, A-8020, Graz, Austria*
[c] *HyGear BV, Westervoortsedijk 73, 6827 AV Arnhem, the Netherlands*

ARTICLE INFO

Article history:
Received 11 December 2020
Received in revised form
14 August 2021
Accepted 28 August 2021
Available online 1 September 2021

Keywords:
Biomass gasification
High temperature gas cleaning
Water gas shift reaction
Side reactions
Contaminants removal

ABSTRACT

High temperature biosyngas cleaning is more efficient when the end user operates at elevated temperature, as in biomass gasifier solid oxide fuel cell systems. However, there is not much experience with this technology and low temperature gas cleaning is usually adopted. This paper advances current knowledge by presenting the results from the investigation of side reactions catalysed by commercially available sorbents involving biosyngas main components, and the results obtained with the pilot plant developed within the Horizon2020 project “Flexifuel-SOFC”. K_2CO_3, used for HCl removal, appeared catalytically active towards the water gas shift reaction. Under conditions representative of a real system, the residence time was not sufficient for the gas composition to reach thermodynamic equilibrium. ZnO–CuO, used for H_2S removal, showed a catalytic activity significantly higher. Both sorbents seemed not active towards the methanation reaction. The pilot plant tests confirmed the occurrence of the WGS reaction in the HCl removal reactor. The sorbents decreased H_2S and HCl below the target value of 1 ppmv for H_2S and 5 ppmv for HCl. The catalytic activity of sorbents and the heat released by these reactions should be carefully considered in the design phase of high temperature gas cleaning units.

1. Introduction

Integrating biomass gasifiers with solid oxide fuel cells is potentially a highly efficient method to transform biomass chemical energy into heat and electricity. In these systems, solid biomass is converted into a gaseous mixture called biosyngas, with CO, H_2, CH_4, CO_2, H_2O and N_2 as main components. Biosyngas also contains some minor species, among which sulphur, chlorine, tar and particulate matter, which can harm downstream equipment, hence they are removed before feeding the gas to the Solid Oxide Fuel Cell (SOFC). Biosyngas can be cleaned at high or at low temperatures, with the former helping to decrease the system energy losses [1–3]. Moreover, low temperature gas cleaning is characterized by the production of wastewater that requires additional treatments. Therefore, biomass gasifier SOFC systems are more efficient and less complex when adopting high temperature gas cleaning. However, at present there are not many systems employing this method since it is considered not sufficiently mature, especially for sulphur and chlorine removal.

In biosyngas, sulphur is mostly present in the form of COS and H_2S. However, due to the presence of steam, which converts COS in H_2S via the hydrolysis reaction, high temperature sulphur removal focuses mainly on H_2S [4]. Even at low ppmv levels, this compound is adsorbed on SOFC Ni active sites affecting the fuel oxidation and catalytic reactions [5,6]. Metal oxides can be used for high temperature hydrogen sulphide removal according to the sulfidation reaction (1). Usually, Ca based sorbents are used inside the gasifier (primary method) for bulk sulphur removal, while Zn, Cu, and Ce based sorbents are used in fixed-bed reactors downstream the gasifier (secondary method). These sorbents can decrease H_2S concentration to around 1 ppmv in the operating window 300 °C–450 °C [7]. Ceria based sorbents can achieve this cleaning efficiency even at higher temperatures when they are reduced to Ce_2O_3 [8].

---

* Corresponding author.
E-mail address: a.cavalli@tudelft.nl (A. Cavalli).

https://doi.org/10.1016/j.renene.2021.08.114
0960-1481/

$$Me_xO_y + yH_2S \rightarrow Me_xS_y + H_2O \quad (1)$$

Sulphur removal has been extensively studied. Only a brief overview is given here, and more information can be found in Refs. [9,10]. Already in 1976, Westmoreland et al. screened the thermodynamic potential of more than twenty solids for sulphur removal at temperatures up to 1500 °C. From the analysis, they identified Fe, Zn, Mo, Mn, V, Ca, Sr, and Ba based sorbents [11]. Tamhankar et al. developed and tested, in the temperature interval 538–650 °C, several regenerable sorbents based on ZnO, CuO, $ZnO-Fe_2O_3$, $CuO-Fe_2O_3$, $CuO-Al_2O_3$, and $CuO-Fe_2O_3-Al_2O_3$. Interestingly, H_2S concentration was lowered below 1 ppm, that is lower than the expected equilibrium concentration of 4.2 ppm. They explained the results with the formation of a sulfide layer on the surface with free energy lower than the bulk sulphide [12]. Naturally occurring minerals as dolomite, limestone [13,14] and modified clay [15] and olivine [16] have also been studied. A large amount of work has been done to improve sorbents properties as sulphur adsorption capacity, regeneration effectiveness, and thermal stability of the sorbents and of the complex formed after the contaminant removal reactions [17–20]. Sanchez-Hervas et al. studied the effect of space velocity, temperature, and pressure on the sulphur capacity of a zinc oxide-based sorbent with nickel oxide as promotor. Besides affecting the sorbent utilization, the space velocity affected Boudouard reaction, that appeared favoured below 2000 h^{-1}. An increase in temperatures from 400 °C to 500 °C had only a minor positive effect on sorbent capacity [21]. Gupta et al. investigated the influence of up to 1500 ppmv HCl on H_2S removal with a zinc titanate sorbent at temperatures ranging from 538 to 750 °C. Hydrogen chloride had no deleterious effects on the sorbent capacity and part of the HCl was also removed. However, at 750 °C, some zinc loss occurred with low-steam concentration [22]. However, the presence of steam appeared to decrease the capacity of two sorbents, Cu-ceria and manganese-based, developed by Cheah et al. [23].

Chlorine is also mostly found bound to hydrogen in biosyngas. Hydrogen chloride can affect SOFC, even though the tolerance limit appears to be higher than that for H_2S [24,25]. At high temperatures, the concentration of this contaminant can be decreased below 1 ppmv with sodium and potassium based sorbents [26]. Alkaline earth metals compounds also have been studied for HCl removal [27]. The sorbents can be in the form of oxide, hydroxide or carbonate, and the cleaning reactions generate a metal chloride, as illustrated in reactions (2) - (4). The operating temperatures should be kept below 650 °C to avoid the evaporation of alkali chlorides above the ppmv level.

$$Na_2O + 2HCl \rightarrow 2NaCl + H_2O \quad (2)$$

$$NaOH + HCl \rightarrow NaCl + H_2O \quad (3)$$

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O \quad (4)$$

Weinell et al. investigated $Ca(OH)_2$ and $CaCO_3$ for HCl removal in the temperature range 60–1000 °C. Above 200 °C, HCl conversion appeared independent of the water concentration. The sorption capacity of both sorbents showed a maximum at 550 °C with a sorption capacity exceeding 90% for $Ca(OH)_2$ and about 25% for $CaCO_3$ [28]. A similar trend was observed by Li et al. when testing sorbents made from natural mineral and alkali compounds [29]. When testing calcium and sodium sorbents, Duo et al. found that the optimum temperature was between 400 and 500 °C. They also observed that, in the temperature range 300–600 °C, the concentration of CO_2 affects HCl sorption by Ca sorbents but not that of Na sorbents [30]. Krishnan et al. developed sorbents using nahcolite powder and bentonite or sodium silicate binders. When tested in a fixed bed reactor at 300 °C with 1750 ppm HCl and a space velocity of 3000 h^{-1}, HCl concentration decreased below 1 ppm and the maximum chloride content was 55 wt% [31]. A $NaAlO_2$ sorbent prepared by Ohtsuka et al. reduced HCl in an air-blown gasification gas from 200 ppm to less than 1 ppm at 400 °C. The sorption capacity decreased when more than 200 ppm H_2S was added to the simulated gas [32]. A large body of work was performed by Dou et al., who developed sorbents based on $NaHCO_3$, $Mg(OH)_2$, $Ca(OH)_2$, capable of reducing HCl level to less than 1 mg/m^3 up to 550 °C [33]. The same author developed also other sorbents [34,35], and studied the distribution of chlorine in the bed and found that at breakthrough, the inlet of the bed was nearly saturated while the outlet contained less than 2 wt % [36].

