

Biogas Desulfurization by Pelletized Biomass Ash in a Fixed Bed Arrangement

Lapp F.^{1*}, Kraft T.¹, Schmutzler F.¹, Brück F.¹, Liebich T.², Lang M.³, Theilen U.¹ and Weigand H.¹

¹ Competence Centre for Sustainable Engineering and Environmental Systems (ZEuUS), THM University of Applied Sciences, Wiesenstr. 14, 35390 Gießen, Germany

² GUT Gesellschaft für Umwelttechnologie mbH, Usinger Str. 32, 61169 Friedberg, Germany

³ LANG Bioenergie GbR, Andreshof, 35625 Hüttenberg, Germany

*corresponding author:

e-mail: florian.lapp@lse.thm.de

Abstract The removal of H₂S is a prerequisite to the energetic valorization of biogas in combined heat and power (CHP) plants. Conventionally, the final step in desulfurization involves filtration over granular activated carbon (GAC). Rising market prices for GAC have fostered research on alternative filtration media. Here we investigated the feasibility of globally available biomass ash (BA) as a cost-efficient alternative. A filter column ($V = 2.4$ L) was loaded with 800 g BA (10 % moisture) and upstream-fed with a total of 2.76 m³ raw biogas sampled from a food waste fermentation plant. At the outlet H₂S, O₂, CO₂ and CH₄ were monitored. The H₂S was completely sequestered by the filter material and no breakthrough was observed, resulting in a load of 0.26 wt.-% H₂S. XRF analyses suggested even further potential. First tests with a new, static batch reactor using a feed of >99 vol.-% H₂S and pelletized BA achieved H₂S uptakes of up to 4 wt.-%, outweighing the reported uptake capacity of conventional GAC. Further investigations are underway to assess the pelletized BA under flow-through conditions. Results will pave the way to scale up the system and test it under real world conditions at a food waste fermentation plant.

Keywords: Biogas, desulfurization, biomass ash, wood ash, pelletizing

1. Introduction

Biogas is a pillar of the transition towards renewable energy supply. Its use has been increasing throughout the EU in recent years (EurObserv'ER 2022). Controlled fermentation of biomass produces a mix of CH₄, CO₂ and traces of H₂S, which may be either directly used as a fuel for combined heat and power (CHP) plants or upgraded to biomethane (Weiland et al. 2015). Prior to combustion in CHP plants desulfurization is mandatory, as combustion of H₂S leads to heavy corrosion (Weiland et al. 2015; Andrade et al. 2018). The final desulfurization step typically involves the use of granular activated carbon (GAC) filters (An-

drade et al. 2018). To increase GAC performance impregnation is often employed, e.g. with potassium hydroxide or iodine salts (Weiland et al. 2015).

A disadvantage is that spent GAC cannot be regenerated and must be disposed of. Furthermore, the energy-intensive production of impregnated GAC has caused rising market prices (Alavi-Borazjani et al. 2020) and is associated with considerable environmental pollution (Fernández-Delgado Juárez et al. 2018). This has fostered research on alternative filtration media. One promising candidate are biomass ashes (BA). This waste stream is globally available with growing production in recent years and has shown promising performance in H₂S removal (Alavi-Borazjani et al. 2020). Furthermore, spent filter BA may be valorized as potential forestry fertilizer due to its generally high contents of essential plant nutrients (Zimmermann et al. 2002) and additional biogas-borne sulfur, which is increasingly lacking at forest sites (Thoms et al. 2018). Figure 1 shows how a BA-based desulfurization system fits into a circular economy set-up.

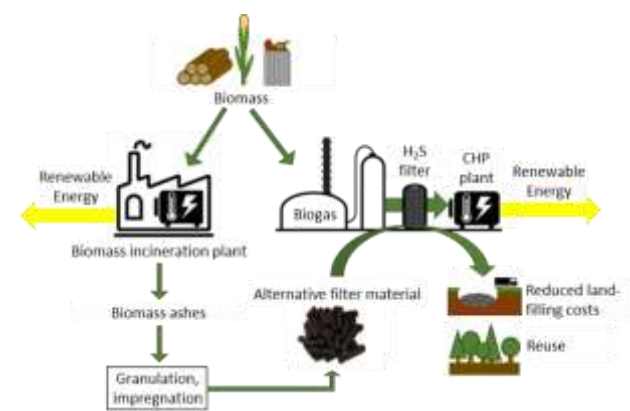


Figure 1. Circular economy of the desulfurization of biogas with biomass ash

In this study we aimed at quantifying the H₂S sequestration capacity of different BA and at improving their filtration performance. To this end, a flow-through column test as

well as static batch tests with a novel pressure-based desulfurization reactor were performed. Therewith we followed the ultimate goal of providing a sustainable alternative to conventional GAC-based H₂S filter systems.

