Desulfurization of Biomass Syngas Using ZnO-Based Adsorbents: Long-Term Hydrogen Sulfide Breakthrough Experiments

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ABSTRACT: Dry-bed adsorptive desulfurization of biomass-based syngas with low to medium sulfur content using ZnO was investigated as an alternative to the conventional wet scrubbing processes. The technical feasibility of ZnO-based desulfurization was studied in laboratory-scale H₂S breakthrough experiments. The experiments were set up to utilize realistic H₂S concentrations from gasification and therefore long breakthrough times. Experiments were performed in a steam-rich model biosyngas in varying conditions. The long-term breakthrough experiments showed apparent ZnO utilization rates between 10 and 50% in the tested conditions, indicating intraparticle mass-transfer resistances partly due to space velocity and particle size constraints as well as the most likely product-layer resistances as evidenced by the large spent adsorbent surface area decrease. An empirical deactivation model to estimate full breakthrough curves was fitted to the laboratory-scale experimental data. Breakthrough experiment in tar-rich syngas was also performed with the conclusion that ZnO performance is not significantly affected by hydrocarbons despite carbon deposition on the particle surfaces.

1. INTRODUCTION

With the increasing need for renewable fuel and energy sources, gasification of woody and herbaceous biomass is of high interest. However, biomass gasification produces also unwanted by-products such as particulates, organic tars, sulfur and nitrogen heteroatom species, and inorganic constituents containing sulfur (H₂S and COS), chlorine (HCl), nitrogen (NH₃ and HCN), and alkali metals. Consequently, cost-effective and efficient purification of syngas is one of the biggest bottlenecks of advanced biomass gasification applications such as fuel or chemicals production through synthesis routes such as Fischer–Tropsch, MeOH, or SNG. Furthermore, large-scale processes have high investment costs and create problems with procurement of biomass feedstock. Decentralized small-scale fuel and chemical production seems thus an attractive alternative approach, but this in turn further increases the need for low-cost purification solutions. Hydrogen sulfide needs to be removed to prevent downstream catalyst poisoning and to protect equipment from corrosion. Biomass contains usually under 0.1 mass % sulfur, that is mostly converted to H₂S in gasification conditions. Raw biosyngas, depending on the biomass feedstock, contains tens to hundreds of ppmv H₂S. The estimates of the target content of sulfur impurities required by downstream synthesis vary by source. For Fischer–Tropsch synthesis (Co- or Fe-based catalyst) Tijmensen et al. report H₂S + COS tolerance below 0.01 ppm, while Boerrigter et al. report a total sulfur tolerance below 1 ppm. Methanol synthesis catalysts (Cu-based) in general have slightly higher poison tolerance than FT catalysts.

Hydrogen sulfide can readily be removed by cold wet scrubbing technologies along with other acid gases such as CO₂. The driving force is the acid gas partial pressure difference between the gas phase and the liquid phase. The processes therefore benefit from higher pressures and lower temperatures, which increase the costs. The main examples of this technology include the physical-solvent-based Rectisol and Selexol processes. These processes are complex and present a high investment cost. Furthermore, the expected H₂S content in effluent of physical absorption systems in general is in the range of 0.1–1 mol-ppm. Adsorptive removal of H₂S using metal oxides is a medium- to high-temperature gas cleaning technology where noncatalytic gas–solid interaction occurs with species combining chemically to the solid material, the adsorbent. Mid- to high-temperature desulfurization avoids the thermodynamic penalty from cooling and heating the gas. It is especially favorable in, for example, IGCC power plants where the gas is fed to combustion turbines that do not need, for example, CO₂ removal, which requires a scrubbing step. Metal oxide adsorbents have traditionally been used in industrial processes as a polishing step for sulfur gases where H₂S levels do not exceed 10–20 ppmv. For streams with higher H₂S concentrations, wet scrubbing processes have been employed.

The desired properties for desulfurization adsorbents can be generalized as (1) high H₂S adsorption capacity [high capacity reduces the required adsorbent quantity and process equipment size]; (2) fast adsorption kinetics and favorable reaction equilibrium; (3) good mechanical properties; (4) chemical properties [stable in reducing environments and not affected by steam and possibly hydrocarbons]; (5) cheap and readily available. For any adsorption process, the adsorbent should have high H₂S adsorption capacity, high H₂S adsorption rate, and good mechanical stability. Furthermore, the adsorbent should not be reactive with steam or hydrocarbons. Therefore, metal oxide adsorbents such as ZnO are considered the most promising adsorbent systems. ZnO is regenerable by stripping with steam and has high adsorption capacity and high resistance to aging and deactivation. The required performance of ZnO can be generalized as having high H₂S adsorption capacity and high H₂S adsorption rate.
available; (6) ideally the capacity to also remove other S-species, which would present advantages in terms of process simplification; and (7) Ideally regenerable. In Table 1, a comparison between common metal oxide adsorbents is presented.