Most of earlier research activities have focussed on the development of high temperature sorbents, and only a limited amount of knowledge is available on the possible interactions between sorbents and biosyngas main compounds. Moreover, experiences with operating high temperature gas cleaning systems have hardly been reported in literature. This paper advances present knowledge on high temperature gas cleaning by investigating, under operating conditions reproducing those of a real system, the catalytic activity of commercially available sorbents towards reactions involving biosyngas main components. Moreover, the paper presents some of the results obtained with the integrated biomass gasifier SOFC pilot plant built within the Horizon2020 project “Flexifuel-SOFC”. The scope of this study was limited to the interactions between the sorbents and biosyngas main compounds and does not cover the effects that biosyngas contaminants such as tar might have on these processes.

To the best of the author knowledge, there are no studies in literature investigating the catalytic activity of high temperature sorbents towards reaction involving biosyngas main components. Moreover, results of pilot systems adopting high temperature gas cleaning unit tests are not available in literature due to the limited number of these systems and to the difficulty of carrying out measurements in tar-containing biosyngas. Hence, only a limited comparison with existing knowledge is possible. The insights presented are expected to help the further development of high temperature gas cleaning sorbents and units, and the commercialisation of biomass gasification-based energy conversion systems. Moreover, the detailed explanation of the equipment used and methodology followed to measure contaminants concentration in real biosyngas is expected to substantially help the researchers involved in similar activities.

2. Methodology

Within the European Union's Horizon 2020 project “FlexiFuel-SOFC”, aiming at the development of a highly efficient and fuel flexible biomass gasifier solid oxide fuel cell micro combined heat and power system, HyGear and TU Delft were responsible for the design of the high temperature gas cleaning unit (GCU), while TU Delft led the testing of the GCU. The approach followed is presented in Fig. 1. The first step to design the gas cleaning unit was to characterize the biosyngas quality and the tolerance limits of the solid oxide fuel cell. The second step was to identify from literature and previous experience sorbents and catalysts available, and to determine suitable operating conditions. Thermodynamic equilibrium calculations were used to establish the GCU operating windows in terms of temperature allowing to achieve the cleaning target values, and of steam content required to avoid carbon deposition. The results of the first two steps can be found in a previous work, where a detailed analysis of the tar species generated in the gasification process is also presented [37]. A series of

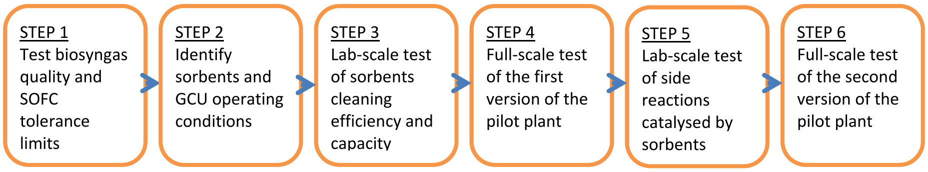

Fig. 1. Representation of the step-wise approach followed for the GCU development.

commercially available sorbents based on Na_2CO_3 and K_2CO_3 for HCl, and ZnO and CuO for H_2S removal were then screened for cleaning efficiency and sorbent capacity and a first design of the GCU vessel was carried out as third step. A first version of the full-scale pilot plant built within the project was tested in the fourth step. Following the lessons learnt during the operation of the pilot plant, the fifth step consisted in investigating with lab-scale tests if the selected sorbents were catalytically active for side reactions that might occur in the GCU under operating conditions simulating those of the real system. Ultimately, the sixth step involved the testing of an improved version of the full-scale pilot plant, modified according to the results obtained in the previous steps.

This paper presents the results of the last two steps of the process and focuses exclusively on the interactions between sorbents and main gas components (lab-scale tests) and on the assessment of the sorbents selected in terms of residual contaminant concentration (pilot plant tests). The paper does not cover issues related to tar, despite these compounds might interact with HCl and H_2S sorbents affecting the cleaning performance, the interaction of the sorbents with the main gas compounds, and the overall operation of the gas cleaning unit. Therefore, tar measurements results are not reported in this manuscript.

The catalytic activity of the selected commercial sorbent, K_2CO_3-based, was analysed by feeding simulated biosyngas (51.5% H_2O, 15.2% CO, 4.7% CO_2, 2.4% CH_4, 8.1% H_2 and 18.0% N_2 in volume) through the sorbent bed consisting of 177 g of the sorbent. First, a blank test was done with Al_2O_3 beads to verify that the observed side reactions were indeed being catalysed by the K_2CO_3 sorbent. Second, the effect of temperature between 350 and 450 °C, and of biosyngas steam content between 40.8 vol% and 56.1 vol% were investigated. The amount of liquid water injected was varied while keeping constant the flow rates of the other gas species; as a consequence, also the space velocity changed between 1065 and 1438 h^{-1}. Last, the space velocity was varied between 150 h^{-1} and 750 h^{-1} by changing the gas flow rate and the effect of this variable on the side reactions was studied. The space velocity was calculated as the ratio between the total gas flow rate at normal conditions and the section of the reactor's volume hosting the sorbents. The blank test with Al_2O_3 was performed only at 400 °C, with a SV of 150 h^{-1} and a steam content of 51.5% in volume.

Similarly, a combination of a commercial ZnO sorbent (158 g) for coarse sulphur removal, with an additional commercial ZnO–CuO sorbent acting as guard bed (47 g), was used to study the catalytic reactions occurring in the sorbent bed by monitoring the changes in the outlet gas composition when simulated biosyngas was fed into the reactor. The effect of temperature in the interval 200–425 °C was investigated. Table 1 presents a summary of the operating conditions of the lab-scale tests performed.

Lastly, the potassium-based sorbent and the zinc oxide sorbent with copper oxide guard bed where tested in the pilot plant built at BIOS Bioenergiesysteme in Graz, Austria. For the scope of the test, poplar chips and miscanthus pellets were used as fuel for their high content of sulphur and chlorine compared to wood chips or wood pellets. The HCl and H_2S cleaning reactors were operated at approximately 400 °C and the residual contaminant concentrations were measured to monitor the proper operation of the gas cleaning unit. The gas composition before and after the reactors was also measured to verify the occurring of side reactions.

2.1. Setup and equipment

2.1.1. Lab-scale tests

A tubular stainless steel reactor with an inner diameter of 4 cm and a height of 50 cm was used for the lab-scale tests. Fig. 3 shows the P&ID of the setup and a picture of the reactor without insulation. A distributor plate at the bottom of the reactor held the sorbent in position. A heating wire was wrapped on the outer wall of the reactor, and on the inlet and outlet pipes. The heating wire is controlled by a thermocouple inserted into the sorbent bed. An additional thermocouple free to move vertically along the central axis of the reactor was used to monitor the bed temperature. The reactor was closed at the top with a flange sealed using a graphite gasket. Glass wool and vermiculite were used for insulating the reactor. Once heated, the reactor presented a temperature gradient along the height of the sorbent bed. Therefore before starting with the actual test, the effects of temperature set point and gas flow rates on this gradient were carefully assessed.

The flow rates were regulated using mass flow controllers Bronkhorst EL-FLOW F201C (Bronkhorst, The Netherlands). Liquid water was injected with a peristaltic pump BT100-2J (Longer Precision Pump Co., China). The temperature of the pipe where the liquid water was injected was kept at 125 °C. A ceramic cartridge was inserted inside the stainless steel pipe to help the dispersion and evaporation of the liquid water.

