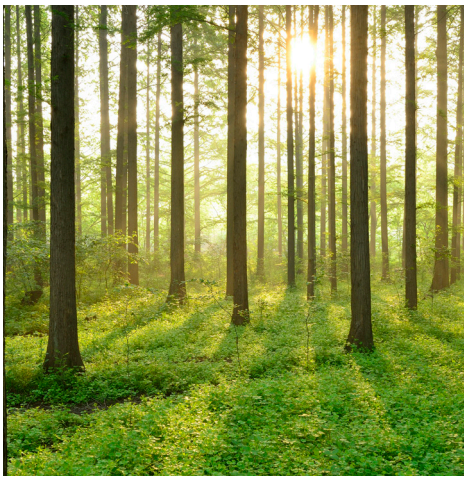
REMOVAL OF SULPHUR SPECIES USING INDUSTRIAL RESIDUAL STREAMS

REPORT 2020:665



BIODRIVMEDEL FÖR SVERIGE 2030

Energiforsk

Removal of Sulphur Species using Industrial Residual Streams

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Foreword

The project has been conducted within the Energiforsk programme Biofuels for Sweden 2030 (Biodrivmedel för Sverige 2030), with the goal to contribute to the development of biofuels for the transportation sector and a fossil-free transportation fleet by 2030.

The programme has been financed by EON Gas Sverige AB, Gasnätet Stockholm AB, Göteborg Energi AB, Neste AB and the Region Skåne.

Within this project, the possibility for using industrial residual streams such as fly ash, green liquor dregs and lime have been investigated for the removal of sulphur species derived from biomass gasification. An experimental study has been performed in which four different sulphur species, amongst others H_2S, have been removed. The experiments have been performed as an experimental, explorative part within the project Co-Generation of BioJet in CHP Plants (Energiforsk report 2020:664), which has had the overall focus of designing and estimating the investment and operational costs for constructing an integrated biojet plant in an existing combined heat and powerplant.

Emil Gammelgaard and Christian Hulteberg have both been involved in planning of the experiments and Emil performed the actual experimental work. Christian and Emil performed the data evaluation and compiled the report. Anton Larsson, Gabriel Gustafsson and Christer Gustavsson have conducted the work in main project, presented in the Energiforsk report 2020:664.

The reference group for the project had the following members: Raza Naqvi, Karlstad University, Jan Brandin, Linnaeus University, and Bertil Wahlund/Anton Fagerström (Energiforsk). The reference group is gratefully acknowledged for invaluable contribution to the project.

Stockholm May 2020

Bertil Wahlund Energiforsk AB

Sammanfattning

Det finns flera utmaningar när det kommer till produktion av syntetiska bränslen från fasta, kolbaserade bränslen så som biomassa. En av dessa utmaningar är den svavelhalt som finns i biomassan och den effekt som detta svavel har på omvandlingen av biomassan till logistiska bränslen. Framförallt gäller detta för de katalytiska steg som ingår i omvandlingen.

I denna rapport redogörs för möjligheten att använda industriella biprodukter, som flygaska, grönlutslam och mesa för att ta bort de svavelämnen som bildas vid förgasning av biomassa. En experimentell studie har jämfört hur väl fyra olika svavelämnen, bl.a. svavelväte, tas upp av dessa biprodukter. I rapporten återges prestandan för dessa material, med olika förbehandlingar, och den bäst fungerande biprodukten verkar vara flygaskan från biomassaförbränning. Detta framförallt efter den har behandlats med vatten i en så kallad släckningsreaktion. För att kunna fungera väl som svavelavskiljningsmedel måste dock den ström som ska behandlas vara relativt fri från koldioxid, då den aktiva substansen i askan, kalciumhydroxid, också reagera med koldioxid. Givet dessa resultat och förutsättningar förefaller det troligt att det går att använda denna typ av biprodukter som ett komplement till traditionell svavelavskiljning och på så sätt sänka totalkostnaden för reningen.

Experimenten har genomförts som en utforskande del inom ramen för projektet kraftvärmeintegrerad flygbränsleproduktion som redovisas separat (Energiforskrapport 2020:664, ”Co-Generation of BioJet in CHP Plants”). Denna rapport innefattar design av hela systemet från biomassainmatning till färdigt flygbränsle. Det experimentella arbetet som redovisas här är en del av detta.

Det återstår dock en hel del arbete för att kunna kommersialisera tekniken, både experimentellt arbete och arbete med utrustningsdesign. Dock förefaller ett principkoncept som bygger på slangfilter ge en bra möjlighet för kontinuerlig in- och utmatning av svaveladsorbenten. Genom att placera detta filter innan en traditionell, zinkoxidbaserad gasrening kan den totala driftskostnaden troligen sänkas för vissa typer av anläggningar.

Summary

There are several challenges when it comes to producing synthetic fuels from solid carbonaceous material such as biomass. One of these challenges is the sulphur content of the biomass and its impact on the downstream processing of the biomass into logistic fuels. This in particular applies to the catalytic unit operations in the transformation of the biomass into fuels.

In this report, the possibility for using industrial residual streams such as fly ash, green liquor dregs and lime have been investigated for the removal of sulphur species derived from biomass gasification. An experimental study has been performed in which four different sulphur species, amongst others H_2S, have been removed. The performance of different materials is reported, and the best alternative seems to be the use of fly-ash from biomass combustion, after slaking it with water. The system requires a relative carbon dioxide-free gas as the active compound in the ash, calcium hydroxide, also readily reacts with carbon dioxide. However, this clearly indicates that the use of the correct side-product to remove sulphur can provide a rather low-cost complement to traditional sulphur removal.

The experiments have been performed as an experimental, explorative part within the project Co-Generation of BioJet in CHP Plants (Energiforsk report 2020:664), which has had the overall focus of designing and estimating the investment and operational costs for constructing an integrated biojet plant in an existing combined heat and powerplant.

For providing a suitable engineering solution, more work is required, both experimentally and with respect to scale-up. However, a first general solution based on baghouse filters is suggested to provide a possibility for continuous generation and regeneration of the sulphur removal. This upstream sulphur removal is used in conjunction with traditional hot sulphur removal, e.g. in ZnO.

List of content

1 Introduction

Sulphur is a major problem in the synthesis of renewable fuels and chemicals from synthesis gas and therefore, finding a low-cost solution to removing the sulphur-compounds is desirable. One way of removing the compounds are via chemical adsorption, and this report will investigate the adsorption of sulphur species using industrial residual streams as adsorbent materials.

Hulteberg Chemistry & Engineering AB has, together with BioShare AB, investigated various aspects of producing synthetic logistics fuels in existing fluidized biomass boilers in a project with the overall focus of designing and estimating the investment and operational costs for constructing an integrated biojet plant in an existing combined heat and powerplant, reported in a separate report Co-Generation of BioJet in CHP Plants (Energiforsk report 2020:664). As a part of the project, the possibility to use different industrial residual streams, e.g. biomass boiler ash, green liquor dregs and lime, as an adsorbent for a desulphurization unit-operation upstream a Fischer-Tropsch process was experimentally verified. To investigate this possibility, the different residual streams were assessed with respect to composition and expected active compounds, and a few were selected for in-detail experimental investigation, with the reasoning that they will be representative for most of the cases.

The experimental investigation was performed as an initial screening of the adsorption of four different sulphur species (with special attention to H_2S) at three different temperatures. The screening was performed at high space velocity conditions for enabling rapid screening and comparison between the samples. As a point of reference, a commercial zinc oxide sample was used. In addition to the adsorption tests, the ash samples have been evaluated as catalysts for the hydration reaction of COS and CS_2 for the potential reaction to H_2S.

$$COS + H_2O \rightleftharpoons H_2S + CO_2 \qquad \text{Eq. 1}$$

$$CS_2 + 2\,H_2O \rightleftharpoons 2\,H_2S + CO_2 \qquad \text{Eq. 2}$$

The report starts by giving a background to the work performed and goes on describing the experimental methods used for performing the screening experiments, including the experiments performed, the adsorbents used and analysis methods. This is followed by a recollection of the results generated in the experimental work, for each individual ash. Finally, conclusions are drawn, and suggestions on future work is given.

2 Background

Sulphur removal from gas is a mature technology, and the problem can be handled in two ways. Either the sulphur is removed from the gas via adsorption, i.e. by contacting it with a material that strongly interact with the sulphur specie. Or the removal can be done using absorption, i.e. contacting the gas with a liquid that has higher solubility for the sulphur species (caused by chemical or physical means) than the other gases, figure 2.1 [1].