Zinc oxide is perhaps the most widely used adsorbent for H₂S removal from gas streams such as natural gas or syngas. It has high capacity due to its fast intrinsic kinetics at mid to high temperatures (200−450 °C) and good stability under reducing conditions. The zinc oxide sulfidation reaction is reported to have first-order kinetics with respect to H₂S. The exothermic sulfidation reaction for ZnO is depicted as:

\[
\text{ZnO}(s) + \text{H}_2\text{S}(g) \rightleftharpoons \text{ZnS}(s) + \text{H}_2\text{O}(g) \quad \Delta H_{400\text{°C}} = -75.5 \text{ kJ mol}^{-1}
\]  

(1)

For sulfidation, assuming there is excess metal oxide, the equilibrium constant can be expressed as the ratio of the gas phase species; Bakker et al. suggested an extension to this by assuming that mainly surface sites act as acceptor sites during the sulfidation. Surface site concentrations are not constant, and therefore the surface phase could be included in the equilibrium expression:

\[
K_{eq} = \frac{[\text{H}_2\text{O}][\text{ZnS(surface)}]}{[\text{H}_2\text{S}][\text{ZnO(surface)}]} 
\]

(2)

Thus, for effective desulfurization, the equilibrium constant should be high or the sorbent should have a high surface area that results in a good surface capacity.

In this study, experimental investigation into zinc oxide as a bulk desulfurization adsorbent for biomass-based gasification syngas was conducted. Long-term breakthrough tests in laboratory scale using model syngas with realistic hydrogen sulfide concentrations present in biosyngas were performed.

### 2. MATERIALS AND METHODS

The laboratory-scale experiments were conducted in a continuous atmospheric quartz packed bed reactor. The laboratory-scale experimental setup diagram is presented in Figure 1. The inner diameter of the quartz tube was 1.8 cm, with a thermocouple pocket of 0.4 cm in diameter in the bottom center of the bed. The bed length was up to 6 cm, and the reactor was placed in a 45 cm tall furnace. The gases were dosed using Bronkhorst mass flow controllers and water fed to an evaporator with a HPLC pump. The bottled gases were mixed with the vaporized water in a heated inlet line. The effluent gas was cooled in a condenser tube with a cooling water jacket. Tar containing gas was furthermore condensed in water wash bottles.

#### 2.1. Methods

The experiments were conducted in a wet gas flow rate, \( V'_g = 1.5−2.5 \text{ N dm}^3 \text{ min}^{-1} \) and inlet H₂S concentrations, \( c_{\text{H}_2\text{S,in}} \), of 100−120 ppmv, which resulted in up to mult WEEK breakthrough times. Before each run the GC was recalibrated, the system was leak-tested to an overpressure of 200 mbar, the feed H₂S concentration, \( c_{\text{H}_2\text{S,pre}} \), was analyzed, and the Teflon tube analysis lines were saturated with H₂S-rich gas.

The run was started by switching the gas stream from the reactor bypass to the preheated reactor line. The breakthrough curves were formed by non-interrupted operation. If any interruptions of the gas

### Table 1. Comparison between Different Metal Oxides for Desulfurization at Mid to High Temperatures

|          | Zn  | Fe  | Cu  | Mn  | Ca  | rare earth (Ce, La) |
|----------|-----|-----|-----|-----|-----|-------------------|
| thermal stability\(^{14}\) | +   | −   | +   | +   | +   | +                 |
| reductive stability\(^{14,15}\) | low T | high T | high T | +   | +               |
| sulfidation performance\(^{13,15}\) | +   | +   | −   | +   | −   | +                 |
| price\(^{16}\) | low  | low | medium | medium | very low | high              |

Figure 1. (A) Laboratory-scale experimental setup schematic diagram. (B) Experimental setup photograph.
flow to the reactor occurred, the reactor was flushed with N₂ and closed-off in the set point temperature.

After each run the reactor was cooled in nitrogen and the adsorbent material was visually inspected, photographed, and weighed.

The gas compositions used in the laboratory-scale experiments are presented in Table 2. Syngas 1 represents a gas that is obtained from a fluidized bed gasification process with almost complete reforming of the gas. Syngas 2 represents a pre-reformed gasification gas that includes a higher amount of CO₂ and CH₄ and C₂H₄ and the tar mixture. Syngas 2 as pre-reformed gas has also a slightly higher H₂S concentration.

The conditions listed in Table 3 are referred to as the standard conditions in this study, utilizing syngas 1. The breakthrough experimental data conducted in these conditions in Figure 3, Figure 4, and Figure 7 are depicted with blue dots.

