

Final report

1.1 Project details

Project title	Regenerative Sulfur Removal from Biomass Gasifiers
Project identification (program abbrev. and file)	EUDP 14-II- journal nr. 64014-0530
Name of the programme which has funded the project	EUDP 14-II
Project managing company/institution (name and address)	Technological Institute Gregersensvej 1 2630 Tåstrup
Project partners	Haldor Topsøe A/S, Haldor Topsøe Alle 1 2800 Lyngby ChimneyLab Europe ApS, 8370 Hadsten
CVR (central business register)	5697 6116
Date for submission	10/10-2019

1.2 Short description of project objective and results

The project objective is to develop a method for removing H₂S by absorption using the well-known metal oxide absorption technology and apply this with the possibility of regenerating the metal sulfide to metal oxide. This will involve developing a regeneration technique initially in laboratory scale. Included in the project is fieldtests at Skive Fjernvarme where the absorbent is exposed to H₂S-rich gasification gas taken as a slipstream from the 15 MW gasifier at Skive Fjernvarme and then regenerate the absorber at the laboratory facilities at DTI.

The requirements to the regenerative absorption mass are:

1. High Sulphur absorption capacity
2. Fast absorption kinetics minimizing the absorption front length
3. Retention of the high Sulphur capacity after several regenerations using steam and air
4. Fast desorption kinetics at not excessive temperatures

Based on initial and preliminary small-scale tests these criteria seemed to be met and the economic and technological viability was calculated to be competitive.

The experimental work carried out in Work Package 1 and especially in the field test experiments in Skive in Work Package 2 has, however, demonstrated that in particular criteria 2 and 3 were not fulfilled. Calculations of the needed absorber volumes and required regeneration temperatures makes the concept too capital intensive and less attractive than foreseen.

The conclusion is unfortunately therefore that the concept is not viable with the present absorption materials in tar containing gases and until better candidates has been identified, there are not incentives to commercialize the technology.

1.3 Executive summary

In this project a process for removing hydrogen sulfide (H₂S) from gasification gas has been investigated. The process uses the well known technique of removing H₂S using a metal oxide absorbent that during the process is converted to a metal sulfide, but instead of discarding the metal sulfide after saturation, a process for converting the metal sulfide back to the oxide form is investigated.

1.4 Project objectives

The purpose of this project is to develop a new technique for removal of H₂S at high temperatures using a metal oxide absorbent that can also be regenerated after saturation.

The common technique for removal of high concentrations of H₂S from gasification gas is by using amine scrubbing, where the gas must be cooled down to 60°C. By this temperature, the water in the gas will condense out, and to be able to perform the water-gas-shift reaction later in the process, the water must be added subsequently. The inlet temperature for the water-gas-shift-reactor is typically 200-300°C and this cycling of the gas temperature from 800°C from the tar reformer down to 60°C in the amine scrubber and then up to 200-300°C will result in a significant heat loss. A part of this project will include absorption studies measurements on a side stream of Sulphur containing gasification gas from Skive Fjernvarmes bubbling bed gasifier. The gasification technique used in Skive is ideal for large scale production of synthetic fuel, and a successful demonstration of the Sulphur removal at Skive Fjernvarme will give Haldor Topsøe A/S an industrial reference, that is valuable in the commercialization of the high temperature Sulphur removal absorbents.

1.5 Project results and dissemination of results

WP1: Development of sulfur absorption- and regeneration procedure using metal oxide absorbers

Description of the regeneration- and sulfidation setup

In this workpackage, a regeneration setup was built in the laboratory at DTI in Tårstrup. The purpose of setup was to perform studies of regeneration of the Sulphur-exposed absorbents. A diagram of the setup is shown in Figure 1. As can be seen, the setup is built so that a mixture of nitrogen, hydrogen, water and mixture of H₂S in nitrogen can be added into a hot reactor that contains the absorbent. The pressure can be adjusted using a backpressure valve downstream the reactor. Part of the gas can be sent to a Gas Chromatograph (GC) that is able to analyze the gas using three detectors. These detectors are respectively a:

Flame ionization detector, FID: This detector can detect combustible hydrocarbon gases, not used in this project.