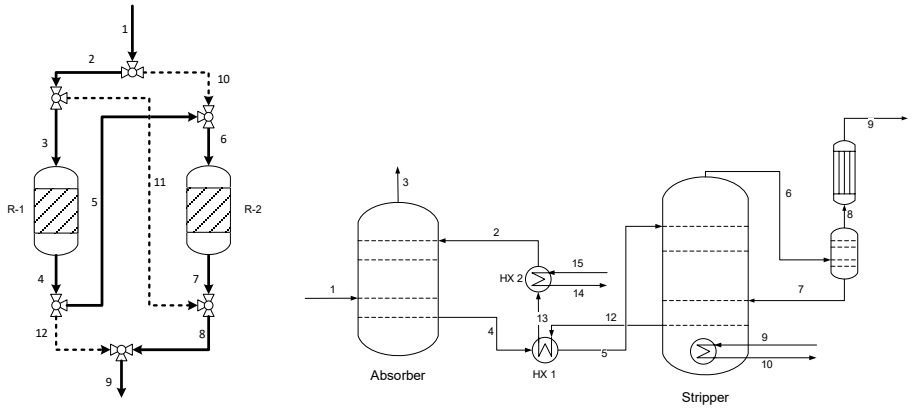

Figure 2.1 Schematic depiction of a lead-lag system for sulphur adsorption on the left and for sulphur absorption on the right.

The sulphur present in gas phase, when processing both natural gas and after biomass gasification, is normally in the form of hydrogen sulphide, carbonyl sulphide and carbon disulphide, with the majority of the sulphur being present as hydrogen sulphide [2-9]. The adsorption uses solid material (adsorbent) for the removal of the incoming sulfur. This can be done in one out of two ways, either at low temperature using activated carbon, a common approach for biogas purification, or at higher temperature using zinc oxide-based adsorbents [10-15].

The choice of method has several influencing factors, where the first thing is if the stream to be treated is high tempered or not. If the input stream is low in temperature, e.g. natural gas, the cleaning can be performed in all three ways described above, low temperature adsorption, high temperature adsorption and absorption. The deciding factor then comes down to sulphur levels in the gas and the size of the stream to be processed. For high concentrations and high flowrates, the use of absorption is preferred. For lower concentrations and low flowrates, adsorption in activated carbon is preferred, as is the industrial standard in biogas separation. For high flowrates and low concentrations, the hot adsorption in zinc oxide is preferred.

For a hot gas stream, e.g. syngas from gasification, the trade-offs are different. Here the energy density of the gas also influences the choice of technology. In the case, low-energy gases, such as when starting with gasified biomass, heating and cooling is not an option, and the hot adsorption is the preferred method of choice. For high-energy cases, such as in the case of coal gasification, with high sulphur

content, there are less restrictions, and both absorption and low-temperature adsorption is an option, as is high temperature adsorption. In the particular case, a high-temperature adsorption is preferred given the low sulphur content of the gas and the desire to avoid excessive heating and cooling of the gas.

As already stated above, the preferred hot adsorbent in industry is ZnO, which is transformed into ZnS. Zinc is quite reactive and can hold significant amounts of sulphur, upwards toward 30% by weight. When assessing the composition of the industrial residual stream available, it is clear that Zn is not a major compound in the mix, table 2.1

Table 2.1 The elemental composition of various industrial residual stream [16, 17].

Element	Green liquor dregs	Biomass ash	Lime
Ca	210 g/kg	350 g/kg	714 g/kg
Si	7.7 g/kg	2 g/kg	n/a
Mg	56 g/kg	200 g/kg	n/a
Na	52 g/kg	50 g/kg	n/a
Mn	17 g/kg	n/a	n/a
Zn	2.2 g/kg	n/a	n/a
K	n/a	150 g/kg	n/a

As revealed in the table, there is very little zinc in the different industrial streams, which is the major compound used in desulphurisation. Indeed, the major compound in all steams appears to be calcium. The lime is of course more or less pure lime (CaO), and the green liquor dregs usually have lime added to it for ease of separation [17]. The use of calcium (in both the oxide and the hydroxide form) for removal of hydrogen sulphide is know; in the latter case, as a part of a chemical scrubbing operation [1, 18]:

$$CaO + H_2S \rightarrow CaS + H_2O \qquad \text{Eq. 3}$$

$$Ca(OH)_2 + 2\,H_2S \rightarrow Ca(HS)_2 + 2\,H_2O \qquad \text{Eq. 4}$$

There is thus reason to believe that it is possible to use the various residual streams for removal of the sulphur via hot adsorption. Due to the similarities of the materials, one material, in this case, biomass ash was selected for further testing. As a trade-off between purity and proximity, the biomass ash was selected for testing as it is generated on the same site as the purification is to be performed. The lime can be reacted into slaked lime ($Ca(OH)_2$) rather conveniently by contacting it with water at elevated temperature (50-100 °C) and the slaked lime is stable to about 600 °C.

It should, however, be stressed that the adsorption must be performed in a CO_2-free environment, as the formation of $CaCO_3$ is rapid from the slaked lime.

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad \text{Eq. 5}$$

3 Experimental

This section presents the experimental procedure, describes the performed experiments and the sorbents tested.

3.1 EXPERIMENTAL SET-UP

In the experimental set-up, two gases have been pre-mixed and passed through a pre-heater. Thereafter, the gas-mixture is passed through the reactor and then onto the analysis equipment for analysis. Mass flow controllers control the flowrates of the gases. The set-up is illustrated in figure 3.1.

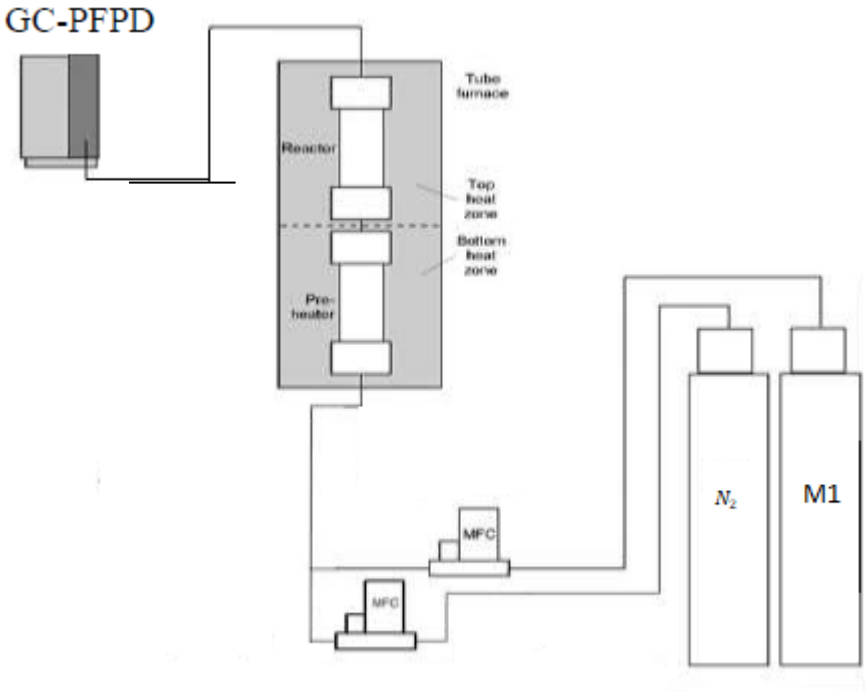

Figure 3.1 Schematic figure of the experimental setup. M1 is the gas mixture described below. For the later stages of experiment, a Coriolis was added to pump distilled water into the preheater and reactor, and another gas mix and MFC was also added as described.

The pre-heater and the reactor are situated in a vertically divisible, two-zone tube furnace. The two temperature-zones in the oven are controlled independently of each other, and the temperatures are set such that the inlet temperature of the adsorbent bed is as close as possible to the desired temperature. The temperature is monitored by a thermocouple in the inlet of the reactor; this temperature has been set to 150, 250 or 350 °C during all experiments. The gas used was supplied by Strandmøllen, and a brief specification of it is shown in table 1. The gas was diluted before use, giving 10 ppm of each sulphur compound into the reactor. In the last stages of this experimental verification, the ashes catalytic activity towards sulphur species hydration was investigated. An additional gas mixture was connected with a mass flow controller to the system. A container with liquid

distilled water was also connected to feed water via a Coriolis flowmeter into the reactor in this later stage.

Table 3.1 The qualities of the used gas.

	Gas mixture 1 [M1]	
Content	H_2S	100 ppm
	COS	100 ppm
	Tert-butyl thiol (TBT)	100 ppm
	Tetrahydrotiophene (THT)	100 ppm
	CH_4	Balance
	Gas mixture 2 [M2]	
	CS_2	100 ppm
	Dimethyl sulphide	100 ppm
	Dimethyl disulphide	100 ppm
	CH_4	Balance

The experiments were performed at 150, 250 and 350 °C and ambient pressure, and the ashes were tested at a space velocity of 20,300 h^{-1}. The reactor was 9.5 mm in inner diameter, and 6 ml of adsorbent was used. In the event of testing slaked limes, the water-slaked ashes were prepared by adding 10 wt% (based on sample weight) of distilled water to the sample, which was then was mixed in a glass beaker. Aluminium foil was fitted on the beaker with the sample and was placed in an oven for drying and reaction at 95 °C for about 12 h.