The standard reaction temperature is 400 °C, GHSV is 21000 h⁻¹, bed length-to-diameter ratio is 2.5, and particle size distribution is 1.0–1.25 mm.

The system pressure was a few hundred millibars above atmospheric pressure in the inlet side, which is taken into account in calculating the real space velocity GHSV and flow rate. The real GHSV converted to nominal GHSV (at STP) in reference conditions using ideal gas laws was around 10000 h⁻¹. The reported sieved particle size distribution diameter is considered roughly equal to the equivalent spherical diameter, Dₑq.

### Table 2. Model Gas Compositions in the Laboratory-Scale Experiments

|         | syngas 1 | syngas 2 |
|---------|----------|----------|
| H₂ (vol %) | 38.01    | 31.17    |
| CO (vol %)  | 19.00    | 13.94    |
| CO₂ (vol %) | 13.50    | 16.43    |
| CH₄ (vol %) | 0.50     | 6.47     |
| N₂ (vol %)  | 0.19     | 0.10     |
| H₂S (ppmv)  | 100      | 120      |
| H₂O (vol %) | 28.79    | 30.03    |
| C₂H₆ (vol %) | 1.59     |          |
| tars (g N m⁻³) | 14.81    |          |

### Table 3. ZnO Laboratory-Scale Experimental Standard Conditions (Blue Dots)

|        |          |
|--------|----------|
| T (°C) | 400      |
| P (bar) | 1.0–1.2 |
| GHSV (h⁻¹) | 21000 |
| V̇₀ (N dm³ min⁻¹) | 2      |
| e₂₃₅₆ (wet gas) (ppmv) | 100    |
| bed L/D | 2.5     |
| Dₑq (mm) | 1.0–1.25 |

¹D = particle size distribution.

The tested ZnO adsorbent was commercial adsorbent of the type Actisorb S2 manufactured by Clarient, hereafter called adsorbent 1. According to the manufacturer, it consists of 90% ZnO and 10% alumina binder. The full-sized pellets of 4.5 mm D were crushed and sieved to the desired particle size distribution of either 1–1.25 mm or 2–2.38 mm.

### 2.3. Analytics.

An online gas analyzer (Sick Mahrk S710) was used for continuous analysis of the effluent dry gas composition. The analyzer included a TCD for H₂ and an oxygen cell and a nondispersive infrared adsorption detector (NDIR) for CO, CO₂, and CH₄. The online gas analyzer was used to verify steady gas feeding and that no permanent gases were being consumed or formed in the reactor.

H₂S was continuously measured from the wet effluent with a gas chromatograph Agilent 7890B with a FPD detector and a GS-GASPRO 30 m x 0.53 mm D column using carrier gas He. The sample line from the setup to the GC was heated. The GC calibration was conducted for H₂S in the range between 7 and 71 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 relative error of ±2% through gas diluter Pierburg 2000B with N₂ as diluant. As a reference, Dräger test tubes of type H₂S 2/A were used for manually measuring the H₂S concentration of the condensed gas. Dräger tubes are quantitative colorimetric chemical sensors, which react with H₂S to form mercury sulfide, HgS. The reported standard deviation of this analysis method is ±5–10%. Dräger tubes were used to determine concentrations below 7 ppmv. Since the breakthrough was determined at 2 ppmv outlet H₂S concentration, Dräger tube results were used to determine the breakthrough time, tₑ. Breakthrough curves were presented in this study using the FPD-GC data. For the experiment with syngas 2, only Dräger tubes were used for H₂S analysis due to the limitations of the GC analyzers with tar-rich gas. As the Dräger samples were taken from dry gas, the results were corrected for wet gas H₂S composition to be comparable with FPD-GC results.

Adsorbent BET surface areas were measured using a Micrometric Tristar 3000 analyzer using N₂ adsorption isotherms at 77.3 K. For spent adsorbent analysis the samples were taken from the upper first half of the bed. Scanning electron microscopy (SEM) was performed with a Carl-Zeiss Merlin scanning electron microscope. Chemical compositions of the samples were determined by energy dispersive X-ray spectroscopy (EDS). The microscope was equipped with a Thermo-Fisher UltraDry energy dispersive X-ray spectrometer (Silicon drift detector). Acceleration voltages used for imaging varied from 3 to 7 kV; for EDS 5, 7, and 10 kV were used. Adsorbent 1 was sampled before crushing and sieving in its original form of 4.5 mm D. The sample was placed on an Al stub for imaging.

### 2.4. Calculation Methods.

Outotec HSC 8 software was used for the chemical equilibrium calculations. The software-derived equilibrium constant data were used to graph the equilibrium concentrations of reaction products as a function of temperature.

Generally, the allowed breakthrough concentration is defined to be usually between 1 and 5% of the inlet adsorbate concentration. In this study, 2 ppm H₂S in the effluent was chosen as the breakthrough concentration, roughly equaling a 98% removal rate.

