Experimental Bench-Scale Study of Residual Biomass Syngas Desulfurization Using ZnO-Based Adsorbents

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ABSTRACT: Dry-bed adsorptive desulfurization of biomass-based syngas with a low- to medium sulfur content using ZnO was studied as an alternative to conventional wet-scrubbing processes for a small- to medium-scale biomass-to-liquid process concept. Following laboratory-scale long-term H2S breakthrough experiments in a previous study, desulfurization tests were scaled-up to bench-scale with actual bio-syngas to verify the lab-scale results under more realistic process conditions. A desulfurization unit was constructed and connected to a steam-blown atmospheric pilot-scale fluidized bed gasifier. Two successful 70+ h test campaigns were conducted with H2S removal below the breakthrough limit using full-sized ZnO adsorbent particles. Scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy elemental analysis, and Brunauer–Emmett–Teller (BET) surface area characterization of the fresh and spent adsorbent pellets were performed. SEM micrographs displayed the outward enlarging particle size in the sulfided layer. Characterization showed significant core–shell sulfidation behavior with a few hundred micron-thick sulfided layer leaving the majority of ZnO unutilized. Adsorbents lost most of their porosity in use, which was evident from BET surface area results. Simultaneous COS removal was found possible by the hydrolysis reaction to H2S. Furthermore, evidence of minor chlorine adsorption was found, thus highlighting the need for a dedicated HCl removal step upstream of desulfurization.

1. INTRODUCTION

With the need to shift away from nonrenewable fossil-based energy and fuel sources, biomass gasification combined with Fischer–Tropsch (FT) synthesis is an attractive option for producing liquid transportation fuels from renewable feedstocks. The major challenge in this process is the efficient and low-cost gas ultracleaning to meet the stringent gas purity requirements of downstream synthesis catalysts. Sulfur compounds are considered to have some of the most problematic impurities, which, along with other acid gases, are traditionally removed using wet-scrubbing processes.

In a gasification process, sulfur can be removed in two stages: (A) in situ (in the gasifier) or (B) downstream of the gasifier.1 Calcium-based adsorbents, such as the typical gasification bed materials, limestone (CaCO3), or dolomite (CaCO3·MgCO3), are known H2S adsorbents at gasification conditions, especially in their calcined form.2 Calcium oxide forms a sulfide3

$$\text{CaO} + \text{H}_2\text{S} \rightleftharpoons \text{CaS} + \text{H}_2\text{O} \tag{1}$$

Half-calcined dolomite can form a sulfide

$$\text{CaCO}_3 + \text{H}_2\text{S} \rightleftharpoons \text{CaS} + \text{H}_2\text{O} + \text{CO}_2 \tag{2}$$

Full-syngas desulfurization requires a sufficient Ca/H2S molar ratio and gas–solid contact time, which is not achievable in a typical fluidized bed gasification reactor. According to these reactions, a high steam content is disadvantageous for desulfurization as well. Because of these constraints, in situ desulfurization in fluidized bed gasifiers using calcium-based beds is only found to be useful for partial H2S removal.2,4

| fuel                  | H2S (ppmv) | COS (ppmv) | other organic S-species (ppmv) |
|-----------------------|------------|------------|------------------------------|
| woody biomass         | 20–250     | 0.1–5      | <1                           |
| herbaceous biomass    | 100–500    | 1–20       | <10                          |

The authors estimated syngas exhibits the sulfur content, as presented in Table 1 for a fluidized bed gasifier with in situ partial H2S removal.

The sulfur contents in bio-syngas presented in Table 1 are significantly lower than that for fossil coal and coke gasification. The reducing conditions present in gasification dictate that H2S is the main sulfur species in the gas, with other species being carbonyl sulfide (COS), carbon disulfide (CS2), mercaptan (CH3SH and CH3CH2SH), and thiophene (C6H5S).5 All of these sulfur species are poisons for cobalt- and iron-based FT catalysts because they irreversibly stick to active sites and thus need to be removed to sub-ppmv concentrations before the synthesis step.6

Wet-scrubbing processes have the benefit of potentially removing all acid gases (H2S, COS, and CO2) present in...
syngas in one process. They are highly efficient but suffer from high capital and operating expenditures. The relatively low H₂S concentration in biomass-derived syngas could allow for the cost-effective bulk removal of H₂S by dry-bed adsorption with zinc oxide, as shown in the biomass-to-liquids (BtL) concept in Figure 1. In our previous study, H₂S removal with ZnO in the bio-syngas model was evaluated in lab-scale breakthrough experiments. The conclusion was that with sufficient gas–solid contact time between the reactants, selective H₂S removal is feasible to sub-ppmv concentration.

In this experimental work, the feasibility of zinc oxide as a bulk desulfurization adsorbent for low-sulfur residual biomass-derived gasification syngas was studied. In a continuation to the lab-scale desulfurization experiments in our previous study, the H₂S breakthrough tests in this study were conducted in actual bio-syngas at bench-scale to verify the results in lab-scale and to gain new understanding of desulfurization under more realistic conditions. Additionally, the breakthrough behavior of COS was investigated.