The gas analysis was performed using a Scion 456-GC Gas Chromatograph equipped with a 500 µl inert steel sample loop 1/16" for Valco injection valve, a Rtx-DHA-50 Cap. column 50m, 0.20mm ID, 0.5µm and a PFP-detector with Electrometer (S and P Modes). Calibration was done using 1.5, 5.5 and 10 ppm of each of the sulphur species. The injector temperature was set to 280 °C; the split ratio was 20, the oven was set at a temperature of 120 °C for 8 min and then increased to 180 °C using 20 °C/min increase and was held at this temperature for 3 min. The overall analysis time was 14 min. The retention times for the sulphur compounds are given in table 3.2, for some of the samples, there were an unknown specie formed, which is also given in the table.

Table 3.2 The retention times of the used sulphur species.

	Gas mixture	
Content	H_2S	4.01 min
	SO_2	4.10 min
	COS	4.17 min
	Unknown sulphur specie	4,85 min
	Dimethyl sulphide	5.94 min
	CS_2	6.58 min
	Tert-butyl thiol	7.31 min
	Unknown sulphur specie	9.39 min
	Dimethyl disulphide	11.11 min
	Tetrahydrotiophene	12.85 min

When investigating the ashes catalytic activity towards hydration, gas mixture 1 and 2 is used, as specified in table 3.1. The gas flow is initiated through the adsorption bed and maintained until a stable outlet concentration is achieved. When stable, a water flow is pumped into the preheater which is instantly vaporized and feed to the reactor equivalent to 5% by volume. Following the water input, a shift in outlet concentration profiles may be detected in the gas chromatograph due to hydration of the sulphuric species effectively increasing the concentration of H_2S instead of reducing it through adsorption. The desired reactions are given below:

$$CS_2 + H_2O \rightarrow COS + H_2S \qquad \text{Eq. 6}$$

$$COS + H_2O \rightarrow H_2S + CO_2 \qquad \text{Eq. 7}$$

3.2 ADSORBENTS INVESTIGATED

Several adsorbents were investigated for the removal of various sulphur species listed in table 3.1 and the investigated industrial residue-based adsorbents were compared to a commercial zinc-oxide-based one.

3.2.1 Zinc oxide

As a point of reference, a commercial adsorbent has been run under similar conditions to the ashes to compare performance. The adsorbent is a zinc oxide material provided by a major chemical company.

3.2.2 Biomass ash

Ashes was tested from two different power plants operated by Karlstad energi AB, Heden 2 and Heden 3. Bottom-sand and fly-ash samples was tested from each plant. The bottom-sand is a coarser fraction compared to the fly-ash and contains

mainly sand (SiO_2). The ash from Heden 2 was loaded in the reactor without pre-treatment since it was homogeneous in texture, the ash from Heden 3, however, was fractioned to between 20-30 mesh (0.6-0.85 mm) before testing. Below follows a specification of the trace substances in bottom-sand in table 3.3 and fly-ash in table 3.4. As the ashes is of biomass, the trace compounds concentration varies, and so will probably the results:

Table 3.3 The specification of trace substances present in bottom-sand Karlstad Energi analyses samples from the ashes annually and these intervals is from tests made 2011 – 2018 [19].

Compound	Heden 2 [mg/kg TS]	Heden 3 [mg/kg TS]
Ca	49,000	40,700
K	44,300	59,100
Mg	7,180	8,260
P	3,380	2,100
Sb	3.92	0.474
As	6.03	1.66
Ba	1,100	1,190
Pb	26.2	15.1
Cd	0.495	0.0334
Cu	97.9	47.3
Cr	98	38.7
Hg	0.02	0.02
Ni	19.8	14
Zn	1,100	1,080

Table 3.4 The specification of trace substance intervals in the tested fly-ash. Karlstad Energi analyses samples from the ashes annually and these intervals is from tests made 2011 – 2018 [19].

Compound	Trace substance [mg/kg TS]
Si	140,000
Ca	120,000- 220,000
K	36,000 – 69,000
Mg	14,000 – 25,000
P	8,400 – 15,000
As	2.6 – 14
Zn	7,800
B	22 - 260
Cu	50 - 100
Pb	47 - 140
Cr	38 - 88
V	26 - 49
Ni	24 - 54
Cd	6.7 – 20
Hg	0.046 – 0.25

As can be seen from the analysis, the ash is composed to a rather high extent of Ca-species. Indeed, Ca constitute 4-5% of the bottom-sand and 12-22 % of the fly-ash.

3.2.3 Test matrix and test specification

The tests are named so that the process conditions are specified in each name. The following example illustrates the test specification:

Consider test: **H2ASHW250**

- H2, H3 – Specifies if the ash is from Heden 2 or Heden 3.
- ASH, BOT – Specifies if the sample is fly-ash or bottom-sand.
- U, W – Specifies if the sample is unslaked (U) or slaked with water (W).
- 150, 250, 350 – Specifies the reactor temperature during the test.

In the table below the test matrix of this project is presented. The slots are marked with dates when the test was done, and the unmarked slots is tests that was eliminated from the matrix (table 3.5) for the following reasons:

- The bottom-sand proved to be ineffective to adsorb the sulphur species.
- The ammonia slaked test was eliminated because the process where the adsorbent is applicable, does not tolerate ammonia downstream of the adsorption bed.

Table 5 Test matrix, each test is specified with parameters accordingly, and with the date (MM-DD) the test was performed

	Sample	Unslaked			H_2O slaked			Hydration activity	
		T150	T250	T350	T150	T250	T350	T150	T250
Heden 2	Bottom-ash	3-may							
	Fly-ash	2-may	03-may	06-may	21-aug	21-may	21-may		
Heden 3	Fly-ash	7-may	07-may	08-may	23-may	22-may	23-aug	28-aug	29-aug

4 Results and Discussion

In this section, the results from the various adsorption experiments have been reported. First some general remarks about the experiments. COS and THT break through the adsorption bed first in every experiment and does not seem to be able to adsorb to the ashes under the tested conditions. TBT does not break through the adsorption bed in any experiment with temperature 350 ℃ and is hypothesised to be consumed in reaction at this temperature. H_2S concentration in the outlet is higher than the inlet concentration in every 350 ℃ test except one. Indicating reaction in the bed producing more H_2S than is fed to the reactor. Slaked fly-ash is much more efficient in adsorbing H_2S than the unslaked ashes but slaking does not affect COS or THT adsorption. At the end of this section, the implications of the findings on a possible system design concept are discussed.

The experiments discussed here, have been performed as an experimental, explorative part within the project Co-Generation of BioJet in CHP Plants (Energiforsk report 2020:664), which has had the overall focus of designing and estimating the investment and operational costs for constructing an integrated biojet plant in an existing combined heat and powerplant.

4.1 ADSORPTION CAPACITY FOR UNSLAKED AND SLAKED SAMPLES

Below the results from testing the unslaked and water slaked samples is presented, a comparison is made between the tested samples, and the best candidates are chosen and compared.

4.1.1 Unslaked Samples

The bottom-sand was tested first with standard sample testing conditions and then with twice the sample mass, and the results were the same. No adsorption of the sulphur species resulted in the series of bottom-sand was eliminated from the test matrix, figure 4.1.

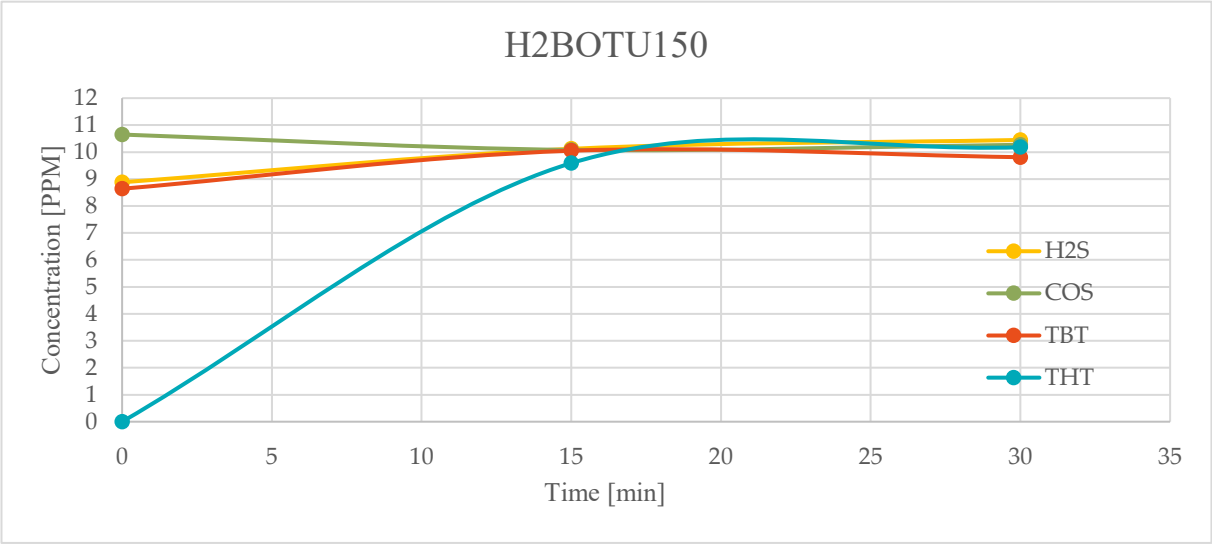

Figure 4.1 No adsorption of the sulphur species in the bottom-sand. Tested at 150 ℃, 21,000 h^{-1} and ambient pressure.