The sulfur adsorption capacity, Sₑq, is the sulfur captured per mass of adsorbent at breakthrough. It is a useful metric for determining the desulfurization performance of a given adsorbent. It can be calculated according to eq 3.

\[ Sₑq = \frac{tₑVₑqSₑqMₑ}{VₑqMₑads} \]

where \( Sₑq \) is the sulfur adsorption capacity (\( \text{mg of S g of adsorbent} \)), \( tₑ \) the breakthrough time (min), \( Vₑq \) the total gas flow rate (\( \text{N dm}^3 \text{ min}^{-1} \)), \( e₃₅₆ \) the wet gas H₂S concentration (ppmv), \( Mₑ \) the molar mass of sulfur, \( Vₑq \) the molar volume, and \( mₑads \) adsorbent weight (g).

The adsorbent utilization percentage describes the amount of sulfur captured relative to the adsorbent theoretical maximum. Pure ZnO has a maximum \( Sₑq \) of 394 \( \text{mg of S g of adsorbent} \), based on the stoichiometry of reaction 1. A 100 wt % adsorbent ZnO content was assumed in the utilization rate calculations.

Deactivation models, which predict the decrease of activity of the solid reactant in gas–solid reactions, can be used to estimate the
breakthrough curves in desulfurization. These models are used in literature by several authors including Yayyeli et al.,22 Suyadal et al.,23 and Garces et al.,24 and they have been found to be more accurate than, for example, the theoretical unreacted shrinking core and the adsorption isotherm models. The deactivation model assumes isothermal conditions and neglects external mass-transfer limitations and that the deactivation of the adsorbent is first-order with respect to the solid surface. It can be described in terms of an exponential decrease with time in its available surface as

$$-\frac{da}{dt} = k_d C_n a^n = k_d a$$

(4)

where $-\frac{da}{dt}$ is the rate of change of activity of the adsorbent, $k_d$ is the deactivation rate constant, $C_n$ is the concentration of H$_2$S in the gas phase, and $a$ is the solid active sites. Deactivation of the adsorbent is first-order with respect to the solid active sites, $n = 1$, and zero-order for the concentration of H$_2$S, $m = 0$.

The equation is integrated with $i_0$ being 1 at time zero, and pseudo-steady state is assumed. After some rearranging the following equation in linearized form is obtained:24

$$\ln \left( \frac{a}{C_n} \right) = \ln \left( \frac{k_m a_0}{V_s} \right) - k_d t$$

(5)

The left side of the equation can be plotted vs time using experimental breakthrough data, and a straight line should be obtained with a slope of $-k_d$ and an intercept equaling $\ln \left( \frac{k_m a_0}{V_s} \right)$. Thus, the adsorption rate constant and deactivation rate constants are obtained.

3. RESULTS

3.1. Chemical Equilibrium Calculations. Equilibrium calculations for the main sulfidation reaction and H$_2$S reactions with syngas components to form COS were performed with equilibrium constant data from HSC 8 software. Figure 2 graphs the results as a function of temperature in biomass-derived syngas per Table 2, syngas 1.

The sulfidation equilibrium favors low temperatures. At 400 °C with the model syngas 1 composition, the equilibrium H$_2$S concentration is 400 ppb (mole basis). Lower steam content in the gas favors desulfurization. In addition, steam could compete for adsorption on the ZnO surface, as was hypothesized by Novochinski et al., further negatively affecting desulfurization performance.

Equilibrium calculations for the COS forming reactions, the reverse COS hydrolysis and reverse COS hydrogenation, suggest that the presence of COS is possible. The equilibrium calculations suggest that the reverse COS hydrogenation is more significant compared to the reverse COS hydrolysis in the desulfurization conditions.

3.2. Breakthrough Experiment Results. The reference conditions for the long-term breakthrough experiments with ZnO in laboratory scale are listed in Table 3. The gas composition was syngas 1 according to Table 2.

The effects of space velocity, reaction conditions, particle size, and bed length on the H$_2$S breakthrough are presented in Figure 3. The figures present the effluent H$_2$S concentration as a function of time. The experiments were conducted up to around 30–60% H$_2$S breakthrough completion with focus on initial breakthrough determination. The reference condition run according to Table 3 is indicated with blue dots. The breakthrough capacity of 2 ppmv is indicated as a horizontal red line as the basis for calculating the sulfidation capacity. The calculated sulfidation capacity is layered in text format on top of the indicated breakthrough curve.