The side reactions occurring in the reactor were evaluated by analysing the outlet gas composition using a microGC Agilent 490 with a CP-Molsieve 5 Å capillary for measuring CO, H_2, N_2 and CH_4 and a PoraPlot U capillary for measuring CO_2 (Agilent, USA). Before reaching the microGC, the gas was passed through a condenser and a desiccator containing silica-gel to remove the moisture contained in the gas. The outlet flow rate was back-calculated from the inlet N_2 flow rate and the N_2 outlet concentration measured with the microGC. This was then used to calculate the flow rates of H_2, CO, CO_2 and CH_4.

2.1.2. Pilot plant tests

The pilot plant consisted of three sections: 1. a fixed-bed updraft gasifier coupled with a 2-stage gas burner and a hot water boiler; 2. the gas cleaning unit consisting of a ceramic filter, an HCl removal reactor, an H_2S removal reactor and a tar reformer; 3. a SOFC system for electricity production and off-gas heat recovery. A suction fan downstream the SOFC off-gas heat recovery section was used to extract part of the biosyngas via a side stream through the gas cleaning unit, while the remaining biosyngas gas was burned in the burner to produce hot water in the boiler. The cleaned biosyngas was fed to the SOFC. Hot off-gases from the SOFC-system were partly used to heat the GCU, and then supplied to the heat recovery section. Fig. 2 shows a schematic representation of the system. More details of the pilot-scale system can be found in the presentations given during the final workshop of FlexiFUel-SOFC

Table 1
Summary of the lab-scale tests performed and of the operating conditions.

Test	Sorbent	Gas flow rate (NmL/min)	Gas composition (vol%)	Space velocity (h^{-1})	Temperature (°C)	Steam content (vol %)
Side reactions in HCl-cleaning reactor	K_2CO_3	650	51.5 H_2O	150	350–450 in 25 °C steps	56.1
	177 g	1300	15.2 CO	300		51.5
	Extruded ring 5 × 2.5 mm	1950	4.7 CO_2	450		47.0
		2600	2.4 CH_4	600		40.8
		3250	8.1 H_2	750		
Side reactions in H_2S-cleaning reactor	ZnO	3000	18.0 N_2	1000	200–425 in 25 °C steps	51.5
	158 g					
	Extrudates 4 mm					
	+					
	ZnO–CuO 47 g Tablets 5 × 3 mm					

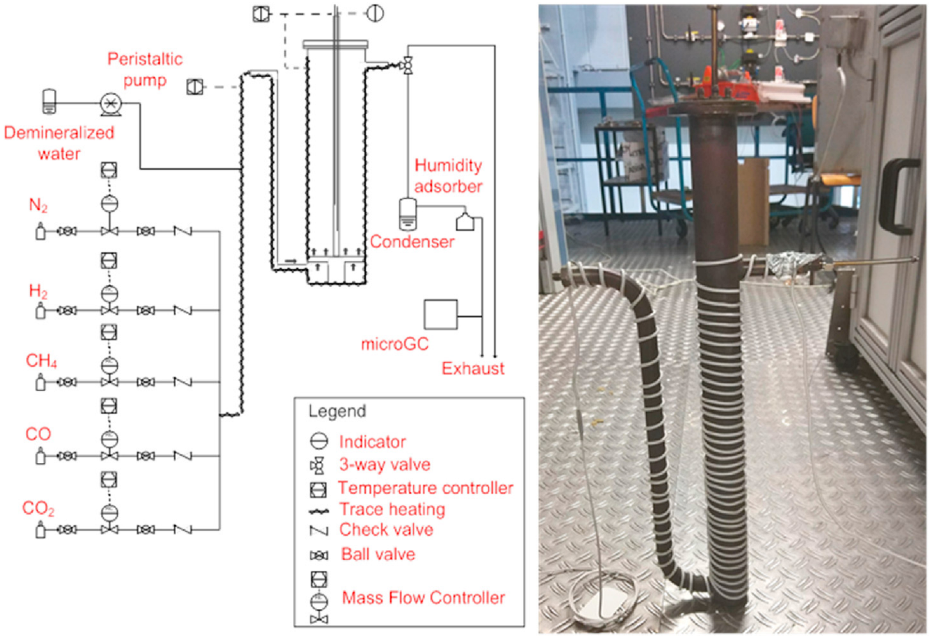

Fig. 2. Schematic representation of the second version of the FlexiFuel-SOFC system [39].

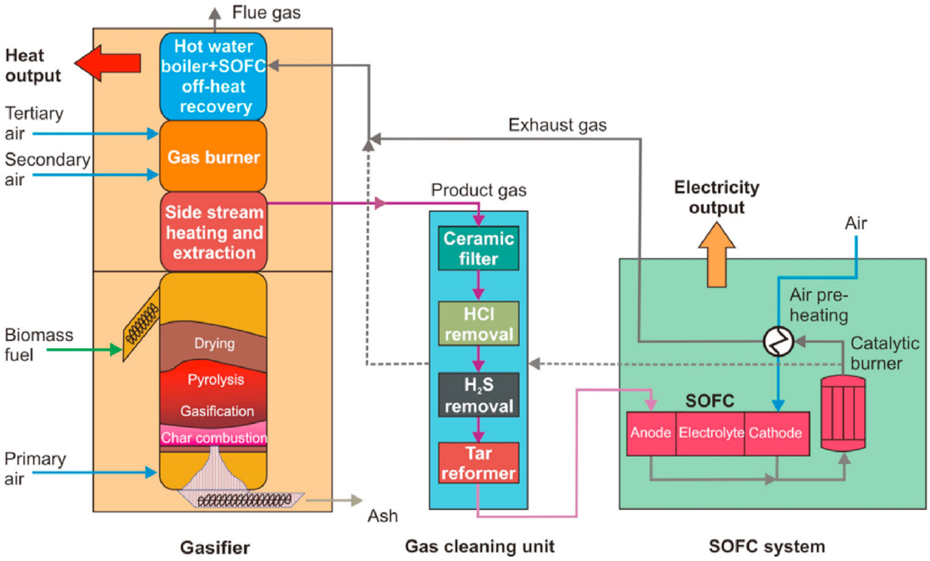

Fig. 3. P&ID of the setup used in the lab-scale tests and a picture of the reactor with the trace heating wire.

project. The documents are available for download on the project website [38].

It is important to mention that the system operates below atmospheric pressure; therefore, some expedients were necessary to prevent air from entering the system and to extract the gas from the system piping.

The residual contaminants concentrations were measured at the end of the GCU. Hydrogen chloride was measured also downstream the HCl cleaning reactor, while hydrogen sulphide downstream the H_2S cleaning reactor. The sampling port was equipped with a high temperature ball valve. The sampling train, illustrated in Fig. 4, started with a lift check valve that was connected to the sampling points; the valve was a safety measure to prevent any back flow of air into the system. The gas extracted passed first through a tar filter containing glass wool and kept at 150 °C. The line connecting the sampling point and the tar filter was heated to 350 °C to avoid condensation of water and tar, which might have clogged the line. The temperature of the filter was carefully selected to condense as much tar as possible and at the same time avoiding any cold spot where water could condense since liquid water highly affects the measurement of HCl. After the tar filter, the gas passed through two impinger bottles for wet sampling of the biosyngas followed by an empty bottle to collect water vapour condensing due to biosyngas cooling down while flowing in the piping. The gas passed then through two bottles containing activated carbon and silica gel to remove volatile compounds and further dry the gas, and then it reached the pump. After the pump a three way valve was installed allowing to vary the post processing of the sampled gas. In one direction, the train continued with a rotameter to adjust the flow rate and a flow totalizer to measure the total amount of gas sampled. A pressure and a temperature indicators were positioned before the flow totalizer to measure the gas conditions in order to correct the flow sampled depending on temperature and pressure. In the other direction, after a ball valve, a specific connection to sample the gas using Tedlar® bags was positioned.