2. Material and Methods

2.1 Ash Characterization and Preparation

A sampling campaign was conducted at three wood-fueled heating plants in Middle Hesse, Germany in 2022. All three facilities use a grate furnace for combustion with a dry discharge system for the bottom ash. Flue gas is treated with a cyclone and subsequent baghouse filters. All three facilities used pine wood chips as feedstock. At each location, both biomass bottom (BBA) and fly ash (BFA) were collected from their discharge containers using shovels, giving a total of 6 samples which are denoted BBA1–3 and BFA1–3. Subsamples were ground in a ball mill (Fritsch, Germany) at 350 rpm for 4 min and analyzed for elemental composition by X-ray fluorescence spectrometry (XRF).

For the preliminary H₂S sequestration test, as received finely grained BFA was used. For all further tests, the ashes were screened for compliance with German fertilizer regulations based on their XRF results. Selected ashes were then sieved and the ≤2 mm fraction was pelletized to supply a filter material meeting the demands of decreased pressure loss and dust formation. An exemplary batch of pelletized BBA is shown in Figure 2.



Figure 2. Pelletized BBA sample (fraction ≤2 mm)

2.2 Preliminary Column Test

For the proof of concept 800 g BFA were mixed with 80 g of deionized (DI) water and loaded in a PVC filter column ($d_i = 89$ mm, $h = 210$ mm). The column was upstream-fed with raw biogas sampled from a food waste fermentation plant before passing the GAC filter. The total operating time for the laboratory column was 28 h. The total flow was 2.76 m³, giving a mean flow rate of 1.64 L·min⁻¹. Using a biogas analyzer (Multitec 540, Sewerin, Germany), the output concentrations of H₂S, O₂, CO₂ and CH₄ were measured continuously, while the input concentration was measured once per retrieved gas sample bag. The volumetric flow was monitored using a drum gas meter (Ritter, Germany). Temperature at different column levels was measured along the outer shell with an infrared thermometer (Voltcraft, Conrad Electronic, Germany). After the experiment, the column was dismantled and sampled in six

sections along its filling level to allow for depth-resolved total sulfur analysis by XRF.

2.3 Static Desulfurization Tests

After the proof of concept, a static batch reaction system was designed to quickly test the H₂S sequestration capacity of different BA pellets under varying conditions. To accelerate the H₂S sequestration, a gas cylinder of 99.5 % pure H₂S (Nippon Gases Deutschland, Germany) was used as input feed. A PI diagram of the test stand is shown in Figure 3. All piping and sealing elements were made of stainless steel/PA and EPDM/PTFE, respectively.

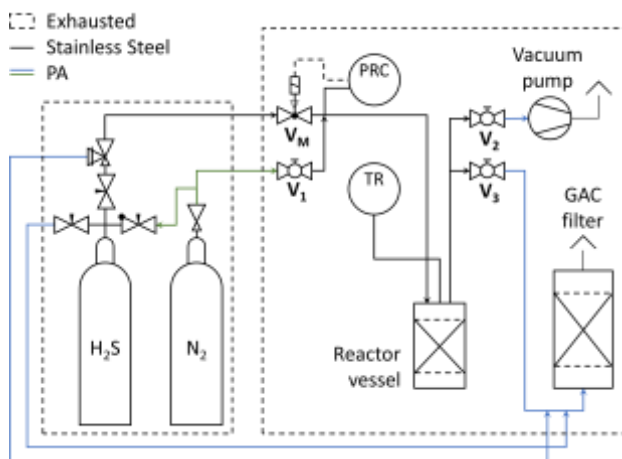


Figure 3. PI diagram of the static pressure desulfurization test stand

For the experiments, pelletized BA (~60 g) was manually hydrated to W/S ratios of 0–0.15 with DI water, placed in a sampling rack and weighed. The rack was placed inside a stainless steel vessel ($d_i = 60$ mm, $h = 100$ mm) and sealed. To generate an H₂S rich atmosphere, the system was flushed with N₂ for 2 min before a vacuum of roughly 50 mbar was generated using a vacuum pump (ILMVAC, Germany). The H₂S was then fed through a magnetic valve (END-Armaturen, Germany) and the pressure drop caused by uptake of H₂S from the gas phase was monitored with an inline pressure sensor (model A-10, WIKA, Germany). Temperature was also recorded inline (model TR36, WIKA, Germany). The reactor pressure was regulated between two setpoints using an analogue signal meter (Digalox DPM72-MPPA, TDE Instruments, Germany) as control unit for the feed valve. The valve would open when the reactor pressure dropped below 0.95 bar and close once it reached 1.15 bar. After 2 h, the experiments were terminated and the system flushed with N₂ for another 2 min. The H₂S uptake was calculated from the resulting intermittent pressure drops according to equation (1):