Focus was now shifted to the fly-ashes from the two different boilers. Heden 2 fly-ash was tested at 150 ℃ (figure 4.2) and 250 ℃ (figure 4.3) without much difference. The H_2S breaks through the bed at the same time (30 min) for both tests, however, in the higher temperature case, the H_2S concentration in the outlet flattens out at a lower value than the lower temperature case, indicating a higher capacity than at lower temperature.

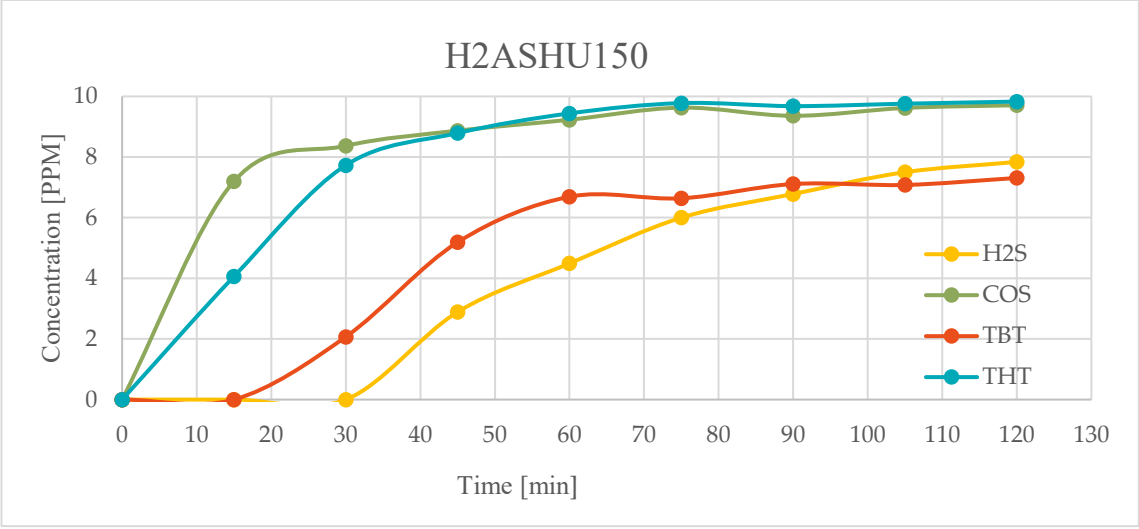

Figure 4.2 Heden 2 unslaked fly-ash is tested at 150 ℃ at 21,000 h^{-1} ambient pressure. The breakthrough of H_2S is at the 4th GC injection (test time/GC injection 14 min).

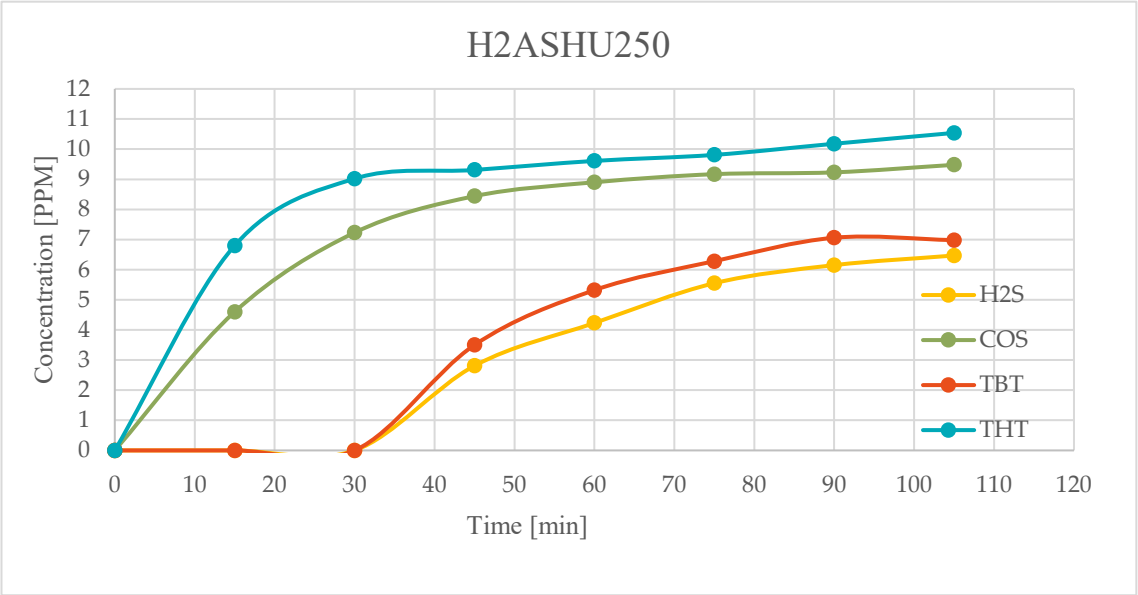

Figure 4.3 Heden 2 unslaked fly-ash is tested at 250 ℃ at 21,000 h^{-1} ambient pressure. The breakthrough of H_2S is at the 4th GC injection (test time 14 min) same as the test at 150 ℃. The concentration of H_2S in the end of testing is lower than in the 150 ℃ case.

The 350 ℃ test is different as the H_2S breakthrough is 60 min (7th GC injection); twice as high as the two former cases. However, the H_2S concentration in the outlet does not stabilize before reaching 13 PPM, which is higher than the inlet concentration of 10 PPM. The TBT does not breakthrough at all during the test, which implies that the adsorption bed has turned into a reaction site for the species converting TBT to H_2S.

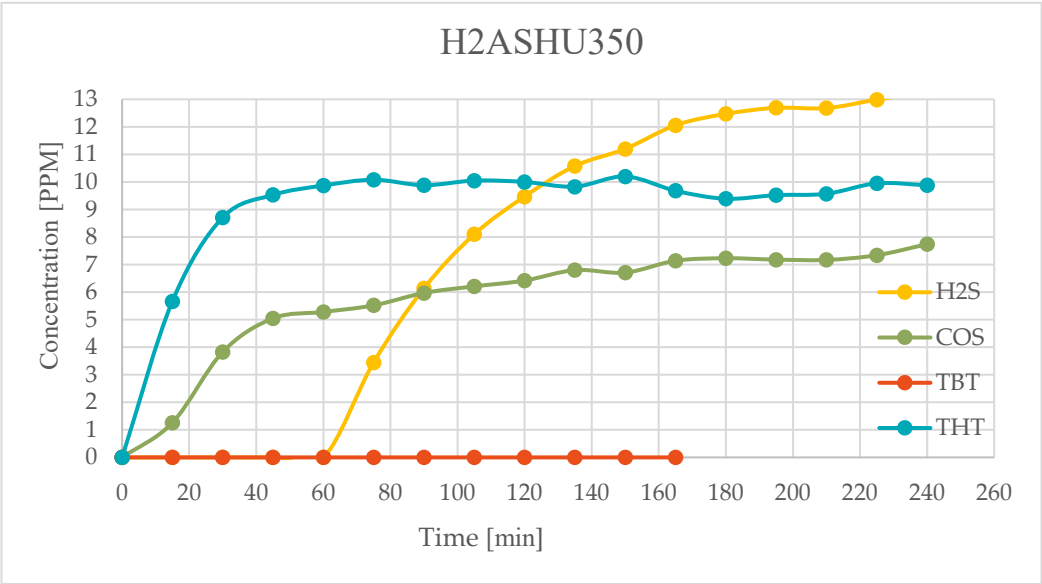

Figure 4.4 Heden 2 unslaked fly-ash test shows an outlet concentration higher than the inlet concentration of H_2S indicating reaction in the adsorption bed tested at 350 ℃, 21,000 h^{-1} and ambient pressure.

Heden 3 tests at 150 °C and 250 °C show the same behaviour as Heden 2 tests at the same temperature. The breakthrough time of the H_2S is the same 30 min, but the outlet concentration of H_2S stabilizes on higher levels quicker for the Heden 3 samples, indicating a lower capacity for these materials.