An increase in the space velocity decreases the sulfidation capacity as indicated in Figure 3 A). The sulfidation capacity, $S_{\text{up}} (2 \text{ ppm})$, drops from the low space velocity experiment of 176 mgS g$_{\text{adsorbent}}$ to 67 mgS g$_{\text{adsorbent}}$, most likely indicating significant intraparticle mass-transfer limitations in the tested range. Gas–solid mass-transfer limitations in the reactor scale cannot completely be ruled out, as the space velocities in these experiments were high. Even though the experiments were performed with long breakthrough times to simulate more realistic adsorption conditions of industrial scale, the space velocity is still much higher in all experiments than is generally recommended as a design basis for large adsorption reactors.

The reference run 2 ppmv breakthrough capacity was 124 mgS g$_{\text{adsorbent}}$, which assuming a 100 wt % adsorbent ZnO concentration equals to 32% utilization rate. In the runs presented in Figure 3 D) the space velocity was varied by changing bed length, and the effect of the small bed length was not only evident in the early breakthrough but also in the high subsequent H$_2$S breakthrough concentrations. With the bed length of 2.5 cm the reactor length to diameter-ratio was 1.4 and the $S_{\text{up}} (2 \text{ ppm})$ was 45 mgS g$_{\text{adsorbent}}$. As the mass-transfer zone and the residence time is shorter, the breakthrough will be more intense. The sharp drop in capturing capacity with the 2.5 cm bed suggest strong outlet effects due to the mass-transfer zone being longer than the bed. Since the 4.5 cm bed was the longest bed length tested, it is unknown if this bed length suffers from
the same problem. From the results presented in Figure 3B it is evident that the effect of reaction temperature between 300−400 °C was relatively small on the sulfidation capacity. The best performance at 2 ppmv H₂S breakthrough level was found to be at 300 °C, with Scap of 159 g adsorbent mg⁻¹. The effect of temperature can especially be seen in the slope of the breakthrough curve, with the lower temperatures showing a steeper slope. At a higher breakthrough level of 7 ppmv H₂S, the best desulfurization performance was at 400 °C. The tests presented in Figure 3C indicated substantial decrease of adsorption capacity with increased particle size. With the 2.0−2.38 mm particle size Scap was 29 g adsorbent mg⁻¹. Channeling effect cannot be ruled out due to the large particle size to reactor diameter- ratio. Despite this, strong mass-transfer resistances for gas diffusion in to the particle can explain the results.

The effect of tars on desulfurization performance was studied by feeding Syngas 2 (Table 2). Figure 4 presents the breakthrough curves for the experiments with Syngas 1 and Syngas 2; conditions are found in Table 3. For Syngas 1 in addition to the FPD-GC results, the Dräger H₂S tube results are presented.

For the reference run, the FPD-GC and Dräger tube breakthrough results agree well. The main difference is the sampling interval, which for Dräger test tubes is more irregular and longer. Dräger results for both experiments were used for breakthrough capacity determination. The breakthrough capacity for the tar-rich gas syngas 2 was 126 mg of S g⁻¹ adsorbent.
which is virtually equal to the reference run with syngas 1. The breakthrough curve for syngas 2 is steeper than for syngas 1.

3.4. Adsorbent Characterization. The SEM micrographs of the fresh adsorbent sample were used to investigate the zinc surface morphology and are presented in Figure 5.

The images reveal a fine surface structure of adsorbent 1. Aluminum is visible, but minimally present. The fresh adsorbent EDS analysis is presented in Table 4.

The fresh adsorbent 1 analysis indicated in addition to Zn and O around 0.9 wt % Al and 0.5 wt % Si. No other species were detected by the EDS analysis.

Table 4. EDS Elemental Analysis Results for Fresh Adsorbent 1

| composition | wt % | at. % |
|-------------|------|-------|
| Zn          | 82.9 | 55.1  |
| O           | 15.7 | 42.6  |
| Al          | 0.9  | 1.5   |
| Si          | 0.5  | 0.8   |
| total       | 100  | 100   |

The presence of hydrocarbons had a clear visual effect on the adsorbents, which is evident from Figure 6 showing the fresh and spent adsorbents.

Figure 5. SEM micrographs of fresh adsorbent 1, with magnifications of (A) 5000 and (B) 25000.

Figure 6. Photographs of (A) fresh adsorbent 1, (B) spent adsorbent 1 used in syngas 1 at 400 °C, and (C) spent adsorbent 1 used in syngas 2 at 400 °C.

The syngas 2 run adsorbent particles have a darker surface coloring, while the syngas 1 spent adsorbent is only slightly darker than the fresh sample. The BET results in Table 5 reveal a slight decrease in surface area compared to the syngas 1 run, which, however, is not significant compared to the general spent vs fresh surface area difference.

The main contributor to surface area decrease according to these results is thus the sulfidation reaction. Fresh sample had a surface area of 42.6 m² g⁻¹, and the spent syngas 2 sample 16.9 m² g⁻¹ and syngas 1 sample 18.2 m² g⁻¹. It is likely that a carbon layer from the syngas 2 tars form the deposits to the adsorbent surface. The bed mass increase is similar after both experiments at around 12–13%, suggesting carbon deposition is not significant.