$$\zeta_{\text{H}_2\text{S}} = \sum_{i=1}^k \frac{(p_i - p_{i+1}) \cdot V_{\text{Gas}}}{R \cdot T_i} \cdot \frac{M_{\text{H}_2\text{S}}}{m_{\text{Sample}}} \cdot 100 \quad (1)$$

where p_i is the absolute reactor pressure at interval i [Pa], V_{Gas} is the effective reactor volume (pipes plus reactor volumes minus sample and sample rack volumes) [m³], R is

the ideal gas constant [$8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$], T_i is the reactor temperature at interval i [K], $M_{\text{H}_2\text{S}}$ is the molar mass of H_2S [$34 \text{ g}\cdot\text{mol}^{-1}$] and m_{Sample} is the dry sample mass.

3. Results and Discussion

3.1 Elemental Composition

All bottom and fly ash samples had dry matter contents above 99.6 wt.-%, which conforms to the dry discharge systems at the incineration plants. The most abundant elements in the samples were Ca (12.3–30.1 wt.-%), Si (5.5–15.8 wt.-%) and K (6.1–22.7 wt.-%) followed by varying amounts of Mg, Mn, Al, Fe and S (0.6–4.0 wt.-%). These

values are within the range reported in literature (Schnabel et al. 2021; Teker Ercan et al. 2023; Trivedi et al. 2016). In terms of these macroelements, the bulk composition of both ash types was similar, with bottom ashes showing accumulation of Si and Ca and fly ashes showing enriched K and S contents. Microelements, which are displayed in Table 1, varied among the ash types. Since spent filter BA may potentially be used as a forestry fertilizer, the microelemental contents were evaluated in regards to German fertilizer regulations (Anlage 2, DüMV, Germany). In terms of potential fertilizer application, BFA seems generally unfavorable due to exceedingly high Pb, Cd and Hg contents. From this ultimate application perspective, the bottom ashes BBA2 and BBA3 were chosen for future biogas desulfurization tests.

Table 1. Elemental composition of BA samples (given by XRF) compared to regulatory limits of German fertilizer legislation (Anlage 2, DüMV, Germany). Green = Complies, Yellow = May comply, Red = Does not comply

Sample	Micronutrients / $\text{mg}\cdot\text{kg}^{-1}$					Pollutants / $\text{mg}\cdot\text{kg}^{-1}$					
	Fe	Mn	Cu	Zn	Ni	As	Pb	Cd	Cr	Hg	Tl
BBA1	$2.5\cdot 10^4$	$2.1\cdot 10^4$	170	198	160	<1.0	2.10	<4.0	258	<1.5	<1.0
BBA2	$2.0\cdot 10^4$	$3.4\cdot 10^4$	112	59.3	55.9	<1.0	<1.5	<4.0	232	<1.5	<1.0
BBA3	$3.1\cdot 10^4$	$1.4\cdot 10^4$	135	37.8	59.6	<1.0	16.9	<4.0	258	<1.5	<1.0
BFA1	$1.8\cdot 10^4$	$1.8\cdot 10^4$	204	2673	195	<3.0	191	152	305	<1.5	<1.0
BFA2	$1.3\cdot 10^4$	$1.6\cdot 10^4$	253	6730	30.6	<3.0	242	77.3	137	4.70	<1.0
BFA3	$1.7\cdot 10^4$	$0.6\cdot 10^4$	166	2759	47.2	<3.0	146	20.8	133	5.90	<1.0
Limits	-	-	900	5000	80	40	150	1.5	450	1	1

3.2 H_2S Sequestration

A total of 8 gas sampling bags each holding $\sim 300 \text{ m}^3$ of raw biogas were successively fed to the BFA filter. The input composition ranged from 360–1100 ppm H_2S , 0.0–0.9 vol.-% O_2 , 22–40 vol.-% CO_2 and 46–61 vol.-% CH_4 . The presence of O_2 in the raw gas is expected since in the sampled food waste fermentation plant, oxygen is added just before the impregnated GAC-filter to promote catalytic H_2S reduction. Figure 4 shows the results of the test. No H_2S breakthrough was observed within 28 h. The cumulated H_2S sequestration of the filter was 0.26 wt.-%, which is consistent with the total sulfur increase as determined by XRF (data not shown). The depth-resolved XRF analyses revealed that sulfur was only enriched in the first 100 mm of the column, suggesting much higher H_2S removal capacity. The achieved H_2S sequestration is higher than the 0.04 wt.-% reported by Mostbauer et al. (2015) for a lab trial with biomass bottom ash.