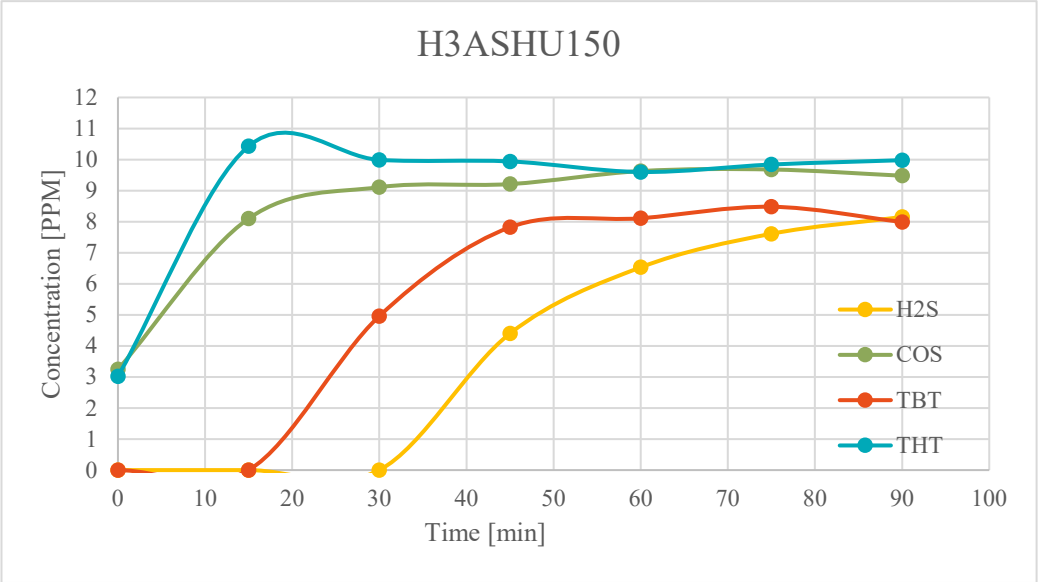

Figure 4.5 Heden 3 tested at 150 °C, 21,000 h^{-1} and ambient pressure unslaked fly-ash show same behaviour as the similar test with Heden 2.

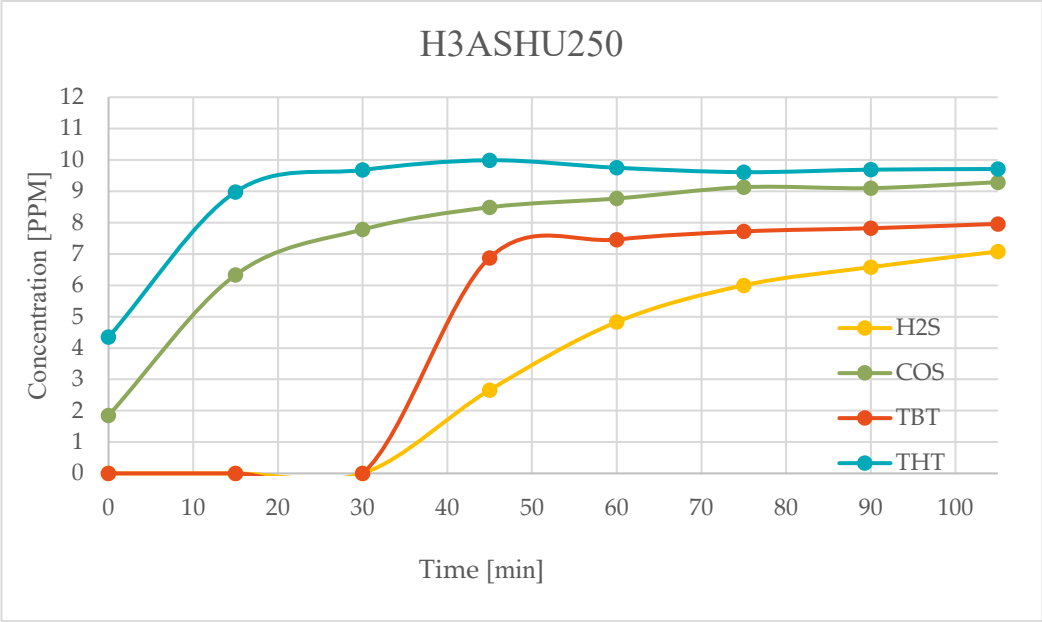

Figure 4.6 Heden 3 unslaked fly-ash 150 °C, 21,000 h^{-1} and ambient pressure test show same behaviour as the similar test with Heden 2 fly-ash.

The test on 350 °C has a H_2S breakthrough of 30 min, which is half of the breakthrough time of the same test on the Heden 2 sample. Just as the Heden 2

sample at 350 °C, the H_2S reaches higher outlet concentrations than inlet and the TBT does not break through, indicating reaction in the bed. One other thing to note is the COS outlet concentration. The breakthrough of the COS is fast, but as the test is done on 350 °C, the outlet concentration increases much slower. This indicate more adsorption sites for this specie becomes active at higher temperatures, figure 4.7.

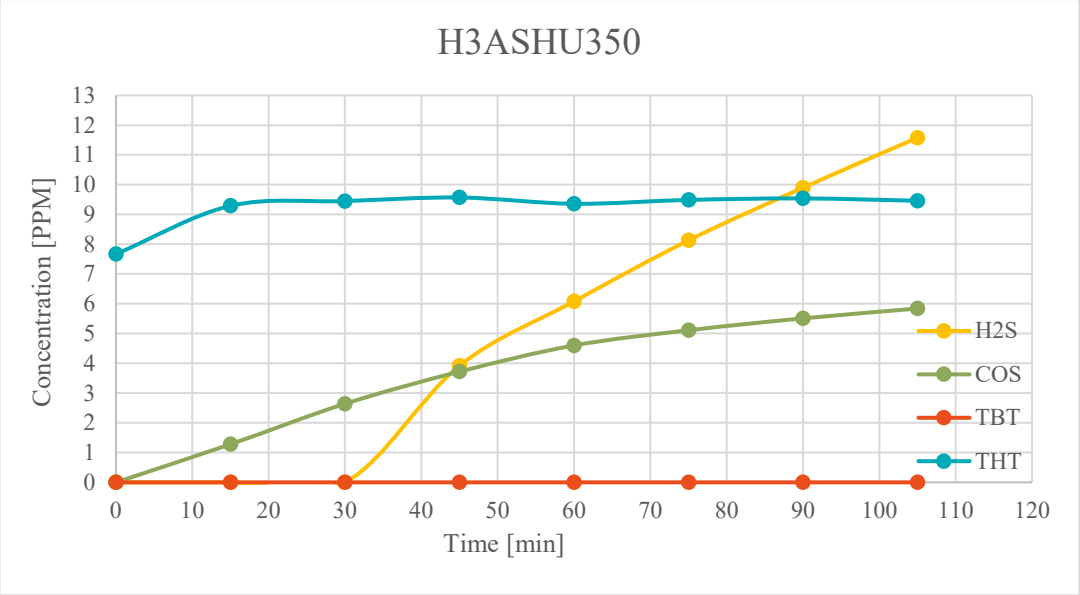

Figure 4.7 Fast breakthrough of H_2S and higher outlet concentrations than inlet indicate reactive environment for the sulphur species in the bed tested at 350 °C, 21,000 h^{-1} and ambient pressure.

4.1.2 Water-Slaked Samples

The water-slaked samples is much more effective adsorbents of H_2S, and the breakthrough time is 135 min (10th GC injection), 2.25 times higher than the best results with unslaked fly-ash, figure 4.8. The concentration in the outlet stabilizes at a quite low concentration of H_2S by the end of testing.