2. DESULFURIZATION IN THE BTL CONCEPT

VTT is developing a BtL plant concept that has investment costs in the range of 200–300 M€ and is suited for “intermediate” scale of 100–150 MW biomass input, so that biomass conversion to FT products can be realized in units that are located close to biomass sources. Heat is integrated to industrial sites or district heating networks, and final refining of FT hydrocarbons into transportation fuels takes place in the existing oil refineries; thus, a double integration benefit is realized. The concept block diagram is shown in Figure 1.

Biomass residues are converted in a dual fluidized bed (DFB) gasifier operated at a low temperature (750–820 °C) and close to atmospheric pressure. The gasifier in the concept utilizes steam and air as fluidizing gases instead of oxygen, eliminating the need to invest in an oxygen plant. Further cost reduction offered by the BtL concept is based on simplified gas cleaning solutions, where only partial CO₂ removal is realized and adsorptive desulfurization replace wet-scrubbing processes.

The spent ZnO adsorbent can either be (A) disposed of or (B) regenerated (on-site or off-site). In the regeneration process, zinc sulfide is converted back into metal oxide by oxidation. However, stable zinc sulfates can be formed under excess oxygen availability which decrease the adsorbent surface area and affect performance negatively. Regeneration of adsorbents add complications to the process. Regeneration is usually performed in air or oxygen, and SO₂ is the main product. SO₂ is a regulated pollutant and has to be converted in the Claus-type process to elemental sulfur. If adsorbent materials can be sourced cheaply, for example, Zn-rich industrial waste streams from steel industry, the economics of nonregenerable desulfurization processes are clearly favored. A solution to the issue with once-through adsorbents, cost-incurring landfilling, or appropriate disposal could be to integrate the spent adsorbent to a zinc smelting plant, as shown in Figure 2.

3. MATERIALS AND METHODS

A bench-scale desulfurization unit was constructed and connected to the bypass stream of a 200 kWth DFB gasification pilot plant. The pilot plant can utilize various biomasses as fuels and steam and air or oxygen as gasification agents. Figure 3 illustrates the plant configuration.
The gasifier consisted of a steam-blown circulating fluidized bed (CFB) gasifier and a bubbling fluidized bed (BFB) oxidizer utilizing air as feed gas. The two reactors were coupled via recycle loops by which bed material circulation between the gasification and combustion sections occurred, thus allowing the bed material to act as a heat carrier. The raw syngas was then led to the sintered metallic filters to remove dust particulates and condensed alkali and halogens. Catalytic autothermal reforming was used to decompose tars and light hydrocarbon gases to CO and H₂ at elevated temperatures.

After the reformer, the gas was cooled to 300 °C, after which the slipstream desulfurization unit was installed. The bench-scale desulfurization unit is described in more detail, as shown in Figure 4A.

The slipstream desulfurization unit consisted of a 5.63 cm inner diameter reactor with two packed beds of lengths 15 cm (upper, bed 1) and 25 cm (lower, bed 2). The resulting L/D ratios were thus for bed 1, 2.7 and for bed 2, 4.4. The volume of bed 1 was 0.373 dm³ and bed 2 was 0.622 dm³. K-type thermocouples were installed inside each bed. The reactor was placed in an 80 cm tall electric furnace. Gas sampling was performed both after the first packed bed and after the second bed to achieve H₂S breakthrough curves for both beds. The unit also included a condenser column with quartz glass Raschig rings and circulating water wash operated by a small peristaltic pump. The condensed water was collected to a tank with a pressure sensor indicating the fluid level. The condenser unit was followed by a condenser tube with a cooling water jacket also connected to the condensate tank. The driving force of the gas from the gasifier was a peristaltic pump by Masterflex.

3.1. Methods. The construction of the desulfurization unit was followed by hot commissioning in a DFB gasification validation test. After commissioning, two noninterrupted week-long gasification test runs, campaign I and II, were conducted with the slipstream unit coupled to the plant and used to study the desulfurization performance of ZnO in bio-syngas.

The desulfurization experiments were performed in conjunction with gasification validation tests at various gasifier setpoints including different fuels and gasification agent settings. During the tests, the CFB gasifier temperature range was between 780 and 830 °C and the steam-to-fuel mass ratio was varied between 0.9 and 1.2. The BFB oxidizer was set at 850−900 °C. The metal filters were operated at a temperature of 670−720 °C, and the reforming unit was operated at 850−950 °C. More details about the gasification, filtration, and reforming test campaigns are available in the report by Kurkela et al. with campaign I denominated as “DFB7/10” and campaign II as “DFB17/17.”

Before each test campaign, the following procedures were performed for the slipstream unit: the peristaltic pump (rpm as a
function of the gas flowrate) was calibrated with N2, the process was leak-tested to an overpressure of 200 mbar, and the furnace was preheated. The gas feeding was started by opening the main inlet valve and starting the peristaltic pump. The flowrate was nonconstant and depended on gas composition, pump tube wear, and gasifier pressure changes. The gas pressure after the reformer and cooler units in the piloting plant was +10–30 mbar above atmospheric pressure, and the suction of the pump caused a small underpressure after the adsorbent reactor. During the run, the operators took Dräger samples from the inlet gas and effluent, adjusted the peristaltic pump speed according to the pressure levels indicated before and after the reactor with the intention to keep flowrate as stable as possible, and emptied the condensate tank at regular intervals. The aimed wet gas flowrate was 25–35 N dm\(^{-3}\) min\(^{-1}\), and the reactor bed temperatures were maintained stable at 400 ± 20 °C during both the campaigns. If gas feeding had to be interrupted, the slipstream unit was flushed with N2 and the reactor was closed-off and maintained at the setpoint temperature. Table 2 summarizes the bed loadings and selected conditions in the two campaigns.