Thermal conductivity detector, TCD: This detector is used to quantify hydrogen, nitrogen

Flame photometric Detector, FPD: This detector can detect H₂S and SO₂ individually.

Furthermore, the setup is equipped with a humidity sensor downstream, that can measure the water content in the gas. This sensor is mainly used to verify that the waterflow is constant.

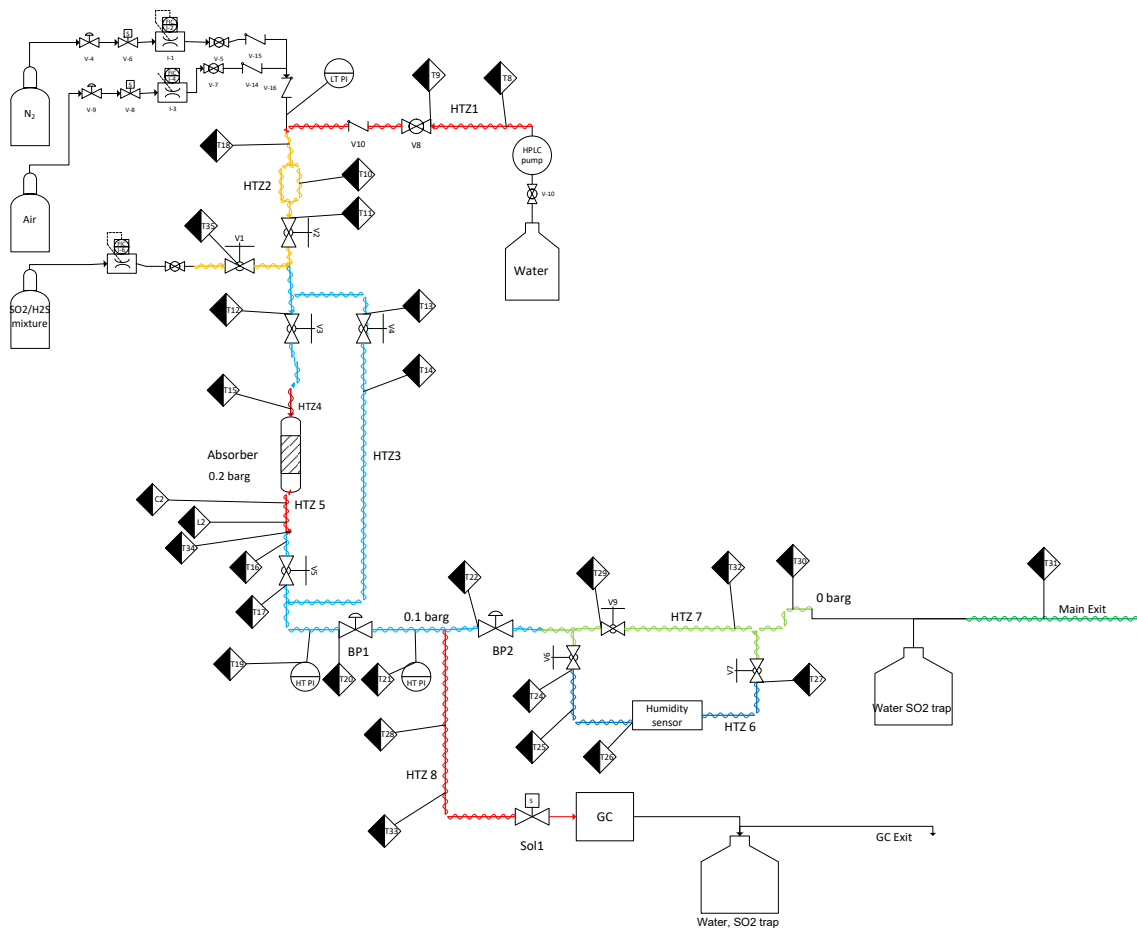


Figure 1. Piping- and instrumentation diagram of the laboratory setup at DTI

The reactor and the oven surrounding the oven is shown in Figure 2, left picture, showing also the inlets and outlets to the reactor. The reactor consists of a steel tube made of a high temperature steel alloy, Sanicro 31HT with welded on fittings from Swagelok in 316L steel. Inside the tube is a grating, consisting of a plate with seven holes, welded onto a thin tube, seen on Figure 2, right. Inside this thin tube is fitted a thermocouple, so that the temperature of just on the grating can be measured. The reactor is loaded from the top with absorbent pellets, that will rest on the grating.