As a side effect, biogas-borne CO_2 was completely sequestered by the BFA within the first 10 min. Partial breakthrough began at minute 15, and output equaled input after 35 min. Simultaneously, the column temperature rose from 24.5 to 39.0 °C and decreased again after full CO_2 breakthrough had occurred. This suggests that the BFA was exothermically carbonated by the biogas-

borne CO_2 . Fernández-Delgado Juárez et al. (2018) observed a similar effect in their pilot-scale BBA-based biogas filter, where CO_2 breakthrough occurred in the beginning phase accompanied by a spike in temperature. Schnabel et al. (2021) demonstrated the potential of BFA to sequester up to 4.36 wt.-% of CO_2 based on carbonation of its high $\text{Ca}(\text{OH})_2$ content.

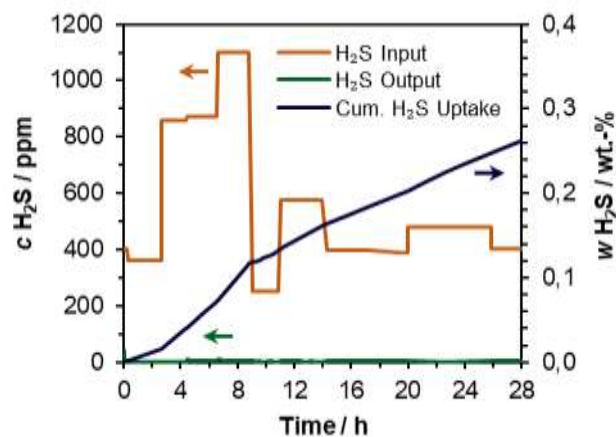


Figure 4. H_2S concentrations and calculated uptake over the 28 h column test of a BFA

In Figure 5 an exemplary run of the static desulfurization test (pelletized BBA, W/S ratio of 0.05) is shown. The

pressure course follows a typical sawtooth characteristic caused by constant H₂S uptake and redosing. The reaction speed notably slows down as the BBA is apparently satiated. After 2 h, the pelletized BBA had sequestered 2.45 wt.-% H₂S, which is a magnitude higher than the 0.26 wt.-% achieved with non-granulated BFA over 28 h in the column test. It was also higher than the 0.5–1.0 wt.-% reported for non-impregnated GAC (Oles et al. 2015). Depending on the W/S ratio, H₂S sequestration of the tested BBA varied between 0.56–4.29 wt.-%, indicating high sensitivity towards the filter conditions. Repeated measurements ($n = 4$) of a BBA sample with constant conditions gave a relative standard deviation of 4.5 %, indicating good repeatability.

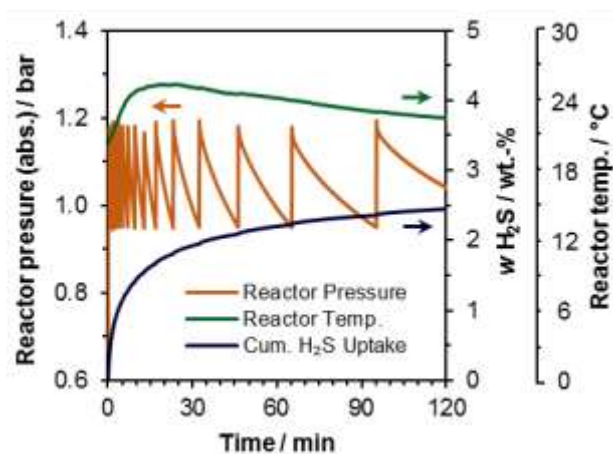


Figure 5. Pressure, temperature and calculated H₂S uptake over a 2 h pressure desulfurization test of a pelletized BBA (W/S = 0.05)

4. Conclusion and Outlook

The results show the potential of biomass ash as an alternative to GAC-based H₂S filter systems. The static batch desulfurization test proved to be viable for quick determination of H₂S sequestration capacity due to high reaction speed. In the light of that, various influences on H₂S removal efficiency (sample origin, agglomeration technique and additives) may be swiftly tested. Current work focuses on the implementation of a synthetic biogas supply to a column reactor to verify the results of the pressure reactor under real life conditions. Variations of H₂S and CO₂ input as well as gas temperature and relative humidity will allow to gain insight into possible reaction mechanisms and interactions. Assuming the uptake capacity is economically met, BA filters may be an interesting alternative to increasingly expensive GAC.

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