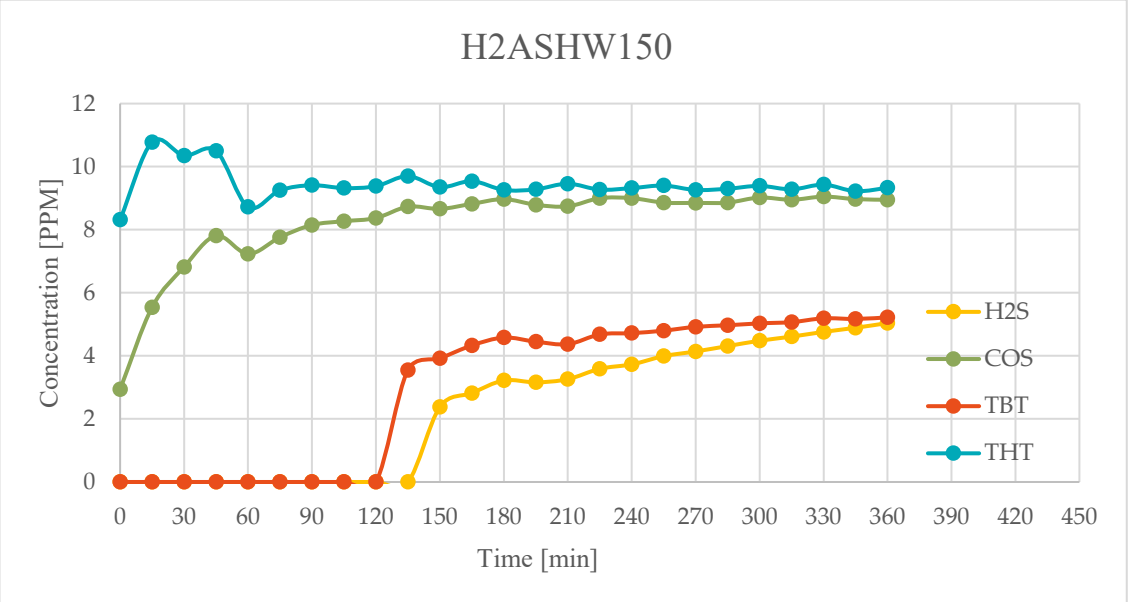

Figure 4.8 Much more efficient adsorption of H_2S with the water slaked samples from Heden 2. Here tested at 150 °C, 21,000 h^{-1} and ambient pressure.

With higher temperature, the adsorption of H_2S is further enhanced to a breakthrough time of 180 min (13th GC injection). Beside that, no other effects can be seen from the results, figure 4.9.

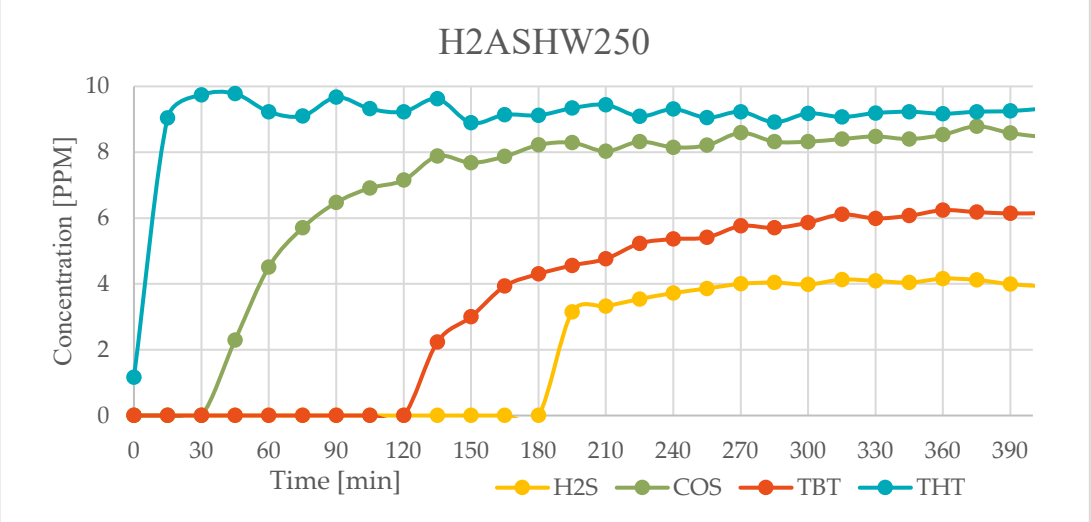

Figure 4.9 Water slaked samples is superior to the unslaked samples in adsorption of H_2S when increasing the temperature to 250 °C even higher breakthrough times can be achieved. This test at 250 °C, 21,000 h^{-1} and ambient pressure.

Again the 350 °C temperature show some unwanted properties, the breakthrough of H_2S is now lower compared to the 250 °C and the 150 °C tests of water-slaked flyash from Heden 2, figure 4.10. This is probably due to the loss of reaction water during the high temperature employed, returning the ash to the oxide rather than

the hydroxide state, despite operating well below the reported 580 °C decomposition temperature.

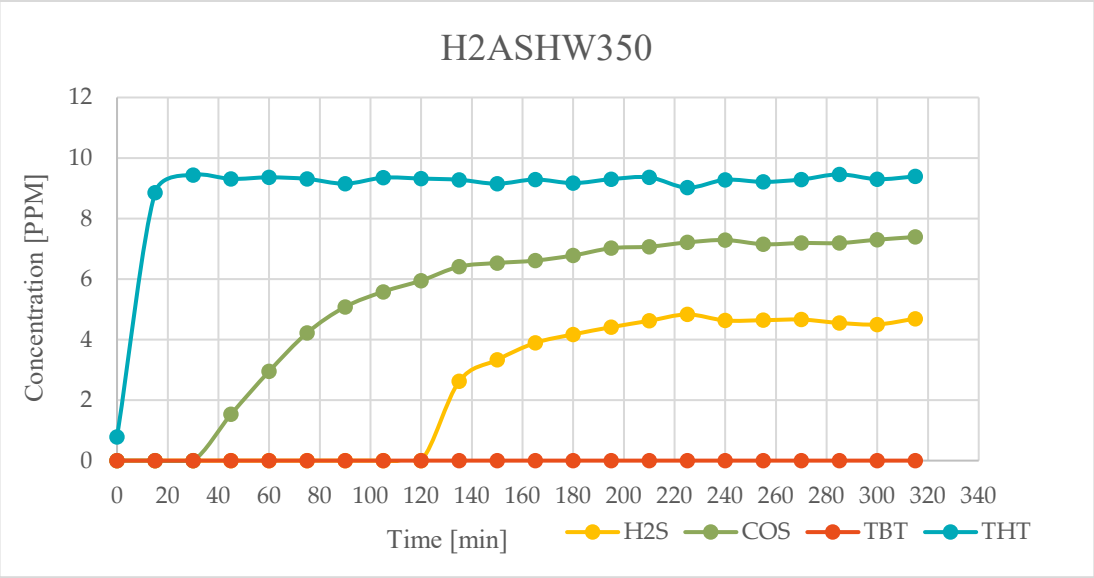

Figure 4.10 Lower breakthrough compared to the lower temperature samples water slaked samples from Heden 2. This test at 350 °C, 21,000 h^{-1} and ambient pressure.

Next, the Heden 3 water-slaked samples is presented. The water-slaked Heden 3 sample tested at 150 °C does not perform better than the best unslaked sample H2ASKU350, figure 4.11.

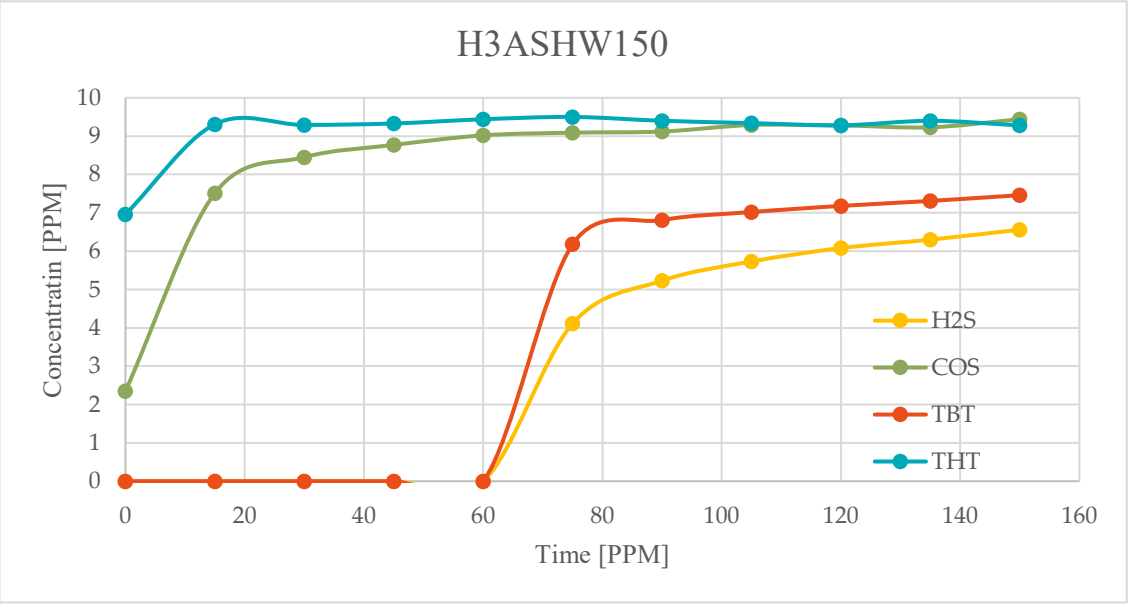

Figure 4.11 The water slaked sample from Heden 3 perform no better than the best of the unslaked samples. This sample at 150 °C, 21 000 h^{-1} and ambient pressure.

Increasing the temperature does not improve the performance of the Heden 3 water-slaked samples, and the breakthrough of H_2S is reduced to 45 min.