3.3. Deactivation Model. A deactivation model of the first-order with respect to the solid surface was used to predict the
breakthrough curves to the saturation point. The breakthrough curve can be thought of as a representation of the non-ideality of the system and shows the global adsorption kinetics, and is thus of interest to model. The FPD-GC breakthrough data from Figure 3(A) GHSV runs and (B) temperature runs were used. Only data from the GC calibrated H$_2$S concentration range from 7 to 70 ppmv were used to derive the rate constants by linearizing the breakthrough data. Panels A and B of Figure 7 present the linearized equation according to eq 5. In Figure 7C,D, the parameters were used to calculate the model breakthrough curve to saturation point \( \frac{C_{\text{ads}}}{C_{\text{eq}}} = 1 \).

In Figure 7A,B straight lines were obtained using the breakthrough data with a slope of \(-k_d\) and intercept \( \ln \left( \frac{k_s V_0}{V_g} \right) \). The linear regression, \( R^2 \), coefficient of determination is between 0.96 and 0.99. In Figure 7C,D using the obtained constants, the full breakthrough curves were plotted against the real breakthrough curves. The derived deactivation rate and initial adsorption rate constants (real basis) are presented in Table 6.

### 4. DISCUSSION

The equilibrium calculations suggest that lower temperatures are preferred for deep H$_2$S removal and that ZnO has the potential for deep H$_2$S removal in biosyngas. In a H$_2$S removal process where bulk desulfurization is conducted at high temperature to encourage maximum mass-transfer rate, an additional ZnO guard bed could be used as a polishing step to achieve deep desulfurization. The guard bed should be operated at lower temperatures to avoid catalyst deactivation.

### Table 5. Laboratory-Scale Experiment BET Surface Area and Bed Weight Change for Samples 1–3 from Figure 6

| Sample | Name          | Fresh adsorbent | Spent, 400 °C syngas 1 | Spent, 400 °C syngas 2 |
|--------|---------------|-----------------|------------------------|------------------------|
| Sample | BED surface area (m$^2$ g$^{-1}$) | 42.6            | 18.2                   | 16.9                   |
|        | BET surface-area change vs fresh (%) | −57             | −61                    |                         |
|        | Spent bed weight change (%) | 13              | 12                     |                         |

### Table 6. Derived Constants from Experimental Data for the Deactivation Model

| Set point variable: GHSV (h$^{-1}$) | $k_d$ (h$^{-1}$) | $k_s$ (dm$^3$ g$^{-1}$ h$^{-1}$) |
|----------------------------------|-----------------|----------------------------------|
| 17000                           | 0.0128          | 808.0                            |
| 21000                           | 0.0117          | 341.2                            |
| 26000                           | 0.0241          | 1091.6                           |

| Set point variable: T (°C) | $k_d$ (h$^{-1}$) | $k_s$ (dm$^3$ g$^{-1}$ h$^{-1}$) |
|----------------------------|-----------------|----------------------------------|
| 300                        | 0.0262          | 2779.3                           |
| 350                        | 0.0162          | 483.4                            |
| 400                        | 0.0117          | 341.2                            |

Figure 7. Linearized deactivation model equation of experimental (A) varying space velocities and (B) varying temperatures. Model breakthrough curves (lines) for (C) varying space velocities and (D) varying temperatures along with experimental breakthrough data (markers) from Figure 3A,B.
at low temperatures of 200–300 °C to ensure deep sulfur removal according to the equilibrium calculations.

The reactions between H₂S and syngas components CO₂ and CO are harmful since COS is hardly captured or converted by zinc-based adsorbents.¹⁸ Sasaoka et al.,²⁶ however, suggest ZnS is active for the catalytic hydrolysis and hydrogenation of COS; thus the spent adsorbent bed part might aid total sulfur removal. Nevertheless, COS formation should not be neglected in the presence of CO and CO₂. Dedicated COS conversion is suggested and usually involves the hydrolysis route and catalysts that include metallic oxides with basic active sites.²⁷

Most industrial gas–solid adsorption processes employ a continuously operated vertical fixed bed reactor design where the bed \( L/D \) is < 5. This was the basis for the experiments in study as well. For typical desulfurization breakthrough capacity studies in literature, high inlet \( \text{H}_2\text{S} \) concentrations to achieve fast breakthrough times have been employed.¹⁷²⁻²⁹ ³⁰ For this study, a realistic \( \text{H}_2\text{S} \) concentration was used and thus longer breakthrough times with the benefit of (A) more accurately representing the breakthrough behavior in a full-scale process and (B) more reliable breakthrough results due to less error in the measurement of the breakthrough time, \( t_b \).