Table 2. Bench-Scale Desulphurization Unit Experimental Conditions and Bed Loadings

| campaign | I | II |
|----------|---|----|
| T (°C)   | 400 | 400 |
| P (bar)  | 0.99−1.1 | 0.99−1.1 |
| bed 1 material | adsorbent 1 | adsorbent 2 |
| bed 1 \(D_{\text{eqv}}\) (mm) | 4.9 | 4.3 |
| bed 2 material | adsorbent 2 | adsorbent 1 |
| bed 2 \(D_{\text{eqv}}\) (mm) | 4.3 | 4.9 |
| bed 1, \(m_{\text{ads}}\) (g) | 309 | 308 |
| bed 2, \(m_{\text{ads}}\) (g) | 704 | 704 |

For campaign I, the desulfurization reactor was packed as follows: adsorbent 1 in bed 1 and 2. For campaign II, bed 1 was packed with adsorbent 1 and bed 2 was packed with adsorbent 2. An estimate of the flowrate of each setpoint was calculated with respect to the condenser tank steam condensation rate. A linear fit (\(R^2 = 0.94−0.99\)) of the tank liquid level increase over time provided the condensation rate. Combined with the average steam content in each setpoint gained from the offline tar sampling, a rough estimate of the total flowrate was obtained. This flowrate measurement method was found to be more reliable than a differential pressure-based flowmeter that was found to be vulnerable to blockage by condensate. The gasification setpoints were carried out with crushed wood pellets, crushed bark pellets, used wood, or straws. The setpoint where straw was used was run when the desulfurization unit was disconnected from the gasification plant and was therefore ignored in this study. The tested biomass fuel dry matter analysis is given in the Supporting Information. The gasification bed material was a mixture of 30% silica sand and 70% dolomite (Myanit B). The reformer was operated using a Ni-based catalyst.

The commercial ZnO adsorbents used in the bench-scale tests were adsorbent 1: Clariant ActiSorb S2 and adsorbent 2: Xi'an Aeromat, extruded pellets. The manufacturer reports that adsorbent 1 consists of 90% ZnO and 10% alumina binder, but according to the energy dispersive X-ray spectroscopy (EDS) analysis in our previous study,\(^{2}\) the adsorbent contained around 2 wt % other elements than Zn or O, namely, Al and Si. The manufacturer reports that the Aeromat adsorbent consists of 100% ZnO. Adsorbent 1 was in a noncrushed pellet form with a diameter of 4.5 mm, and adsorbent 2 was in a 3.5 mm hollow cylinder form. Adsorbent 1 had a spherical equivalent diameter of 4.9 mm, and adsorbent 2 had a diameter of 4.3 mm based on 20 measured pellets.

3.3. Analytics. Dräger test tubes of type H2S 2/A and 2/B, which are quantitative colorimetric chemical sensors that react with H2S to form HgS, were used for manually measuring the H2S concentration in the gas. The reported standard deviation of this analysis method is ±5−10%. In addition to this, 2 dm\(^3\) gas bag samples from the raw syngas and after the desulfurization reactor were gas chromatography analyzed for sulfur species. Gas bag samples in campaign I were analyzed for COS, and in campaign II, COS and H2S were analyzed. The gas was analyzed within 2 h of sampling using GC Agilent 7890B with a flame photometric detector (FPD) and a GS-GasPro 30 m × 0.53 mm D column using carrier gas He. The GC calibration was conducted for H2S in several ranges: for reactor gas desulfurization, between 2−10 ppmv H2S; for COS dry gas, 0.2−1 ppmv; for raw syngas, 20−125 ppmv H2S; and for COS, 0.4−4 ppmv dry gas. Calibration was conducted by feeding gas to the GC from an AGA calibration gas bottle containing 200 ppmv H2S and 20 ppmv COS with a relative error of ±2% using gas diluter Pierburg 2000B with N2 as the diluant.