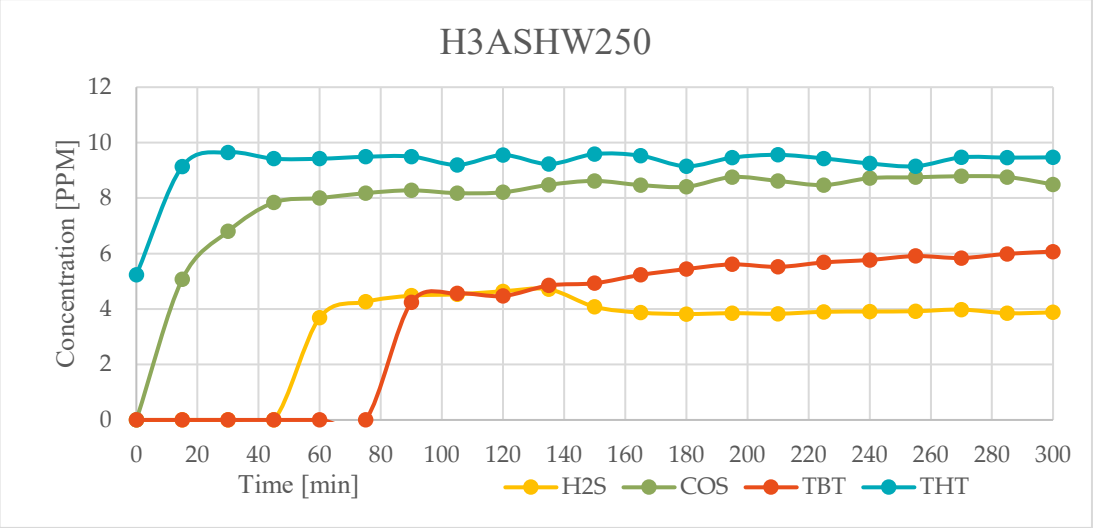

Figure 4.12 Increasing the temperature does not increase the adsorption capacity for the Heden 3 water slaked sample as the breaktrough of H_2S is reduced. This sample at 250 ℃, 21,000 h^{-1} and ambient pressure.

When the temperature is increased to 350 ℃ for the water,slaked Heden 3 sample, a radical shift in equilibrium occurs. As noted with the unslaked samples at 350 ℃, the concentration in the outlet of COS decreases with temperature increase. In the slaked sample case, the COS does not breakthrough at all. Instead, H_2S breaks through the bed at 25 min and stabilizes on a concentration above the inlet concentration, figure 4.13.

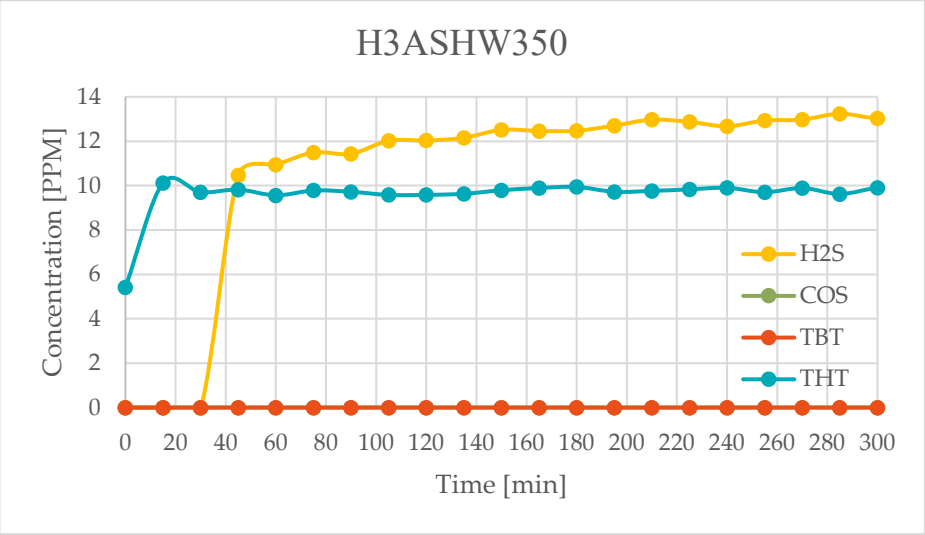

Figure 4.13 Heden 3 slaked fly-ash sample at 350℃ shows very different behaviour compared to all the other tests, several of the other sulphur species are converted to H_2S and adds to the outlet H_2S concentration. GHSV 21,000 h^{-1} and ambient pressure.

4.1.3 Comparison and Capacity Estimate

The best unslaked sample is H2ASKU350, and the best slaked sample is H2ASKw250 with respect to breakthrough time and 50 % breakthrough. Both top candidates are from Heden 2, as the Heden 3 samples has proven to be unreliable and unpredictable. Below the capacity of all the samples are listed, and the two top candidates are highlighted:

Table 4.1 Two best candidates with respect to breakthrough time are highlighted. Outlet concentration of H_2S at test end varies much and must be taken into consideration when making the adsorption unit design.

Sample	Initial breakthrough [min]	50% breakthrough [min]	Outlet concentration H_2S at test end [ppm]
H2ASHU150	30	55	7.84 (120 min)
H2ASHU250	30	50	6.47 (105 min)
H2ASHU350	***60***	***94***	***13.3 (204 min)***
H3ASHU150	30	44	8.15 (90 min)
H3ASHU250	30	56	7.2 (120 min)
H3ASHU350	30	59	11.58 (105 min)
H2ASHW150	135	163	5.04 (360 min)
H2ASHW250	***180***	***189***	***3.93 (405 min)***
H2ASHW350	120	133	4.69 (315 min)
H3ASHW150	60	72	6.56 (150 min)
H3ASHW250	45	53	3.88 (300 min)
H3ASHW350	30	39	12.75 (405 min)

When comparing the initial breakthrough time, the slaked sample is three times better than the unslaked. It is, however, not only the initial breakthrough time that is better in the slaked case. Also, the much higher 50% breakthrough indicate higher overall capacity for the slaked adsorbents. Another observation is that about 75% of the 350 ℃ tests resulted in outlet concentrations of H_2S being higher than the inlet concentration fed to the reactor. This is a strong indication that some of the sulphur compounds are consumed in reaction on this temperature (presumably TBT) and thereby producing more H_2S.

When comparing the breakthrough curve of H2ASKw250 to a commercial sulphur adsorbent, the ash is much less effective as concluded below in figure 4.14 where capacities are compared.

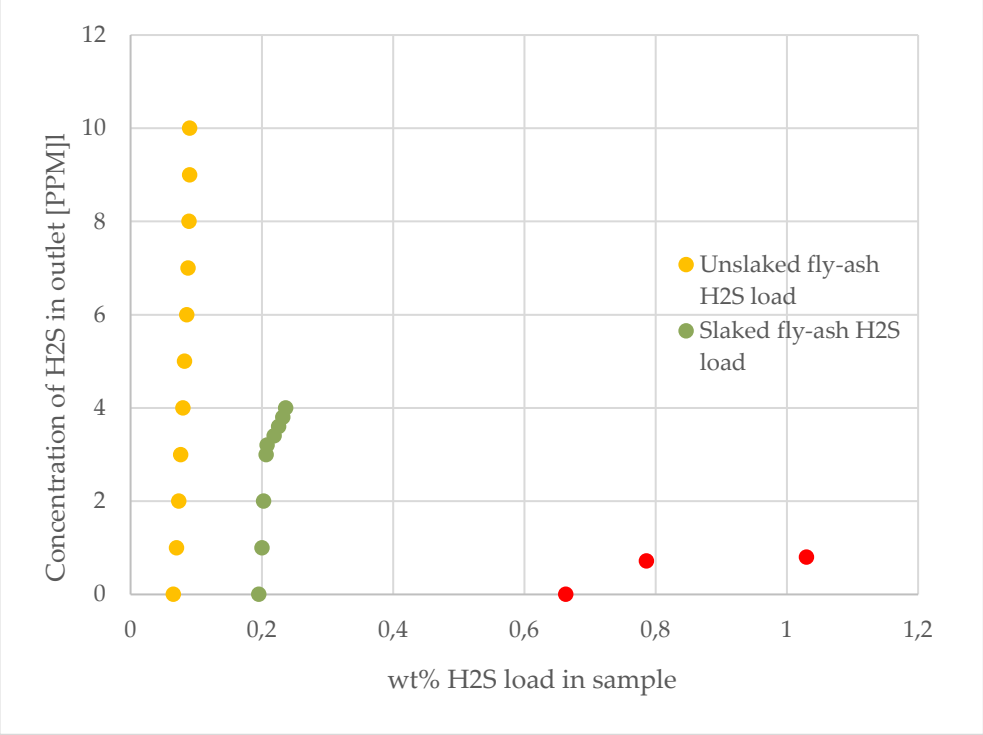

Figure 4.14 A commercial sulphur adsorbent outperforms the slaked fly-ash by a great margin (ca 24 times more capacity). The same gas mixture using 25,000 h^{-1} with 1 ml of adsorbent was used for the test.