Initially, both HCl and H_2S concentrations were measured by wet sampling using two impinger bottles with frit nominal pore size of 100–160 μm (European standard P1). Each bottle was filled with either 30 ml of deionized water for HCl sampling or 30 ml of a NaOH solution for H_2S measurement. However, due to the presence of CO_2 in the gas, the NaOH solution pH quickly decreased and, since H_2S is a weak acid, it did not dissolve in the solution. Therefore, a 2 g/l $Zn(CH_3COO)_2$ solution was used. In this solution, sulphur reacts with zinc forming solid zinc sulphide. The HCl samples collected were analysed by ion chromatography (IC). According to Ref. [40], the zinc acetate solution should be analysed by photometric method following the guideline DIN38405D26. Due to the unavailability of the reactants necessary for the procedure, the liquid samples were analysed using inductively coupled optical emission spectroscopy (IC-OES). However, since ZnS is a solid precipitating on the bottom of the samples, the analysis method does not accurately indicate the sulphur content. Therefore, for H_2S, colorimetric chemical sensors (glass detector tubes) were used (Dräger, Germany). The glass detector tube measurement was performed downstream an FT-IR used to measure the gas composition. This expedient allowed the use of a manual pump to suck the gas through the detector tube since after the FT-IR the gas pressure was above atmospheric pressure. For both contaminants, the inlet concentrations were calculated as the difference between the sulphur and chlorine contained in the fuel and in the ashes remaining after gasification.

2.2. Testing procedure

2.2.1. Lab-scale tests

After having introduced the sorbent in the reactor, the temperature was increased while flushing the reactor with N_2; the gas composition was then changed to simulated biosyngas once the desired temperature was attained. Each test condition was maintained for a minimum of 120 min to reach a steady state condition. During the test, the outlet gas composition was monitored continuously. The tests were not duplicated. However, two testing conditions (K_2CO_3 at 400 °C with SV of 1300 h^{-1} and 3250 h^{-1}) were repeated to verify replicability.

2.2.2. Pilot plant tests

The tightness of the sampling train was checked at the beginning of each sampling procedure. This was done by starting the pump while keeping closed the ball valve of the sampling point and checking if the bubbling in the impinger bottles diminished, thus indicating the removal of the air in the empty volumes of the train. The ball valve was then opened and the gas flow rate was set to approximately 3 NL/min to avoid too vigorous bubbling and liquid being carried over from the first to the second impinger bottle. The gas was sampled for 30 min and, at the end of the sampling procedure, the sampling train, after the tar filer and until the moisture collector (included), was rinsed with de-ionized water. The sampling time was selected based on the expected HCl concentration in the gas and the minimum detection limit of Cl- ions of the chromatograph. The pilot plant system was operated for two days with poplar chips and two days with miscanthus pellets, and for each fuel two measurements were taken. The procedure for H_2S measurement using glass detector tubes was rather straightforward. An empty bottle was placed at the outlet of the FT-IR to collect any condensing moisture that could have affected the measurement by wetting the solid indicator in the glass detector tube. At the outlet

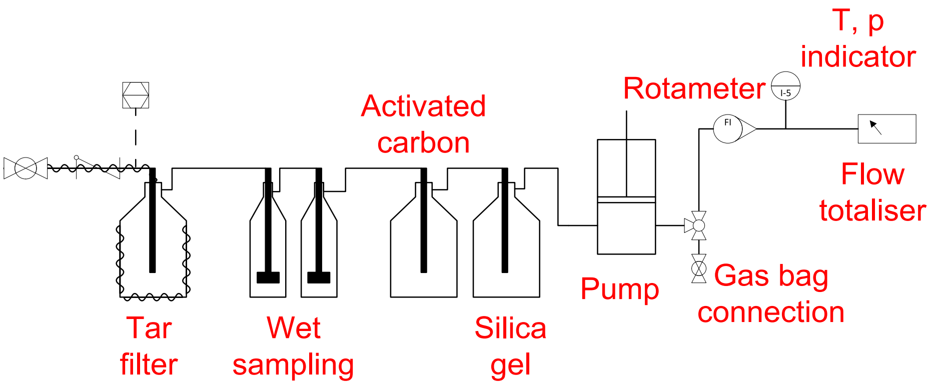

Fig. 4. Sampling train used in pilot-plant tests.

of the bottle, a three-way connection was used to direct the gas to the exhaust and to connect the glass detector tube. Also in this case, two measurements were taken for each fuel. Before each measurement, the gas was passed through the bottle for at least 10 min to be sure that the whole bottle volume was filled with the gas to be sampled.

The main gas composition (CO, CO_2, H_2, CH_4, N_2 and O_2) was measured during a previous series of test runs where wood chips were used as a fuel. Besides a lower content of HCl and H_2S, the different fuel does not affect significantly the main gas composition. Similar to the procedure followed for HCl wet sampling, after having checked the tightness of the sampling train, the ball valve of the sampling point was opened. The gas was first left flowing in the branch of the sampling train where the rotameter was positioned to assure the removal of any air or gas from previous measurements. After having positioned a gas sampling bag, the three-way valve was turned and the ball valve opened. After collection, the gas composition was analysed with a GC-MS (Agilent 3000 Mikro GC). Three bags were collected upstream the HCl cleaning reactor, two bags downstream the H_2S removal reactor and only one bag in between the two reactors.

3. Results and discussion

3.1. Lab-scale tests

Before diving into the results of the side reactions that might be promoted by the gas cleaning sorbents, the results of the reactor characterization are presented. Temperature plays a significant role on reaction rate and it is therefore necessary to know the reactor temperature profile as well as the effect that the operating variables have on it. Therefore, the reactor temperature profile for different temperature set point values, and the temperature of the top of the bed, that is the last part of sorbent bed the gas gets in contact with, were studied using N_2.

Fig. 5 shows the temperature profiles measured along the height of the reactor at different temperature set points when a space velocity of 300 h^{-1} was used. The thermocouple controlling the furnace temperature was kept fixed approximately at the centre of the reactor since preliminary tests showed this position was the one minimizing temperature gradients. At the bottom of the reactor, the temperature was slightly different from the set point, due to the cooling effect of the entering gas. However, by preheating the inlet gas via trace heating wires, placed upstream the reactor inlet, it was possible to keep the temperature gradient within only 15–20 °C. Also the temperature at the top of the reactor was 10–25 °C lower than the set point and this was due to the higher heat losses in the upper part of the reactor. The difference between set point and reactor bottom or top temperature increased when the temperature set point was increased. Fig. 6 gives more insights about the bed top temperature and the effect of the gas flow rates. When the space velocity was increased, also the temperature of the top part of the sorbent bed increased. The same behaviour was observed for the average sorbent bed temperature. However, when the temperature of the bed was set to 450 °C, doubling the space velocity resulted in a decrease of the top part of the bed. This might have been caused by an inaccuracy in the measurement. The insights gained with the reactor characterization tests were taken into account when analysing the results of the sorbents catalytic activity.

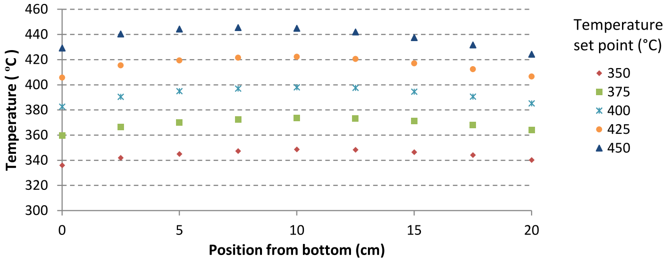

Fig. 5. Temperature profiles measured along the height of the reactor at different temperature set points.

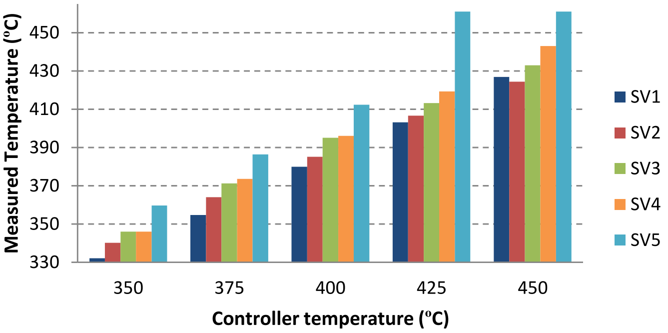

Fig. 6. Temperature measured at the top of the sorbent bed as a function of the space velocity and the temperature set point (SV1 = 150 h^{-1}, SV5 = 750 h^{-1}).