The sampling line consisted of an indirect cooler, a condensate tank, and a suction pump after which a Teflon sampling tube was installed. The raw syngas–gas composition was measured after the reformer with an online gas analyzer (ABB AO2020) and a micro GC [Agilent 3000A equipped with a thermal conductivity detector (TCD)], which sampled every 15 min. The online analyzer was used for real-time process monitoring, while the micro GC was used for analyzing CO, CO2, H2, CH4, O2, N2, and C1−C3 hydrocarbons. According to the European Tar Protocol,\(^{12}\) tars were measured after removing from the gasifier and samples were taken in isopropanol. The samples were analyzed for benzene and S2 tar compounds up to coronene with a GC model Agilent 6890A equipped with the flame ionization detector (FID) and column Agilent 19091B−112 Ultra 2. A GC of model HP 5890 series II with the TCD and column PoraPLOT U was used for quantifying the water content from tar samples.\(^{13}\)

Adsorbent Brunauer−Emmett−Teller (BET) surface areas were measured using a Micrometric Tristar 3000 analyzer using N2 adsorption isotherms at 77.3 K. For BET surface area measurement of the spent adsorbents, noncrushed both darker and noncolored samples were chosen. Scanning electron microscopy (SEM) was performed with a Carl Zeiss Merlin scanning electron microscope. Chemical compositions of the samples were determined by EDS. The microscope was equipped with a ThermoFisher UltraDry energy-dispersive X-ray spectrometer (silicon drift detector). Acceleration voltages used for imaging varied from 3 to 7 kv, and for EDS, 5, 7, and 10 kv were used. Certain ZnO samples were broken in the middle to expose the cross-section and core. Samples were placed in Al stubs for imaging. The sampled particles for SEM−EDS analysis differed from the BET-SA sampled particles. For the spent adsorbent SEM imaging and EDS elemental analysis, darker-colored samples were chosen.

3.4. Calculation Methods. The particle equivalent spherical diameter, for which an irregularly shaped object is the diameter of a sphere of equivalent volume, is calculated as follows

\[
D_{\text{eqv}} = \frac{3D \times H}{D + 2H} \tag{3}
\]

where \(D\) is the pellet diameter and \(H\) is the pellet length (mm).

The sulfur adsorption capacity \(S_{\text{cap}}\) is the sulfur captured per mass of the adsorbent at breakthrough. It is given according to eq 4

\[
S_{\text{cap}} = \frac{t_{\text{b}} \cdot \dot{V}_{\text{g}} \cdot c_{\text{H2S}}}{V_{\text{ads}} \cdot m_{\text{ads}}} \tag{4}
\]

where \(S_{\text{cap}}\) is the sulfur adsorption capacity (\(\text{mg} \cdot \text{s}^{-1} \cdot \text{dm}^{-3}\)), \(t_{\text{b}}\) is the breakthrough time (min), \(\dot{V}_{\text{g}}\) is the total gas flowrate (N dm\(^{-3}\) min\(^{-1}\)), \(c_{\text{H2S}}\) is the H2S concentration (ppmv), \(M_s\) is the molar mass of sulfur, \(V_{\text{ads}}\) is the molar volume, and \(m_{\text{ads}}\) is the adsorbent weight (g).

For breakthrough calculations, the same breakthrough limit as in the previous lab-scale study, 2 ppmv H2S in the effluent, was chosen. The adsorbent utilization percentage describes the amount of sulfur captured relative to the adsorbent theoretical maximum. Pure ZnO
has a maximum $S_{\text{cap}}$ of 394 mg S adsorbent g$^{-1}$. A 100 wt % adsorbent ZnO content was assumed in the utilization rate calculations.

4. RESULTS

4.1. Breakthrough Experiment Results. Two bench-scale desulfurization test campaigns with actual bio-syngas using different residual biomass sources were performed. In campaign I, time-on-stream (TOS) for the desulfurization unit was in total 72 h and in campaign II, the TOS was 75 h. In campaign I and II, gasification tests consisted of validation of a new fuel feedstock with varying H$_2$S contents in the syngas. The fuel feedstock and the average gas composition in the different setpoints are presented in Table 3.

Table 3. Setpoint Average Gas Composition for Each Setpoint in Campaigns I and II, After Reformer (Wet Gas)$^{31}$

| SP | fuel   | H$_2$ (vol %) | CO (vol %) | CO$_2$ (vol %) | CH$_4$ (vol %) | N$_2$ (vol %) | H$_2$S (ppmv) | COS$^a$ (ppmv) | H$_2$O$^c$ (vol %) | C$_2$H$_x$+tar$^c$ (g N m$^{-3}$) |
|----|--------|---------------|------------|---------------|----------------|---------------|---------------|----------------|------------------|-------------------------------|
| A  | bark   | 22.4          | 9.1        | 12.0          | 1.1            | 16.6          | 61            | 38.7           | 0.02             | 216.8                         |
| B  | bark   | 23.2          | 9.9        | 12.1          | 1.5            | 16.6          | 67            | 36.6           | 0.03             | 498.4                         |
| C  | bark   | 21.4          | 9.8        | 13.4          | 1.5            | 16.5          | 75            | 18             | 37.5             | 491.1                         |
| D  | used wood | 17.4         | 6.3        | 10.6          | 0.7            | 24.9          | 54            | 11             | 40.1             | 113.9                         |
| A  | wood   | 29.6          | 12.3       | 11.8          | 0.9            | 15.0          | 8             | 30.4           | 0.01             | 62.8                          |
| B  | wood   | 29.0          | 11.8       | 11.6          | 0.8            | 15.7          | 13$^d$        | 0.3            | 31.2             | 55.1                          |
| C  | wood   | 26.9          | 12.4       | 13.1          | 0.9            | 15.3          | 12            | 31.4           | 0.00             | 54.6                          |
| D  | wood   | 26.3          | 11.6       | 13.4          | 0.7            | 16.1          |               | 32.0           | 0.00             | 30.3                          |
| E  | bark   | 25.0          | 10.9       | 13.1          | 1.5            | 15.4          | 62            | 2.0            | 34.2             | 505.3                         |
| F  | bark   | 27.0          | 10.6       | 11.6          | 1.7            | 14.8          | 76            | 34.3           | 0.02             | 733.9                         |
| G  | bark   | 25.1          | 9.8        | 12.3          | 1.3            | 15.6          | 77$^d$        | 2.0            | 35.9             | 424.3                         |
| H  | used wood | 23.6         | 9.7        | 13.1          | 1.4            | 14.1          | 88$^d$        | 38.1           | 0.02             | 352.4                         |