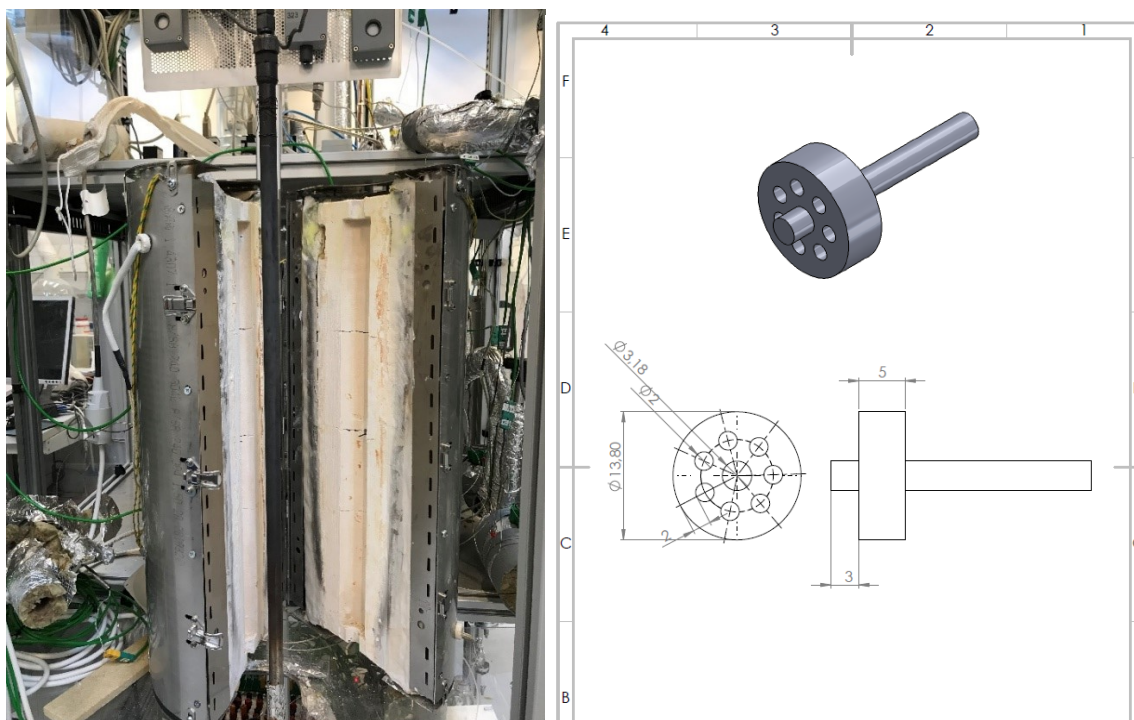


Figure 2. Left: Picture of the regeneration reactor and oven. Right: Drawing of the grating for holding and supporting the absorbent in the reactor

Procedure for Absorption- and regeneration studies of the Sulphur absorbent

The reactor and oven surrounding it was built to hold around 10 grams of absorbents pellets, so the studies of sulfication and regeneration was done on initially 10 gram of pellets. After each regeneration, a sample of 1 gram of absorbent is removed from the reactor and sent to analysis for Sulphur content. In some cases we also removed 1 gram of sample after the sulfidation. The analysis for Sulphur was performed by ALS Minerals using the a LECO Sulfur analyzer.

The sulfidation of the absorbent is described in Table 1.

Table 1. Sulfidation properties in lab experiments

	vol %	
H ₂ O	11.07	
N ₂	74.04	
H ₂ S	7.41E-04	
H ₂	14.82	
GHSV	2044.4	NL/kg.cat/hour
Gram in reaktor	9.9	g
Temperature	400	°C

The regeneration conditions are described in Table 2 in the result-section. All the regenerations experiements are performed addition of water in nitrogen. In some of the regeneration studies, oxygen is added. The temperature during regeneration has also been varied.