Adsorption processes are commonly sized based on the “mass-transfer zone” (MTZ) concept using experimental data. The adsorbent closer to the inlet of the fluid becomes saturated more quickly and develops a concentration gradient beyond the saturated zone called the “equilibrium zone”. The region where the concentration profile with the typical S-shape occurs is called the “mass-transfer zone”, MTZ, and is the sum of bulk and pore diffusional resistances and adsorption/reaction kinetics.²¹ Figure 8 displays a symmetrical mass-transfer front along the length of the bed.

![Figure 8](image-url)

**Figure 8.** Progress of a stable mass-transfer front through an adsorption bed of length \( L \) at breakthrough. \( C_{\text{int,s}} \) is the adsorbed sulfur equilibrium concentration, and \( L_s \) is the saturated bed length.

\[
\text{LUB} = L \left( 1 - \frac{t_b}{t_s} \right) \quad (6)
\]

where \( t_s \) is stoichiometric time; breakthrough time when \( \frac{C_{\text{int,s}}}{C_{\text{in,ext,s}}} = 0.5 \). In theory, the slower the mass-transfer process and the adsorption kinetics are, the longer the LUB and MTZ will be. The stoichiometric front travels with the same velocity as the real front, and the saturation velocity, \( u_s \), can be expressed as

\[
u_s = \frac{L}{t_s} \quad (7)
\]

Now the new bed length of the scaled-up adsorber can be calculated by

\[
L = t_s \mu_s + \text{LUB} \quad (8)
\]

Assuming the wavefront to be symmetric gives \( \text{MTZ} = 2\text{LUB} \).

However, scaleup using the LUB concept can only be used when the length of the overall bed is large relative to the mass-transfer zone, since short beds may have unstable mass-transfer zones.³¹ Estimating the LUB and MTZ from the breakthrough capacity results and the modeled breakthrough curves from this study shows that the mass-transfer zone is between 3.7 and 6.9 cm (5.9 cm in standard conditions according to Table 3) in the tested conditions, and thus the bed length is not sufficient for the LUB sizing concept to be applied to the results in this study. Nevertheless, the mass-transfer zone concept can be useful in interpreting the experimental results in this study.

The experimental results display incomplete sulfidation, below 50% utilization rate, at the tested conditions. The short bed length in all experiments relative to the mass-transfer zone caused diminishing of the utilization rates. This effect is evident from Figure 3D), where the smaller bed length 2.5 cm exhibited an overproportional loss of capacity over the 4.5 cm bed. A significantly taller bed than the current mass-transfer zone in the experiments would have neglected the strong breakthrough effects and increased utilization rates. The sulfidation capacities and utilization rates in this study do not therefore likely represent the equilibrium values and should be regarded as apparent capacities and rates.

The effect of GHSV and especially particle size on desulfurization performance suggested significant intraparticle diffusional limitations. As a comparison, Kim and Park³⁰ studied the effect of GHSV in desulfurization and almost full utilization rate (96%) was achieved at 8000 h⁻¹ (particle size distribution of 150–250 μm) and at above 8000 h⁻¹ the intraparticle mass-transfer limitations even with this low particle size distribution were significant. In the same study the effect of particle size on desulfurization performance was studied. The intraparticle diffusion path is dependent on the particle size, and in a 450–1000 μm particle size distribution range the performance dropped significantly. Since commercial-scale adsorption processes utilize significantly larger particle sizes than 1000 μm due to pressure drop constraints, there can always be assumed to be significant intraparticle diffusional resistances.

In theory, higher reaction temperature improves mass-transfer; however this is not fully evident in the results in Figure 3B). The effect is visible from the breakthrough curve after \( t_b \) in the highest temperature run at 400 °C, which has the lowest gradient S-curve and thus longest MTZ. The 2 ppmv \( \text{H}_2\text{S} \) breakthrough is still dominated by factors other than the product-layer diffusion, and thus the 400 °C had the lowest breakthrough capacity. Since the process is pore diffusion limited, the surface S-species concentration is high and this decreases the driving force for mass transfer from the bulk to the surface. As a result, higher temperatures improve adsorption, while higher space velocities decrease it. Since the inlet gas feed rate was kept constant, the space velocities varied, and the 400 °C run had the highest space velocity, negatively affecting performance.

It can be concluded that in this study the particle size was the limiting factor as also evident from the test with the larger particle size distribution in Figure 3C). Furthermore, during the reaction between ZnO and \( \text{H}_2\text{S}, \text{S}^{2-} \) ions substitute \( \text{O}^{2-} \) in the ZnO lattice.³² Since the formed ZnS occupies a larger volume, sulfidation causes a lack of porosity, as evident by the lowering of the BET surface area found in this study. This also causes

\[
\text{LUB} = L \left( 1 - \frac{t_b}{t_s} \right) \quad (6)
\]
product-layer diffusion resistance, and several studies have attempted to model these diffusion resistances. The fresh adsorbent had a surface area of 46 m$^2$ g$^{-1}$ and spent adsorbents in the range 17–18 m$^2$ g$^{-1}$, Table 5.