Fig. 7 shows the result of the first test performed, that is the measurement of the gas composition at the reactor outlet when activated alumina beads where placed in the reactor and when K_2CO_3 was present. The gas composition expected at the reactor outlet if thermodynamic equilibrium was reached is also presented in the graph. There was a slight difference between set and inlet measured flow rates, which might have been caused by calibration errors of the mass flow controllers and/or of the micro GC. The findings of the study are however not affected by this minor inaccuracy. The comparison between inlet and equilibrium values gives an indication of the possible reactions occurring, which are water gas shift and methanation. From the outlet flow rates measured when Al_2O_3 was present, it is clear that the gas did not go through any significant reaction. In fact, the decrease in CO and the increase in H_2 and CO_2, shows only a minimal occurring of the WGS reaction. The methane flow rate remained unchanged between inlet and outlet, thus indicating the complete absence of methanation. When K_2CO_3 was present, there was a clear decrease in CO flow rate, that was almost halved from its inlet amount. Accordingly, the flow rates of CO_2 and H_2 almost doubled. The catalytic action of potassium carbonate towards water gas shift reaction was evident, but the outlet flow rates were far from the equilibrium values. Indeed, also with K_2CO_3, the methane flow rate remained unchanged, thus

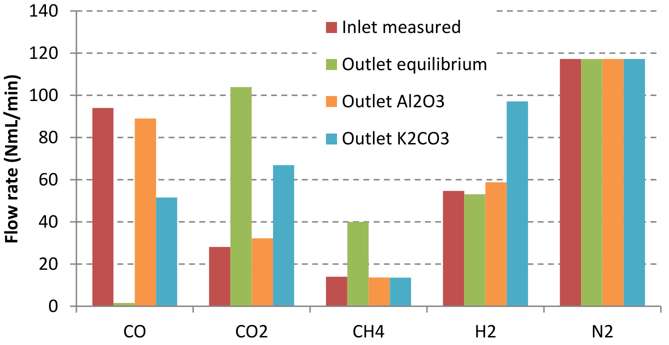

Fig. 7. Gas flow rates experimental results measured at SV of 150 h^{-1} and 400 °C, and equilibrium composition.

Table 2
Comparison between equilibrium and measured flow rate in the presence of K_2CO_3 for different temperatures and a SV of 650 h^{-1}.

Flow rate (NmL/min)	350 °C		400 °C		450 °C	
	measured	equilibrium	measured	equilibrium	measured	equilibrium
H_2	62.6	29.4	97.1	53.2	133.8	85.6
N_2	117.3	117.3	117.3	117.3	117.3	117.3
CO	84.4	0.5	51.6	1.6	14.8	4.5
CH_4	13.3	46.2	13.5	40.0	13.4	31.2
CO_2	33.4	98.8	67.0	103.9	101.9	109.9

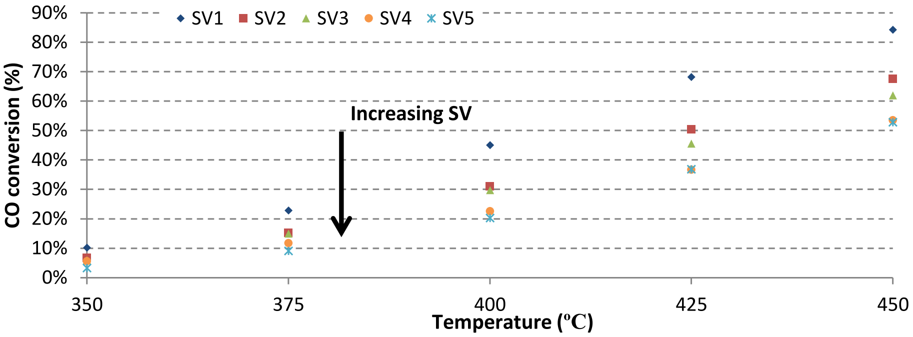

Fig. 8. Carbon monoxide conversion in the presence of K_2CO_3 as a function of temperature and space velocity.

suggesting that potassium carbonate is not a catalyst for the methanation reaction. The occurring of the WGS reaction caused also a temperature increase in the reactor.

After having noticed the catalytic effect of K_2CO_3 on the WGS reaction, the effect of sorbent temperature was investigated. Table 2 compares the measured outlet flow rates and the values expected if thermodynamic equilibrium condition was achieved at the three temperatures. The CO flow rate expected if thermodynamic equilibrium is achieved increases with increasing temperature, since the WGS reaction is exothermic and is therefore favoured at lower temperature. However, the measured values show the opposite trend. This is due to the fact that the WGS reaction was not at equilibrium but was kinetically limited and an increase in temperature accelerated the reaction, thus converting more CO into CO_2 and H_2. Even at 450 °C, K_2CO_3 was not catalytically active for methane formation.

To better illustrate the influence of sorbent temperature, space velocity and steam content, the conversion of carbon monoxide in the different testing conditions was calculated. Fig. 8 shows the effects of the first two variables. As previously mentioned, the WGS reaction rate increases by increasing the sorbent temperature, thus resulting in a higher CO conversion. Conversely, when the space velocity is increased, the conversion decreases since the contact time of reactants and catalyst decreases. The effect of space velocity is more dominant at higher temperatures, with the CO conversion decreasing from 84% to 53% at 450 °C when the space velocity is quintuplicated. The results of the reactor characterisation test showed that at higher space velocities, the temperature of the top part of the sorbent was higher. Since the residence time is not sufficient for the gas composition to reach thermodynamic equilibrium, an increase in temperature results in a higher reaction speed, thus an increase in the CO conversion should be expected. Therefore, the values presented in Fig. 8 are influenced by this effect and, as a consequence, we could expect CO conversion slightly lower than the one measured if the space velocity was not affecting also the reactor temperature.

To study the influence of biosyngas steam content on the WGS reaction, a test was carried out at 400 °C with a space velocity of 1300 h^{-1}. The results presented in Table 3 show that steam has only a minimal effect on the carbon monoxide conversion. This was possibly due to the fact that the steam flow rate was always more than double the stoichiometric amount necessary for converting the carbon monoxide flow rate. The test was not carried out keeping the total flow rate constant and, by increasing the steam content, also the total flow rate increased. As a consequence, also the space velocity raised. From the previous results, it was evident that a higher space velocity resulted in a lower CO conversion, while in this case the opposite effect was observed. This behaviour was caused by the higher amount of steam that pushed the reaction towards the products.

Table 4 compares the equilibrium and the measured outlet flow rates at different temperatures when ZnO–CuO was present in the reactor. Also in this case, the sorbent appeared catalytically active towards the WGS reaction. This material is in fact indicated in literature as a suitable low temperature catalyst for this reaction [41]. Similar to the case of K_2CO_3, the sorbent was not catalytically active for methane formation reaction and the measured outlet compositions were far from the expected equilibrium compositions. However, this was only partially due to the incomplete WGS reaction and to the largest extent to the non-occurrence of methane formation. In fact, if the presence and the formation of methane are neglected, the CO equilibrium outlet flow rate is 15.6 NmL/min at 350 °C and 25.9 NmL/min at 400 °C, while the measured flow rates were 24.4 NmL/min and 29.9 NmL/min. Interestingly, in the case of ZnO–CuO sorbent, the CO conversion as a function of temperature presented a maximum around 350 °C, as shown in Fig. 9. Below this temperature, the effect of temperature on the reaction kinetics was

Table 3
Carbon monoxide conversion in the presence of K_2CO_3 as a function of steam flow rate.