$^a$Raw gas sampled using gas bags and measured with FPD-GC. Results are the average of two gas bag samples. $^b$Sampling using manual Dräger tubes. $^c$Raw gas sampled in water and measured with FID-GC. $^d$Slipstream experiment terminated during the setpoint.

Figure 5. Bench-scale desulfurization unit H$_2$S breakthrough analysis after bed 1: (A) campaign I. (C) Campaign II. H$_2$S and COS analysis after bed 2: (B) campaign I. (D) Campaign II, with GC-analyzed H$_2$S results marked in light blue. Gasifier setpoint (according to Table 3) start and stop times indicated with dashed green and red vertical lines, respectively. Desulfurization experiment termination indicated with black-dashed vertical lines.
composition was calculated for the full setpoint length. The analysis results are corrected for wet gas composition according to the average steam content in each setpoint derived from offline samples. Gas bag samples for H$_2$S and COS analysis were taken for certain setpoints, marked separately. Offline benzene and tar (and water content) samples were taken for each gasification setpoint.

The steam content in the syngas after the reformer varied between 30 and 40 vol %. The gas contained a small amount of C$_2$ compounds and residual benzene and tar. Benzene amounted for over 90% of the tar sample. The other identified compounds in the tar sample were naphthalene in the range of 10–80 g N m$^{-3}$. A less heavy tar content is achieved partly because of the catalyzing effect of the Ca-based bed material in steam gasification as well as the effective tar reforming step.

The analysis indicated for bark fuel setpoints a H$_2$S concentration between 60 and 80 ppmv in the gas after the reformer. Gas bag samples used to analyze H$_2$S and COS with a GC were taken for setpoints utilizing wood fuel and bark. The average COS concentration in wood-derived syngas and bark was 0.3 and 2.0 ppmv, respectively.

The gas flowrate and the space velocity calculations based on the steam condensation rate, as described in the Methods section, is given in the Supporting Information. The average flowrate for campaign I was 36 N dm$^{-3}$ min$^{-1}$, and for campaign II, it was 28 N dm$^{-3}$ min$^{-1}$, resulting in a time-weighted average gas hourly space velocity for bed 1 of 12,000–14,000 h$^{-1}$ and for bed 2 of 8000–9000 h$^{-1}$. As the campaign progressed, the flowrate tended to decrease, which could be attributed to the pump tube wear. In campaign I, the setpoint D unit suffered a peristaltic pump tube failure and the syngas flowrate diminished for a few hours until the tube was changed. The new pump tube that was installed at the end of campaign I was more rigid and of more wear-resistant rubber. Consequently, in campaign II, the average flowrate was lower.

The breakthrough curves for H$_2$S for both beds as well as COS analysis results after the second bed are presented in Figure 5. Offline GC-analyzed H$_2$S results are indicated separately. Results from campaign I are graphed in Figure 9A,B. Results from campaign II are graphed in Figure 5C,D. The setpoint start and stop times are indicated with green- and red-dashed horizontal lines, respectively.

In Figure 5A, the breakthrough behavior of H$_2$S through the 15 cm bed is visualized. A 0.5 ppmv breakthrough is reached before the 10 h TOS mark after which the breakthrough is stable between 0.5 and 2 ppmv till the end of the campaign. No breakthrough curve is formed, indicating that saturation of the bed is not reached. In Figure 5B, the breakthrough behavior of H$_2$S after the second 25 cm bed is shown. Complete H$_2$S removal is not achieved, and a residual concentration of 0.2–0.5 ppmv is left. COS concentration after the reactor is around 1 ppmv, which means that partial COS removal was achieved.

In Figure 5C, the breakthrough of the first bed packed using adsorbent 2 in campaign II is shown. The breakthrough in wood gasification setpoints is expectedly low and increases to 0.5–2 ppmv in bark gasification setpoints. The second bed breakthrough through adsorbent 1 is shown in Figure 5D. The COS removal after the reactor is almost complete. The H$_2$S concentration is around 0.1 ppmv measured using Dräger tubes and around 0.5 ppmv using gas bag GC samples.