During the regeneration, we measured the concentration SO₂, H₂S, H₂ with the gas chromatograph.

An example of the measurements during regeneration is shown in Figure 3. As can be seen, this regeneration takes around 75 hours.

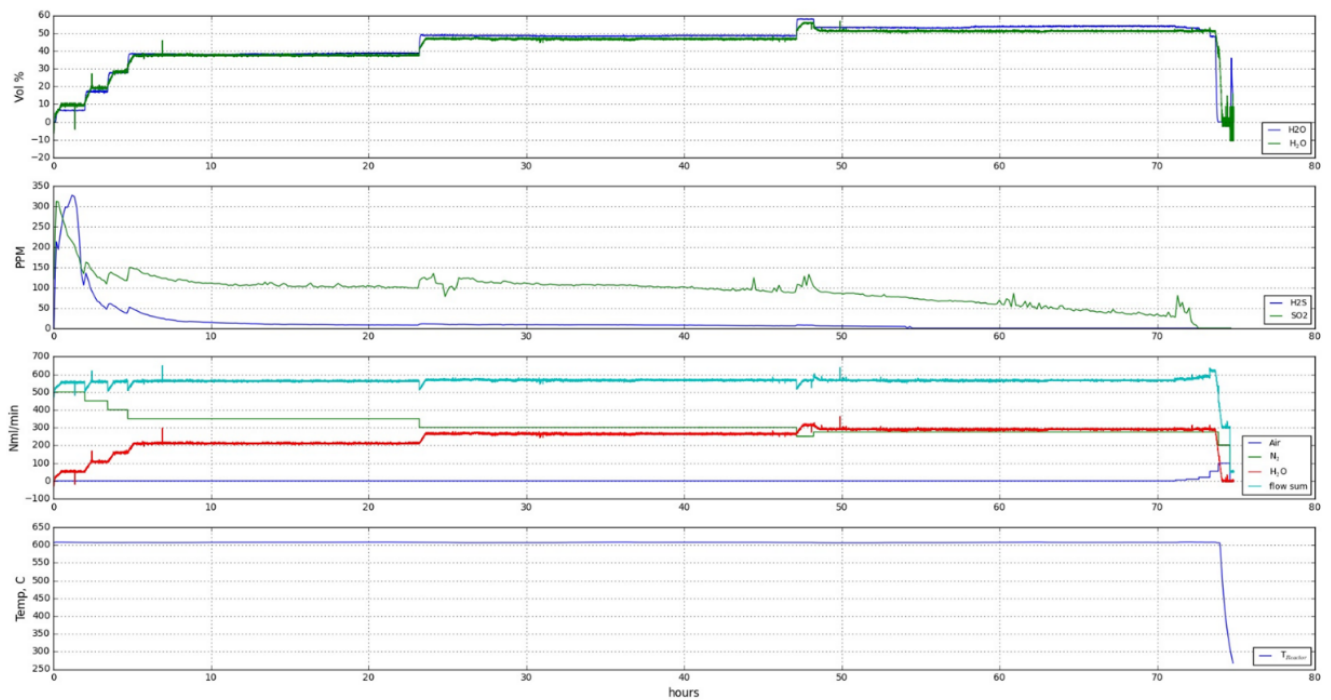


Figure 3. Example of data collected during the regeneration of the absorbent at 600°C

Overview of the absorbing and regenerating properties of the sulphur absorbent:

The result of the most important sulfidation- and regeneration studies are given in Table 2. As can be seen, it is indeed possible to regenerate the samples, and to remove the Sulphur from the absorbents.

Table 2. Results of cycles of sulfidation and regeneration studies

		Sulphur content as % of saturation full
2.1.S	Sulfidation at 400C, sample taken out	100.0
2.1.R	Regeneration at 600C, with H2O	54.5
2.2.S	Sulfidation at 400C, sample NOT taken out	-
2.2.R	Regeneration at 600C with H2O og O2	20.2
2.3.S	Sulfidation at 400C, sample NOT taken out	-
2.3.R	Regeneration at 550C with H2O, og O2 til sidst	40.4
2.4.S	Sulfidation at 400C, sample taken out	96.0
2.4.R	Regeneration at 600C with H2O og O2, sample taken out	39.1
2.5.R	Regeneration at 750C with H2O og O2, sample taken out	23.4

What is observed from the measurements is that the absorbent's capacity is not decreased even after four regenerations. The sulphur content in 2.4.S is 96%.