Inlet tot. flow rate (NmL/min)	1065	1189	1300	1438
Steam content (vol%)	40.8%	47.0%	51.5%	56.1%
H_2O/CO ratio	2.2	2.8	3.4	4.1
CO conversion (%) (CO_{in}-CO_{out})/CO_{in}	27.5%	28.7%	29.0%	30.5%

Table 4
Comparison between equilibrium and measured flow rate in the presence of ZnO—CuO at different temperatures.

Flow rate (NmL/min)	Temperature							
	350 °C		375 °C		400 °C		425 °C	
	Meas.	Equil.	Meas.	Equil.	Meas.	Equil.	Meas.	Equil.
H_2	670.3	135.8	669.2	185.1	665.1	244.9	652.3	314.7
N_2	568.2	568.0	568.2	5678.0	568.2	568.0	568.2	568.0
CO	24.4	2.1	26.2	3.9	29.9	7.0	42.7	12.1
CH_4	71.9	206.0	72.0	193.2	72.0	177.5	72.1	158.7
CO_2	528.4	445.4	521.9	456.3	524.9	468.9	509.6	482.5

dominant, thus resulting in an increasing conversion of carbon monoxide. However, above 350 °C, the CO conversion started decreasing. The effect of temperature on the reaction thermodynamics dominated over its effect on the kinetics since WGS reaction is exothermic. The catalytic activity of ZnO—CuO sorbent was significantly higher than the one showed by the K_2CO_3: at 400 °C and space velocity of 1000 h^{-1} a CO conversion of 93% was achieved. At the same reactor temperature and even lower SV (650 h^{-1}), the CO conversion promoted by the K_2CO_3 was only of 45%.

To the best of the authors knowledge, this study represents the first attempt to investigate whether sorbents used for biosyngas high temperature cleaning interact with the gas main components. Therefore, the results here illustrated are extremely important and helpful for the design of high temperature GCU and in general for biomass gasification based systems. In fact, the observed catalytic activity of K_2CO_3 and the associated temperature increase caused by the catalysed WGS reaction should be considered when designing the reactors and the system. Moreover, the higher catalytic activity of ZnO—CuO towards the shift reaction and therefore the larger amount of heat released, suggests the placing of the HCl removal reactor upstream the H_2S removal reactor since the temperature increase will promote the Zn evaporation: above 450 °C the concentration of gaseous Zn is above the ppbv value [37]. The occurring of the exothermic WGS reaction should be carefully considered when planning the thermal management and the operating temperature of the GCU. The lack of catalytic activity of both sorbents toward the methanation reaction is also an important result due to the high exothermic nature of this reaction that could have also affected the safe operation of the reactors and could have strongly influenced the overall system heat management.

The change in main gas composition occurring over the GCU due to the catalytic activity of these sorbents towards the WGS reaction can also affect the other components of the system, such as the tar reformer or the SOFC where, due to the higher operating temperature, the RWGS reaction is expected to take place. Furthermore, while K_2CO_3 is not expected to react with H_2S, the ZnO—CuO sorbent can react with HCl forming CuCl and $ZnCl_2$. These compounds have low melting point and the limit to avoid catalyst poisoning are on the order of 1 ppb [41]. Nonetheless, these are information obtained by equilibrium calculations and should therefore be verified with experimental tests to understand the kinetic of these reactions.

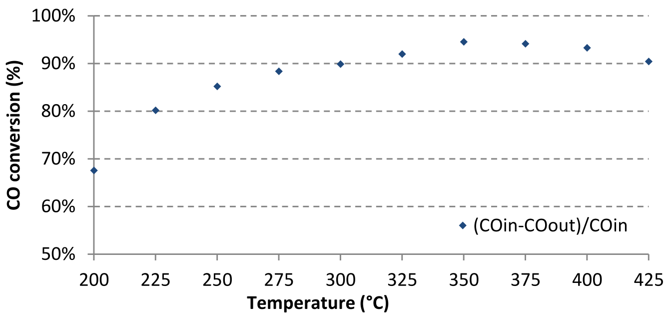

Fig. 9. Carbon monoxide conversion with ZnO—CuO as a function of temperature.

As part of future work, it is suggested to further study the long term catalytic activity towards the WGS reaction since the operating temperature might affect the structure of the sorbents and therefore its activity. As an example, Cu might sinter and the catalytic activity could decrease over time. Moreover, the catalytic activity should be monitored while the sorbents are being used to remove the contaminants. Furthermore, the interactions between HCl and H_2S sorbents and tar compounds should be carefully studied since these compounds might affect the cleaning performance, the interaction of the sorbents with the main gas compounds, and the overall operation of the gas cleaning unit.

3.2. *Pilot plant tests*

The results of the gas sampling to measure the main gas composition are presented in Fig. 10. For the sampling points upstream the HCl removal reactor and downstream the H_2S removal reactor the values are averages of the gas bags collected. As expected, in the HCl removal reactor the WGS reaction occurred, as visible from the increase in the concentrations of hydrogen and carbon dioxide and the decrease in carbon monoxide. This was also confirmed by an increase in temperature of roughly 100 °C measured by the thermocouples positioned inside the reactor. No significant reaction involving the main gas components occurred in the H_2S removal reactor. A minor decrease in the volumetric percentages of CO_2 and an increase in the CO content were observed. However, the change in gas composition was small and could be ascribed to measurement inaccuracies.

Table 5 shows the concentration of HCl and H_2S expected in the biosyngas after the ceramic filter calculated from the difference between sulphur and chlorine content in the feedstocks and in the ashes, and the amount measured by wet sampling and glass tubes

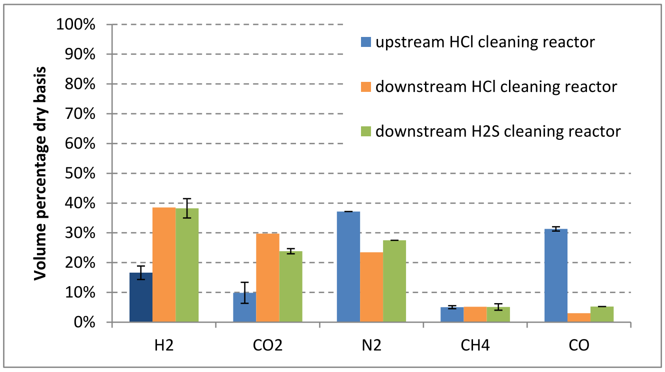

Fig. 10. Main gas composition measured in the pilot plant using wood chips as fuel.

Table 5
HCl and H_2S concentrations measured after the cleaning stage and calculated from fuel and ash analysis.

	HCl concentration (ppmv d.b.)		H_2S concentration (ppmv d.b.)	
	Poplar chips	Miscanthus pellets	Poplar chips	Miscanthus pellets
After filter (calculated)	32.1	126.3	129	183
After HCl reactor	0.2	2.5 ± 0.3		
After H_2S reactor			0.2 ± 0.1	0.2 ± 0.1
After GCU	0.3 ± 0.1	2.2 ± 0.1	0.2 ± 0.1	0.5 ± 0.1

during the experimental campaign. The sorbents were able to decrease the contaminants content below the design values of 5 ppmv HCl and 1 ppmv H_2S with both feedstocks, in accordance with the calculation of Westmoreland et al. and the experiments of Sanchez-Hervas et al. for H_2S removal [11,21]. The residual HCl concentration with poplar chips as feedstock was lower than in the case of miscanthus pellets. This might be due to the lower chlorine content of poplar, or to the lack of the moisture collector in the sampling train. Moreover, it might appear that in case of miscanthus as feedstock, the HCl residual concentration further decrease when the biosyngas passed through the rest of the gas cleaning unit, that is through the H_2S removal reactor and the tar reformer. However, despite it is possible that HCl reacted with the sorbents and catalyst in the reactors downstream, the difference between the residual HCl concentration at the HCl reactor outlet and at the GCU outlet is within the accuracy of the measurement. Similarly, the H_2S residual concentration after the GCU appeared higher than after the H_2S reactor, but also in this case the difference is within the accuracy of the measurement.