Only indicative ZnO-adsorbent breakthrough capacities and utilization rates could be calculated because of the varying flowrate and H$_2$S concentration in the raw gas as well as noncontinuous H$_2$S analysis. Based on the average setpoint flowrates (provided in the Supporting Information) and assuming that Dräger and offline gas bag analysis results represent an average H$_2$S concentration over the setpoint, the campaign I bed 1 sulfidation capacity at the end of the campaign (TOS 72 h) was around 45 $\frac{mgS}{g_{adsorbent}}$, which equals a 12% utilization rate assuming a 100% ZnO content in adsorbent 1. Because of the lower H$_2$S content in wood gasification syngas in campaign II, the sulfidation capacity at the end of the campaign (TOS 75 h) was around 25 $\frac{mgS}{g_{adsorbent}}$, which equals to a 6% utilization rate assuming a 100% ZnO content in adsorbent 2.

4.2. Spent Adsorbent Characterization. The BET surface areas were measured for the fresh and selected particles from bed 1 in campaign I and campaign II. There was clear distinction between individual adsorbent particles in coloring of the surfaces. The effect of the discoloring was studied by taking two samples from the bed: (1) darker- and (2) lighter-colored particles. Photographs of the particles are available, as shown in Figure 6, and the BET surface areas of these samples are available, as shown in Table 4.

Figure 6. Photographs from fresh and spent bench-scale experiment adsorbents: (A) fresh adsorbent 1. (B) Fresh adsorbent 2. Campaign I bed 1: (C) sample 1. (D) sample 2. Campaign II bed 1: (E) sample 1. (F) Sample 2.
The discolored particles had a BET surface area of 24.1 m² g⁻¹, and the lighter-colored particles had a BET surface area of 29.4 m² g⁻¹. In the previous lab-scale experiments, the spent adsorbent 1 surface area shrunk to below 20 m² g⁻¹; however, because the lab-scale experiments were run past the breakthrough limit of 2 ppmv unlike the bench-scale experiments, the lower spent surface area is logical. The fresh adsorbent 2 sample had a surface area of 17.6 m² g⁻¹, which was significantly lower than for adsorbent 1. The spent samples of adsorbent 2 from campaign II bed 1 had surface areas of 15.3 - 15.4 m² g⁻¹, which is a 13% decrease from the fresh sample.

The fresh and spent adsorbent EDS elemental analysis results are presented in Table 5. The EDS spectromograms are provided in the Supporting Information.

Surface samples of the spent adsorbents showed almost complete sulfidation, with significant oxygen replacement. Sulfur occupied up to 40 at. % of the sample. Campaign II bed 1 sample analysis showed other impurities such as Ni and Fe present in 5 at. % quantity. This is believed to be the dust from the desulfurization reactor steel because the fresh sample did not exhibit these impurities. The EDS elemental analysis indicated presence of chlorine in the both adsorbent 1 and adsorbent 2 after campaign I and campaign II, respectively. The indicated Cl concentrations were in the few wt % range, which is not significant but still meaningful because Cl was not detected in adsorbent 1 or adsorbent 2 fresh samples.

The micrographs for a spent particle from campaign I bed 1 are given in Figure 7.

The EDS map for sulfur, as shown in Figure 7A, reveals that the sulfidation has completely occurred in the pellet surface and reaches 50 - 350 μm deep. Small amounts of sulfur are detected in the inner layers of the cross-sectional pellet. In Figure 7C, the EDS-analyzed lighter compounds are shown in a lighter color, and thus, a sharp boundary on the outer layer between the product and the unreacted ZnO is seen. Figure 7B shows the sulfided outer layer microstructure. The surface morphology has completely changed, and the surface grain size is significantly bigger than that in the unreacted inner layer shown in Figure 7D, which is similar in morphology to the fresh sample. The surface particle size increases from fresh <100 up to 500 nm for the sulfided particles.

The EDS map for sulfur, as shown in Figure 8A, displays a similar phenomenon to the spent adsorbent 1, where sulfur is mainly detected on the outer pellet surface reaching a 150-350 μm depth. Furthermore, the hollow cylinder shape facilitates increased sulfidation through the inner walls up to 50 μm deep. In Figure 8C, again a sharp interface of the outer sulfided layer and the unreacted ZnO can be seen. In Figure 8B, the outer sulfided layer microstructure is similar to the adsorbent 1 sulfided layer. The surface grain size according to the micrographs for the fresh sample is around 150 nm, and the sulfided particles in the spent sample can be above 500 nm with size increasing closer to the surface.

The core-shell sulfidation behavior was further studied by quantifying the elemental composition along the radius of the spent adsorbent pellets. The campaign I bed 1 spent adsorbent 1 analysis covered 30 samples to a pellet depth of 1.4 mm. The campaign II bed 1 spent adsorbent 2 analysis included 50 sampling points along the full radial length of the pellet to the hollow core. High error rate samples were removed. The

| Table 4. Bench-Scale Experiment Adsorbent BET Surface Areas for Samples According to Figure 6 |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| sample          | BET surface-area (m² g⁻¹) | BET surface area change vs fresh (%) |
| A               | 42.6             |                  |                  |                  |                  |                  |                  |                  |                  |
| B               | 17.6             |                  |                  |                  |                  |                  |                  |                  |                  |
| C               | 24.1             | -43             |                  |                  |                  |                  |                  |                  |                  |
| D               | 29.4             | -31             |                  |                  |                  |                  |                  |                  |                  |
| E               | 15.4             | -13             |                  |                  |                  |                  |                  |                  |                  |
| F               | 15.3             | -13             |                  |                  |                  |                  |                  |                  |                  |

The indicated Cl concentrations were in the few wt % range.