Another observation, that is also done is that the regeneration depends very much on the regeneration temperature. When the temperature is 550°C, the sample still contains 40%

Sulphur. And in the last regeneration, a regeneration temperature of 600°C, the sample still contains 39% Sulphur. This regeneration was repeated with an increased temperature, 750°C, and the Sulphur content could be decreased to 23%, which is higher than after the initial regeneration at 600°C. So the regeneration seem to require higher temperatures after only 2-3 cycles of sulfidations and regenerations.

Carbon in the absorbents, before and after regeneration

After having removed absorbent pellets from the reactor after the first regeneration with oxygen, it was observed that the absorbents visually changed color from dark grey to light grey, as seen in Figure 4.

John Bøgild from Haldor Topsøes informed us that the black color was due to carbon-remains that was used during processing of the pellets. The absorbents were sent to analysis for Sulphur and Carbon, and the analysis did show that the content of carbon in the sample had decreased to 0.1 w/w%.

The difference between the regeneration for R.2 and R.3 was that R.3 was regenerated with a small amount of oxygen during the last ca. 5 hours of the experiment, and this could explain why the carbon of 2.R.3 was removed, since the O₂ had oxidated/burned away the carbon.



Figure 4. Picture of pellets after regeneration (grey) compared to the non-regenerated pellets (dark grey/black)

Physiontiobed vs. chemisored sulphur

During the regeneration of the sulfidated samples, we observe a very high concentration of H₂S in the exit-gas, and the concentration is so high that the FPD-detector is saturated and the exact concentration of H₂S cannot be determined, this however only is a problem for around 30 minutes, where the H₂S-concentration drops to a measurable level, and after around 30 hours the H₂S-concentration drops below the SO₂-concentration. The SO₂-concentration is remains relatively stable throughout the regeneration, and H₂ is also seen and the regeneration continues.

The first conclusion is, that H₂S is initially released by physiosorbtion. This means that some of the sulphus is not absorbed in the absorbent as ZnS, however the H₂S is absorbed as free molecules

attached more loosely to the surface. The physisorbed sulfur is released as H₂S, the remaining chemisorbed sulfur in the absorbent is released.

It is observed, that the initial spike of H₂S is much lower and less significant in the second regeneration, and even smaller in the third and fourth regeneration. We believe that is due to the fact that during regeneration with O₂, we burn off most of the carbon in the absorbent, and this remaining carbon can act as absorbent of the physisorbed H₂S, in a similar way that active coal does.

Processes during regeneration, formation of hydrogen

Relations between H₂ and SO₂ is shown in Figure 5 and we see that the ration between H₂ and SO₂ is at a level of around 2.5 to 3. This level is almost constant from 10 hours and to the end at 70 hours, even as the concentration levels of H₂ and SO₂ continue to decrease in this time interval. The concentration of H₂S in this time interval drops more significantly relative to the SO₂ and H₂ concentration.