It is important to mention that only sulphur in the form of H_2S was measured. However, a certain percentage of sulphur might have been present in other sulphur compounds. Measurements of the flue gas composition downstream the catalytic afterburner of the SOFC system revealed SO_2 concentrations which were higher than those which would correspond to the combustion of the sub-ppmv H_2S levels measured downstream the gas cleaning unit. Therefore, a detailed study of the sulphur compounds present in biosyngas is suggested as future work.

Summarising, the lab-scale and the pilot plant tests performed indicated that.

- Potassium carbonate appeared catalytically active towards the water gas shift reaction in both the lab-scale and the pilot plant tests.
- Despite the WGS reaction is exothermic, higher temperatures resulted in a higher CO conversion since the residence time was not sufficient for the gas composition to reach thermodynamic equilibrium.
- The zinc-copper oxides sorbent catalytic activity towards the WGS reaction appeared significantly higher than that of potassium carbonate (double, despite a higher SV).
- Both sorbents appeared inactive towards the methanation reaction.
- The sorbents, operated at 400 °C in the pilot plant, were able to meet the target values of 1 ppmv for H_2S and 5 ppmv for HCl.
- Pilot plant tests showed that sulphur might be present in other forms than H_2S to a certain extent which might not get removed by the sorbents selected.

4. Conclusion

At present, there are not many systems employing high temperature gas cleaning and most of earlier research activities have focussed on the development of high temperature sorbents. To advance present knowledge on this topic, this work investigated the catalytic activity of K_2CO_3 as HCl sorbent and ZnO–CuO as H_2S sorbent towards reactions involving biosyngas main components (e.g., the water gas shift and the methanation reactions). A specially-built lab-scale reactor was used to investigate the sorbents catalytic activity under operating conditions simulating those of the pilot plant. Moreover, the ability of these sorbents to reduce HCl and H_2S content below 5 ppmv and 1 ppmv, respectively, was tested in the integrated biomass gasifier SOFC pilot plant built within the Horizon2020 project “Flexifuel-SOFC”.

Both sorbents appeared to be catalytically active towards the water gas shift reaction, with ZnO–CuO beign significantly more active. The occurring of the WGS reaction caused an increase in the reactor temperature. Conversely, none of the sorbents resulted catalytically active towards the methanation reaction. As part of future work, it is suggested to study the long term catalytic activity of these sorbents and how this is affected by the adsorption of the contaminants. When tested in the pilot plant, the sorbents were able to meet the target values of 1 ppmv for H_2S and 5 ppmv for HCl. Such low concentrations of contaminants were measured in tar-containing biosyngas below atmospheric pressure thanks to the sampling train and methodology explained in this paper. A detailed study of the sulphur compounds present in biosyngas is suggested as future study in order to be able to further improve the sulphur removal unit.

In the lab-scale tests with the potassium carbonate sorbent, higher temperatures resulted in higher CO conversions, even if the water gas shift is an exothermic reaction, thus indicating that under the tested conditions the reaction is kinetically limited. Accordingly, at higher space velocities the CO conversion was lower, while steam appeared to have only a minimal effect, probably due to the large concentration present in the simulated biosyngas. The CO conversion with the zinc-copper oxides sorbent as a function of temperature presented a maximum around 350 °C, in accordance with the exothermic nature of the water gas shift reaction.

The results here illustrated are considered extremely helpful for the design of high temperature GCU and are expected to help the further development of biomass gasification-based energy conversion systems.

CRediT authorship contribution statement

Alessandro Cavalli: Conceptualization, Methodology, Experiments, Visualization, Writing- Reviewing and Editing. **Pradeep Chundru:** Conceptualization, Methodology, Experiments. **Thomas Brunner:** Conceptualization, Methodology, Reviewing. **Ingwald Obernberger:** Conceptualization, Methodology, Reviewing. **Ilaria Mirabelli:** Conceptualization, Methodology, Reviewing. **Robert Makkus:** Conceptualization, Methodology, Reviewing. **Purushothaman Vellayani Aravind:** Supervision, Reviewing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

This research is partially supported by the project “FlexiFuel-SOFC”. The project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No. 641229. The authors acknowledge Anamaria Beatrice Teodoru for the help given in carrying out this work. The authors want to acknowledge all the project partners for the good collaboration had, and in particular the team from BIOS Bioenergiesysteme for the help in carrying out the pilot plant tests.

References

[1] A.O. Omosun, A. Bauen, N.P. Brandon, C.S. Adjiman, D. Hart, Modelling system efficiencies and costs of two biomass-fuelled SOFC systems, J. Power Sources 131 (2004) 96–106, https://doi.org/10.1016/j.jpowsour.2004.01.004.

[2] R. Toonssen, S. Sollai, P.V. Aravind, N. Woudstra, A.H.M. Verkooijen, Alternative system designs of biomass gasification SOFC/GT hybrid systems, Int. J. Hydrogen Energy 36 (2011) 10414–10425, https://doi.org/10.1016/j.ijhydene.2010.06.069.

[3] P.V. Aravind, T. Woudstra, N. Woudstra, H. Spliethoff, Thermodynamic evaluation of small-scale systems with biomass gasifiers, solid oxide fuel cells with Ni/GDC anodes and gas turbines, J. Power Sources 190 (2009) 461–475, https://doi.org/10.1016/j.jpowsour.2009.01.017.

[4] P.J. Woolcock, R.C. Brown, A review of cleaning technologies for biomass-derived syngas, Biomass Bioenergy 52 (2013) 54–84, https://doi.org/10.1016/j.biombioe.2013.02.036.

[5] J.F.B. Rasmussen, A. Hagen, The effect of H2S on the performance of Ni-YSZ anodes in solid oxide fuel cells, J. Power Sources 191 (2009) 534–541, https://doi.org/10.1016/j.jpowsour.2009.02.001.

[6] J.P. Ouweltjes, P.V. Aravind, N. Woudstra, G. Rietveld, Biosyngas utilization in solid oxide fuel cells with Ni/GDC anodes, J. Fuel Cell Sci. Technol. 495 (2006) 3, https://doi.org/10.1115/1.2349535.

[7] P.V. Aravind, W. de Jong, Evaluation of high temperature gas cleaning options for biomass gasification product gas for Solid Oxide Fuel Cells, Prog. Energy Combust. Sci. 38 (2012) 737–764, https://doi.org/10.1016/j.pecs.2012.03.006.

[8] Y. Zeng, S. Kaytakoglu, D. Harrison, Reduced cerium oxide as an efficient and durable high temperature desulfurization sorbent, Chem. Eng. Sci. 55 (2000) 4893–4900, https://doi.org/10.1016/S0009-2509(00)00117-2.

[9] X. Meng, W. de Jong, R. Pal, A.H.M. Verkooijen, In bed and downstream hot gas desulphurization during solid fuel gasification: a review, Fuel Process. Technol. (91) (2010) 964–981, https://doi.org/10.1016/J.FUPROC.2010.02.005.

[10] N. Abdoulmoumine, S. Adhikari, A. Kulkarni, S. Chattanathan, A review on biomass gasification syngas cleanup, Appl. Energy 155 (2015) 294–307, https://doi.org/10.1016/j.apenergy.2015.05.095.

[11] P.R. Westmoreland, D.P. Harrison, Evaluation of candidate solids for high-temperature desulfurization of low-Btu gases, Environ. Sci. Technol. 10 (1976) 659–661, https://doi.org/10.1021/es60118a010.

[12] S.S. Tamhankar, M. Bagajewicz, G.R. Gavalas, P.K. Sharma, Flytzani-Stephanopoulos M, Mixed-oxide sorbents for high-temperature removal of hydrogen sulfide, Ind. Eng. Chem. Process Des. Dev. 25 (1986) 429–437, https://doi.org/10.1021/i200033a014.