The surface particle size increases from fresh <100 up to 500 nm for the sulfided particles. The EDS map for sulfur, as shown in Figure 8A, displays a similar phenomenon to the spent adsorbent 1, where sulfur is mainly detected on the outer pellet surface reaching a 150-350 μm depth. Furthermore, the hollow cylinder shape facilitates increased sulfidation through the inner walls up to 50 μm deep. In Figure 8C, again a sharp interface of the outer sulfided layer and the unreacted ZnO can be seen. In Figure 8B, the outer sulfided layer microstructure is similar to the adsorbent 1 sulfided layer. The surface grain size according to the micrographs for the fresh sample is around 150 nm, and the sulfided particles in the spent sample can be above 500 nm with size increasing closer to the surface.

The core-shell sulfidation behavior was further studied by quantifying the elemental composition along the radius of the spent adsorbent pellets. The campaign I bed 1 spent adsorbent 1 analysis covered 30 samples to a pellet depth of 1.4 mm. The campaign II bed 1 spent adsorbent 2 analysis included 50 sampling points along the full radial length of the pellet to the hollow core. High error rate samples were removed. The

| Table 5. Fresh and Spent Adsorbent EDS Elemental Analysis⁴ |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| element         | line | fresh, adsorbent 1 | spent, campaign I bed 1 | fresh, adsorbent 2 | spent campaign II bed 1 |
|                 |      | (wt %) | (at. %) | (wt %) | (at. %) | (wt %) | (at. %) |
| Zn              | L    | 82.9   | 55.1   | 65.0  | 45.7   | 86.7  | 61.5   | 67.7  | 51.2   |
| O               | K    | 15.7   | 42.6   | 2.8   | 8.1    | 13.3  | 38.5   | 1.5   | 4.6    |
| Al              | K    | 0.9    | 1.5    | 0.8   | 1.3    | n.d   | n.d    | n.d   | n.d    |
| Si              | K    | 0.5    | 0.8    | 0.7   | 1.2    | n.d   | n.d    | n.d   | n.d    |
| S               | K    | n.d    | n.d    | 29.0  | 41.5   | n.d   | n.d    | 25.3  | 39.1   |
| Cl              | K    | n.d    | n.d    | 1.7   | 2.2    | n.d   | n.d    | 0.7   | 0.9    |
| other (Ni, Fe)  |      | n.d    | n.d    | n.d   | n.d    | n.d   | n.d    | 4.8   | 4.2    |
| total           |      | 100    | 100    | 100   | 100    | 100   | 100    |

⁴Samples taken from the adsorbent particle surface. Results presented in wt % and at. %.
adsorbent pellets analyzed are not the same, as shown in Figures 7 and 8. The results are graphed, as shown in Figure 9. Figure 9A displays has a similar sulfur concentration profile similar to the EDS map shown in Figure 7A. The concentration of sulfur on the surface and up to 200 μm deep ranges from 20 to 30 wt %. At a depth of 400 μm, there is virtually no sulfur detected. Few samples though were detected up to 4 wt % in the inner layers. In Figure 9B, the spent adsorbent 2 high sulfur concentration layer of 25−30 wt % is 300 μm deep. The hollow tube inner surface-sulfided layer has a sulfur concentration of 5−30 wt %

5. DISCUSSION

Two successful test campaigns where H2S was removed below the breakthrough limit confirm the feasibility of ZnO as a viable desulfurization solution from a technical perspective. Adsorbent discoloring, that is, carbon deposition on the pellets, in the bench-scale campaigns was comparable to the lab-scale tests in our previous study with model tar-containing syngas. Loss of the surface area was verified in comparative BET analysis to nondiscolored pellets, but the conclusion was that the hydrocarbons and tars in the real syngas do not significantly affect desulfurization performance unlike the model gas in lab-scale.16 Compared to the lab-scale study, the indicative utilization rates of the beds were low, 13 and 6% for campaign I and II, respectively. However, full breakthrough was not achieved, and in general, a low utilization rate can mainly be attributed to the large adsorbent particle size, which was intentionally chosen to see the particle size effect.

COS was almost completely removed in both test campaigns. One possible explanation for this phenomenon could be attributed to the COS hydrolysis reaction

\[
\text{COS} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{S} + \text{CO}_2
\]

The equilibrium COS concentration at a desulfurization unit reaction temperature of 400 °C for a feed gas composition according to campaign II setpoint E (available in Table 3) is around 0.2 ppmv in wet gas. The equilibrium gas composition was calculated using Gibb’s free energy minimization in Outotec HSC 8 software.13 The commercial adsorbent 1 contains Al2O3, which is a known COS hydrolysis catalyst typically operated at 200−245 °C.14,15 Therefore, it is feasible to assume catalytic conversion of COS.

A small and early H2S breakthrough of 0.1−0.5 ppmv after desulfurization was detected in both campaigns, which differed from the breakthrough behavior experienced in the previous campaigns. This breakthrough was attributed to the presence of small amounts of COS in the feed gas, which could not be detected using the analytical methods employed in the previous study.