The empirical deactivation model was used to model the laboratory-scale experimental breakthrough curves in this study. FPD-GC data from the calibrated H$_2$S range from 7 to 70 ppmv could be used to derive the constants. The deactivation rate term, $k_d$, has to take into account the changes in surface area, pore volume, and activity of the solid reactant due to sulfidation. Despite these challenges, the deactivation model represents the experimental data well. However, for the sizing of larger adsorbent beds additional experimental data with bigger bed length is required. Adsorbent tests found in literature have mostly been performed in the absence of tars and other hydrocarbon contaminants, using model process gas or H$_2$S with an inert gas. Wakker et al. however, performed deactivation tests for MnO/Al$_2$O$_3$ and FeO/Al$_2$O$_3$ adsorbents in the presence of hydrocarbons CH$_4$, C$_2$H$_6$ and C$_4$H$_10$. At the lowest test temperature of 350 °C there was no deactivation detected due to carbon deposition, but at 600 °C there was brown deposition on the reactor tube that was polymerized or vulcanized H$_2$S with hydrocarbons. The authors note that also CO can cause carbon deposition, but such phenomena were not observed in the conducted tests. Water has also been reported to prevent carbon formation, which further prevents deactivation problems by hydrocarbons in wet syngas. In this work, the effect of biosyngas tars on desulfurization at 400 °C was investigated in wet syngas. The sulfidation capacity presented in Figure 4 was very similar to the reference run without tars. The breakthrough curve for the adsorbent tested in syngas 2 was steeper than in syngas 1, which might be attributed to either the 20% higher initial H$_2$S concentration or competing adsorption of other species onto the surface. However, syngas desulfurization requires a low H$_2$S outlet concentration, and thus breakthrough time and capacity are more important parameters in evaluating performance than the length of the mass-transfer zone. The spent adsorbent particulates from the syngas 2 run showed some carbon deposition on the surface, but the BET surface area analysis indicated only a slight loss of surface area compared to the reference. Thus, the effect of hydrocarbons was minor and desulfurization with ZnO adsorbents in such gas is feasible.

5. CONCLUSION
In this work, the technical feasibility of non-regenerable ZnO-based adsorbents for bulk biosyngas desulfurization was studied. Chemical equilibrium calculations predicted good desulfurization performance of ZnO but also the possible presence of COS, for which ZnO has no adsorptive affinity. Long-term breakthrough capacities of a commercial ZnO adsorbent were determined in laboratory scale using model biosyngas. The results indicated heavy intraparticle diffusional resistances within the tested conditions, with <50% apparent adsorbent utilization rates at 2 ppmv H$_2$S breakthrough. The low utilization rate is partly attributed to the low bed length relative to the mass-transfer zone in the experiments, overstating the breakthrough effects. The BET SA results showed significant loss of porosity due to the sulfidation product ZnS blocking the fine pores. A first-order deactivation model to estimate the full breakthrough curves at specific conditions was applied and found to represent the laboratory-scale results well. The effect of tars on desulfurization performance was found to be small, and the spent adsorbent surface areas were similar to reference adsorbents run in nontar gas even though heavy dark coloring of the particles occurred.

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Abbreviations

$C =$ concentration
$CW =$ cool water
$D =$ diameter
$D_{eqv} =$ equivalent spherical diameter, mm
$EDS =$ energy dispersive X-ray spectroscopy
$FPD =$ flame photometric detector
$FT =$ Fischer–Tropsch (synthesis)
$GHHSV =$ gas hourly space velocity real basis, h$^{-1}$
$HW =$ hot water
$K =$ equilibrium constant
$k_d =$ deactivation rate constant, h$^{-1}$
$k_i =$ initial adsorption rate constant, dm$^3$ g$^{-1}$ h$^{-1}$
$L =$ bed length, cm
$L/D =$ length-to-(inner) diameter ratio
$LUB =$ length of unutilized bed
$MTZ =$ mass-transfer zone
$N =$ nominal (at 273.15 °C and 101 325 kPa)
$n.d. =$ not detected
$NDIR =$ nondispersive infrared adsorption detector
$\Delta S =$ (x ppm) = desulfurization capacity where x is the breakthrough concentration
$SEM =$ scanning electron microscope
$SNG =$ synthetic natural gas
$t_b =$ breakthrough time, h
$t_s =$ saturation time, h

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TCD = thermal conductivity detector
TOS = time on stream, h

V = gas flow rate, N dm³ min⁻¹

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