It should, however, be noted that the commercial adsorbent contain 100 % zinc oxide, whereas the fly-ash is diluted with apparently inert material to about 80-90% (assuming that only Ca is active in the adsorption). Given this, the fly-ash actually have a rather decent performance calculated per active specie.

4.1.4 Hydration Activity of the Ash

In table 4.2 below, the relative area difference from the chromatograph-response is summarized before and after water is added to the feed. A significant increase in H_2S concentration is evident, but not because of the reason hypothesized. COS and CS_2 are approximately the same before and after water addition and are ruled out as the reactants that produce more H_2S. There is an unknown sulphur species that is converted after the water is added and that can be a source of more H_2S in the system, but TBT is also produced (or more likely desorbed) after water is added to the system. The substance that increases the most is dimethyl disulfide, which increases 5.8 times. The most likely explanation is that there is a competitive adsorption behavior with water such that it helps in desorbing the sulphur already adsorbed in the ashes, thereby adding to the outlet concentration of the species.

Table 4.2 The relative change in chromatograph-response in dry vs 5 vol% water environment. COS and C_2S is unchanged by the addition of water to the system. Other substances radically changes as can be observed.

Substance	Area dry $[\mu V \cdot min]$	Area wet $[\mu V \cdot min]$	Change [%]
H_2S	941,4	4051,3	+330
COS	4930,4	4923,7	-0,1
Unknown	2402,0	0	-100
Dimethyl sulphide	3753,9	3833,4	2
CS_2	14690,3	14252,7	-3
Tert-butyl thiol	0	2540	+100
Dimethyl disulphide	2149,5	14561,0	+577
Tetrahydrotiophene	3792,1	3778,3	-0,4

4.2 PROCESS DESIGN CONCIDERATIONS

Fly-ash is an inexpensive alternative to commercial sulphur adsorbents if the sulphur-loading in the incoming gas is low. However, there are several practical handling issues that needs to be resolved before this solution may be implemented. First of all, a solution where the ash can be removed from boiler and adequately slaked have to be developed. Perhaps this is possible to solve using a wet ash removal. Thereafter, the ash has to be well contacted with the gas, and there must be time allowed for the gas to contact the ash. This can perhaps be done using bag filters. The slaked ash can be injected into the gas stream, collected using the bag filters and periodically removed using back-pulsing of the filters. This is not unlike the dry method used for removing SO_2 from flue gases. Finally, the last hurdle to overcome is to recycle the now sulphur-laden ash, as it may no longer be possible to dispose of it as with ordinary biomass ash; this final point needs further investigation.

Given the information in this report, a set-up where a calcium-rich material is used as part of a solution to the sulphur-removal problem can be envisioned. This however assumes that there is a low-cost source available of such material, that the material can be processed (slaked) on-site, that the gas to be processed is virtually CO_2-free and that there is another up-stream sulphur unit with a more traditional type sulphur remocal. To schematically represent the final process, a box-flow diagram of the process can be proposed, figure 5.1.

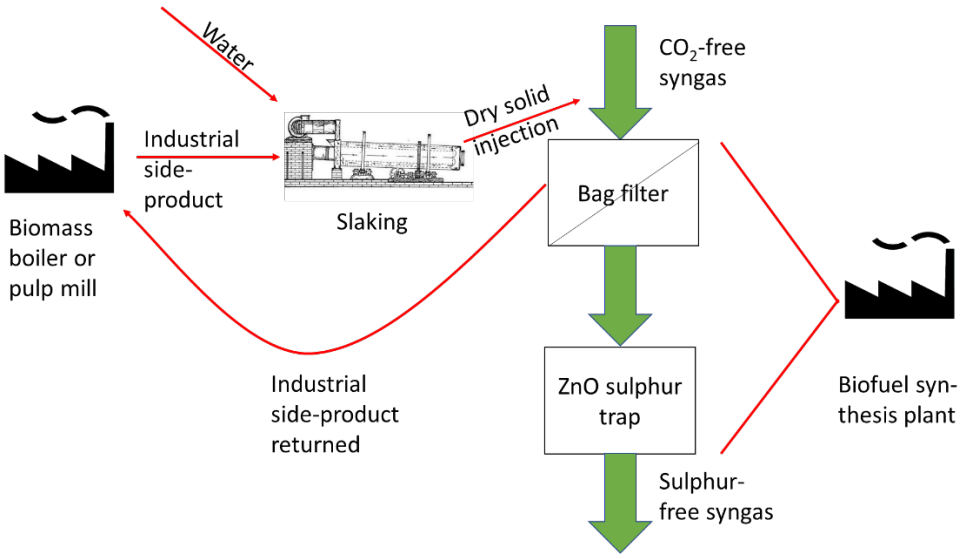

Figure 5.1 The final recommendation of the process given the experimental work.

As can be seen in the figure, the starting point is either a biomass boiler or a pulp mill, producing some kind of calcium-rich material as a side product. This material is processed, e.g. sieved and mixed with water and then heated in a small dryer, for performing the slaking reaction. The resulting fine-powdered dry solid is injected into the CO_2-free syngas stream, to be used in synthesis. The fine powder in separated from the gas stream using a baghouse filter and the majority of the sulphur uptake in the processed industrial side-product will be in the filter-cake. The baghouse-filter is periodically backflushed to release the filter cake, where after it is removed from the system and returned to the normal waste-handling flow. The synthesis gas is then passed through a more traditional zinc oxide sulphur removal step, to ensure a good enough sulphur removal for the downstream processing of the syngas into synthetic fuels.

5 Conclusions

The slaked fly-ashes perform better than the unslaked ones. This is most likely due to the formation of hydroxide species in the ash. The hydroxide of calcium ($Ca(OH)_2$), has proven to be a good candidate for sulphur removal in biogas purification [15], this also happens to be the main trace constituent of the fly-ash. However, the same reference also shows that there is quite some activity for the removal of CO_2 from the gas, forming the carbonate of calcium instead ($CaCO_3$). The best candidate was sample: H2ASHW250. This sample is two times better than any of the unslaked samples, but a commercial adsorbent is approximately 20 times more efficient than the best fly-ash sample. It should, however, be noted that the concentration of the active compound is rather dilute (10-20%) in the ash, leading to a much lower capacity. This final point will make it more likely that lime from a limekiln would be a much better option, after slaking of course, as the calcium content is much higher.

Fly-ash is an inexpensive alternative to commercial sulphur adsorbents if the sulphur-loading in the incoming gas is low. However, there are several practical handling issues that needs to be resolved before this solution may be implemented. First of all, a solution where the ash can be removed from boiler and adequately slaked have to be developed. Perhaps this is possible to solve using a wet ash removal. Thereafter, the ash has to be well contacted with the gas, and there must be time allowed for the gas to contact the ash. This can perhaps be done using bag filters. The slaked ash can be injected into the gas stream, collected using the bag filters and periodically removed using back-pulsing of the filters. This is not unlike the dry method used for removing SO_2 from flue gases. Finally, the last hurdle to overcome is to recycle the now sulphur-laden ash, as it may no longer be possible to dispose of it as with ordinary biomass ash; this final point needs further investigation.

The ashes show no catalytic activity in hydration of carbonyl sulfide or carbon disulfide. This is perhaps not that strange, as this is a reaction that is normally promoted by acid sites, e.g. on alumina [20], and the ash is basic in nature.

The developed technology has a potential for significantly increasing the lifetime of the, rather expensive, zinc oxide-based sulphur adsorbent. However, there are some trade-offs to the done, especially with respect to the size of the plant to be constructed. The smaller the plant, the smaller the gain and the more hazzle with the handling of a solid stream.

It is also important to continue working on the reaction engineering aspects of the sulphur removal, e.g. how can the capacity for sulphur-uptake be increased, how does the presence of CO_2 impact the performance of the system and what impact will a possible breakthrough of solid powder have on the downstream process are all relevant research and development questions to be addressed moving forward from this initial proof-of-concept stage to a fully industrialized concept.

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Keywords
Sulphur removal, fly-ash, green liquor dregs,

REMOVAL OF SULPHUR SPECIES USING INDUSTRIAL RESIDUAL STREAMS

In this report, the possibility for using industrial residual streams such as fly ash, green liquor dregs and lime have been investigated for the removal of sulphur species derived from biomass gasification.

An experimental study has been performed in which four different sulphur species, amongst others H_2S, have been removed. The performance of different materials is reported, and the best alternative seems to be the use of fly-ash from biomass combustion, after slaking it with water. The system requires a relative carbon dioxide-free gas but can provide a rather low-cost alternative to traditional sulphur removal.