Figure 8. Scanning electron micrographs for spent adsorbent 2 (cross-section) from campaign II bed 1: (A) micrograph with overlayed EDS map for sulfur (yellow); (B) outer layer-sulfided microstructure, magnification of 25,000; (C) ZnO−ZnS interface, magnification of 25,000; and (D) adsorbent core microstructure, magnification of 25,000.

Figure 9. Spent adsorbent radial EDS line scan analysis for (A) spent adsorbent 1 from campaign I bed 1 and (B) spent adsorbent 1 from campaign II bed 1.
laboratory-scale study. One reason for the slight, but below the limit, breakthrough of H$_2$S even after the second bed could be attributed to the large particle size and channeling effects. This leads to a longer mass transfer zone, which causes faster breakthrough and an underutilized bed compared to potential equilibrium saturation. Another possible explanation could be attributed to the hydrolysis reaction. The formed H$_2$S might break through, and an underutilized bed compared to potential leads to a longer mass transfer zone, which causes faster inside the particles.10 Either way, the product layer di that ZnO migrates outward because of the presence of voids reported and HCl actually enhanced H$_2$S removal. This was O performance of a zinc titanate sorbent below 550 °f, blocking acceptor sites, was signi- cant morphological and connected to the slipstream of a pilot-scale steam-blown fluidized bed gasifier. Two successful 70+ h test campaigns with real bio-syngas were performed, where H$_2$S was removed below the breakthrough limit in the first adsorbent bed throughout the campaigns. The feasibility of H$_2$S as a bulk desulfurization adsorbent utilizing full-sized particles in real conditions was therefore verified. SEM–EDS analysis of the spent adsorbent pellets showed significant core–shell sulfidation behavior and consequently loss of porosity and product layer diffusional resistances with the majority of ZnO left unutilized. SEM micrographs displayed the outward enlarging particle size in the sulfided layer. Simultaneous COS removal was found possible because of the hydrolysis reaction to H$_2$S with the consequence of a small H$_2$S breakthrough, attributed to the insufficient contact time for adsorption of the formed H$_2$S. Evidence in the EDS analysis of the spent pellets of minor chlorine adsorption was found, thus highlighting the need for a separate HCl removal step upstream of the desulfurization unit.

### 6. CONCLUSIONS

Hydrogen sulfide removal using ZnO-based adsorbents is conceptualized as a simplified, cost-effective alternative to wet-scrubbing processes in small- to medium-scale BTL processes. Following previous lab-scale ZnO studies in model bio-syngas, desulfurization breakthrough tests were conducted in real syngas at bench-scale. A desulfurization unit was constructed and connected to the slipstream of a pilot-scale steam-blown fluidized bed gasifier. Two successful 70+ h test campaigns with real bio-syngas were performed, where H$_2$S was removed below the breakthrough limit in the first adsorbent bed throughout the campaigns. The feasibility of H$_2$S as a bulk desulfurization adsorbent utilizing full-sized particles in real conditions was therefore verified. SEM–EDS analysis of the spent adsorbent pellets showed significant core–shell sulfidation behavior and consequently loss of porosity and product layer diffusional resistances with the majority of ZnO left unutilized. SEM micrographs displayed the outward enlarging particle size in the sulfided layer. Simultaneous COS removal was found possible because of the hydrolysis reaction to H$_2$S with the consequence of a small H$_2$S breakthrough, attributed to the insufficient contact time for adsorption of the formed H$_2$S. Evidence in the EDS analysis of the spent pellets of minor chlorine adsorption was found, thus highlighting the need for a separate HCl removal step upstream of the desulfurization unit.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.9b04277. Photographs and dry matter analysis of the gasification fuels; estimated desulfurization unit feed flowrates and adsorbent bed space velocities; and EDS spectrogram of fresh and spent bench-scale experiment adsorbents (PDF)

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#### Notes

The authors declare no competing financial interest.

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**ABBREVIATIONS**

BtL = biomass-to-liquids  
c = concentration  
CFB = circulating fluidized bed  
CW = cool water  
D = diameter  
D_{eqv} = equivalent spherical diameter in mm  
DFB = dual fluidized bed  
EDS = energy-dispersive X-ray spectroscopy  
FPD = flame photometric detector  
FT = Fischer–Tropsch (synthesis)  
GHSV = gas hourly space velocity real basis in $\text{h}^{-1}$  
H = height-to-diameter ratio  
L/D = length-to-($\text{m}$) diameter ratio  
HW = hot water  
MTZ = mass transfer zone  
N = nominal (at 273.15 °C and 101,325 kPa)  
n.d = not detected  
NDIR = nondispersive infrared adsorption detector  
$S_{\text{cap}}$ ($x$ ppm) = desulfurization capacity, where $x$ is the breakthrough concentration  
SEM = scanning electron microscopy  
$\tau_b$ = breakthrough time in min  
TCD = thermal conductivity detector  
TOS = time on stream in $\text{h}$  
$V = \text{gas flowrate in N dm}^3\text{ min}^{-1}$

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