[13] P. Yrjas, K. Iisa, M. Hupa, Limestone and dolomite as sulfur absorbents under pressurized gasification conditions, Fuel 75 (1996) 89–95, https://doi.org/10.1016/0016-2361(95)00204-9.

[14] A.B.M. Heesink, W.P.M. Van Swaaij, The sulphidation of calcined limestone with hydrogen sulphide and carbonyl sulphide, Chem. Eng. Sci. 50 (1995) 2983–2996, https://doi.org/10.1016/0009-2509(95)91133-J.

[15] K.V. Bineesh, D.-K. Kim, M.-I. Kim, D.-W. Park, Selective catalytic oxidation of H2S over V2O5 supported on TiO2-pillared clay catalysts in the presence of water and ammonia, Appl. Clay Sci. 53 (2011) 204–211, https://doi.org/10.1016/j.clay.2010.12.022.

[16] A. Hachimi, L. Vilcocq, C. Courson, A. Kiennemann, Study of olivine supported copper sorbents performances in the desulfurization process in link with biomass gasification, Fuel Process. Technol. 118 (2014) 254–263, https://doi.org/10.1016/j.fuproc.2013.10.001.

[17] W.F.F. Elseviers, H. Verelst, Transition metal oxides for hot gas desulphurisation, Fuel 78 (1999) 601–612, https://doi.org/10.1016/S0016-2361(98)00185-9.

[18] M. Pineda, J.M. Palacios, L. Alonso, E. Garcıa, R. Moliner, Performance of zinc oxide based sorbents for hot coal gas desulfurization in multicycle tests in a fixed-bed reactor, Fuel 79 (2000) 885–895, https://doi.org/10.1016/S0016-2361(99)00218-5.

[19] L. Alonso, J.M. Palacios, E. Garcıa, R. Moliner, Characterization of Mn and Cu oxides as regenerable sorbents for hot coal gas desulfurization, Fuel Process. Technol. 62 (2000) 31–44, https://doi.org/10.1016/S0378-3820(99)00063-6.

[20] B.S. Liu, Z.Y. Wan, Y.P. Zhan, C.T. Au, Desulfurization of hot coal gas over high-surface-area LaMeOx/MCM-41 sorbents, Fuel 98 (2012) 95–102, https://doi.org/10.1016/j.fuel.2012.03.048.

[21] J.M.M. Sánchez-Hervás, J. Otero, E. Ruiz, A study on sulphidation and regeneration of Z-Sorb III sorbent for H2S removal from simulated ELCOGAS IGCC syngas, Chem. Eng. Sci. 60 (2005) 2977–2989, https://doi.org/10.1016/j.ces.2005.01.018.

[22] R.P. Gupta, W.S. O'Brien, Desulfurization of hot syngas containing hydrogen chloride vapors using zinc titanate sorbents, Ind. Eng. Chem. Res. 39 (2000) 610–619, https://doi.org/10.1021/ie990533k.

[23] S. Cheah, Y.O. Parent, W.S. Jablonski, T. Vinzant, J.L. Olstad, Manganese and ceria sorbents for high temperature sulfur removal from biomass-derived syngas – the impact of steam on capacity and sorption mode, Fuel 97 (2012) 612–620, https://doi.org/10.1016/j.fuel.2012.03.007.

[24] G. Buchinger, P. Hinterreiter, T. Raab, S. Griesser, R. Claassen, D.P. Claassen, et al., Operating microtubular SOFCS with hydrogen chloride and hydrogen sulfide containing fuels and synthetic wood gas, J. Fuel Cell Sci. Technol. 3 (2006) 280–283.

[25] A. Cavalli, R. Bernardini, P.V. Aravind, Influence of primary tar and H2S on solid oxide fuel cell anodes in integrated biomass gasifier SOFC systems, 13th Eur. SOFC SOE Forum 2018 (2018) 41.

[26] G.N. Krishnan, R.P. Gupta, A. Canizales, S. Shelukar, R.E. Ayala, Removal of hydrogen chloride from hot coal gas streams, High Temp Gas Clean 1 (1996) 405–414.

[27] W. Wang, Z. Ye, I. Bjerle, The kinetics of the reaction of hydrogen chloride with fresh and spent Ca-based desulfurization sorbents, Fuel 75 (1996) 207–212, https://doi.org/10.1016/0016-2361(95)00242-1.

[28] C.E. Weinell, P.I. Jensen, K. Dam-Johansen, H. Livbjerg, Hydrogen chloride reaction with lime and limestone: kinetics and sorption capacity, Ind. Eng. Chem. Res. 31 (1992) 164–171, https://doi.org/10.1021/ie00001a023.

[29] Y. Li, Y. Wu, J. Gao, Study on a new type of HCl-removal agent for high-temperature cleaning of coal gas, Ind. Eng. Chem. Res. 43 (2004) 1807–1811, https://doi.org/10.1021/ie034217o.

[30] W. Duo, N.F. Kirkby, J.P.K. Seville, J.H.A. Kiel, A. Bos, Den Uil H. Kinetics of HCl reactions with calcium and sodium sorbents for IGCC fuel gas cleaning, Chem. Eng. Sci. 51 (1996) 2541–2546, https://doi.org/10.1016/0009-2509(96)00111-X.

[31] G.N. Krishnan, A. Canizales, R. Gupta, R. Ayala, Development of disposable sorbents for chloride removal from high-temperature coal-derived gases. Adv. Coal-fired power syst. '96 rev. Meet., U.S. DOE, morgantown energy technology center, 1996.

[32] Y. Ohtsuka, N. Tsubouchi, T. Kikuchi, H. Hashimoto, Recent progress in Japan on hot gas cleanup of hydrogen chloride, hydrogen sulfide and ammonia in coal-derived fuel gas, Powder Technol. 190 (2009) 340–347, https://doi.org/10.1016/j.powtec.2008.08.012.

[33] B. Dou, B. Chen, J. Gao, X. Sha, HCl Removal, Chlorine, Distribution in the mass transfer zone of a fixed-bed reactor at high temperature, Energy Fuels 20 (2006) 959–963, https://doi.org/10.1021/ef060018g.

[34] B. Dou, B. Chen, J. Gao, X. Sha, Reaction of solid sorbents with hydrogen chloride gas at high temperature in a fixed-bed reactor, Energy Fuels 19 (2005) 2229–2234, https://doi.org/10.1021/ef050151t.

[35] B. Dou, W. Pan, J. Ren, B. Chen, J. Hwang, Single Yu T-U, Combined Removal of HCl and Alkali Metal Vapor from High-temperature Gas by Solid Sorbents, Energy Fuels 21 (2007) 1019–1023, https://doi.org/10.1021/ef060266c.

[36] B. Dou, J. Gao, S.W. Baek, X. Sha, High-temperature HCl removal with sorbents in a fixed-bed reactor, Energy Fuels 17 (2003) 874–878, https://doi.org/10.1021/ef010294p.

[37] A. Cavalli, A. Fernandes, P.V. Aravind, Thermodynamic analysis of an improved integrated biomass gasifier solid oxide fuel cell micro combined heat and power system, Energy 120945 (2021) 231, https://doi.org/10.1016/j.energy.2021.120945.

[38] FlexiFuel-SOFC n.d.. http://www2.flexifuelsofc.eu/. (Accessed 5 June 2018).

[39] I. Obernberger, T. Brunner, C. Ramerstorfer, M. Kerschbaum, P.V. Aravind, R. Makkus, et al., Operation experience with a novel highly efficient micro-scale CHP system based on fuel-flexible gasification and a SOFC, 27th Eur. Biomass Conf. Exhib (2019) 504–512, https://doi.org/10.5071/27thEUBCE2019-2BO.2.1.

[40] J. Zeisler, M. Kleinhappl, H. Hofbauer, Reliable sampling of impurities in product gas and syngas, 2010, pp. 1–12.

[41] C. Ratnasamy, J.P. Wagner, Water gas shift catalysis, Catal. Rev. 51 (2009) 325–440, https://doi.org/10.1080/01614940903048661.