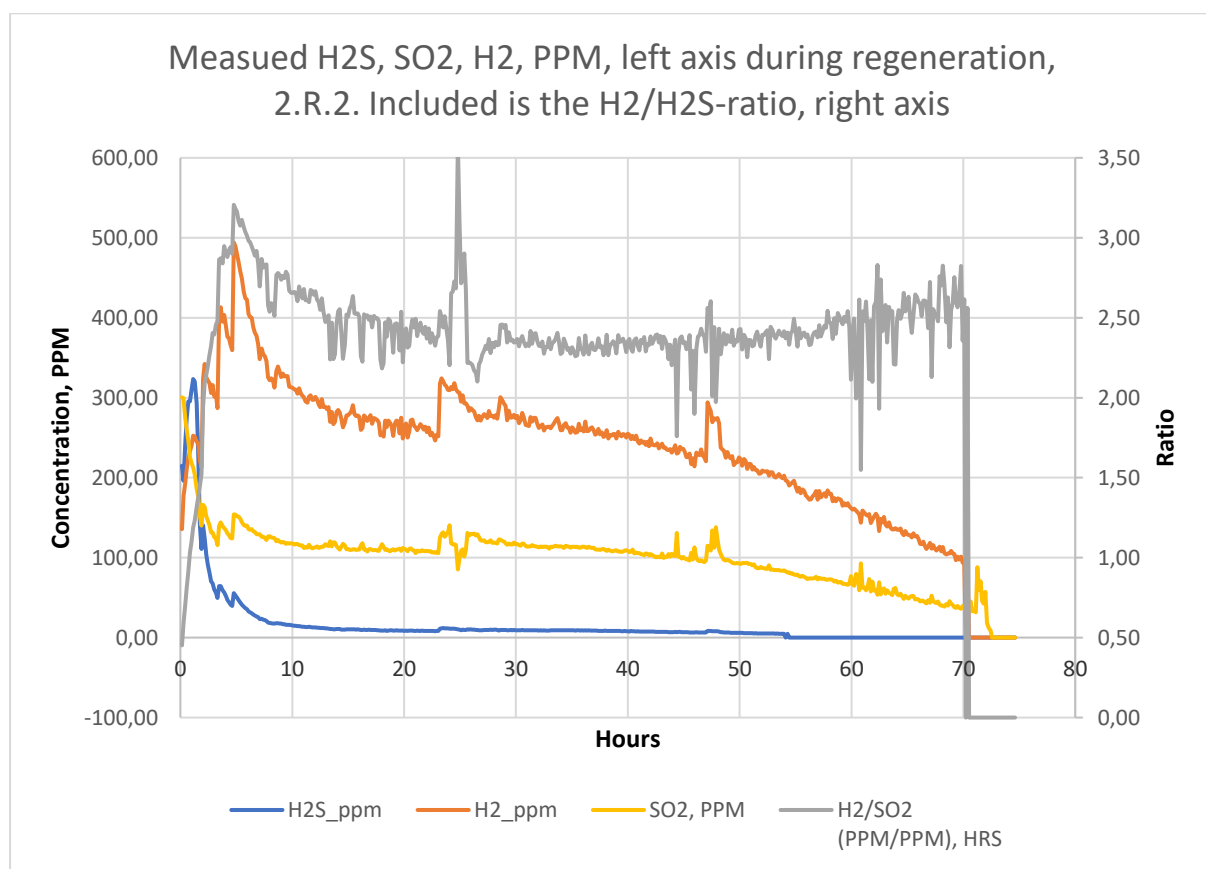
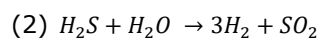
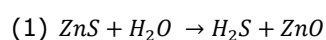


Figure 5. Measured H₂S, SO₂, H₂, PPM, left axis during regeneration, 2.R.2. Included is the H₂/SO₂-ratio, right axis

The reaction that takes place is expected to be reaction (1), and as soon as H₂S is formed, reaction (2) happens, and hydrogen is released. This explains why H₂S and not SO₂ is seen during regeneration.

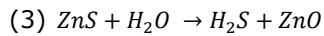


This also explains why the ratio between the measured H₂ and SO₂ concentration stabilize at around 3, even as the concentrations of H₂ and SO₂ decrease.

The limiting reaction here is reaction (1), which is slower than reaction (2). The reason that we do not measure 2.5 and not 3 is believed is due to inaccuracies related to calibrations gases, and the fact that the FPD-detector signal scales quadratically with the SO₂-signal.

Thermodynamic calculations on Sulphur regeneration with water

The reaction with water is investigated:



The aim was to determine the temperature- and water-pressure conditions at which the equation (3) is shifted towards the right, that is towards desorption of Sulphur and the release of H₂S. The equilibrium constant of equation (3) can be calculated using well known relations between Gibb-free energy, equilibrium constants, reaction enthalpy and reaction entropy. However the data available in eg. the rubber handbook (CRC) is not sufficient to fully describe equation (3) at the desired temperature ranges from 200°C to 900°C. In order to access thermodynamic data in this range several sources have been accessed, mostly from NIST-databases. The data used are summarized in annex 1.

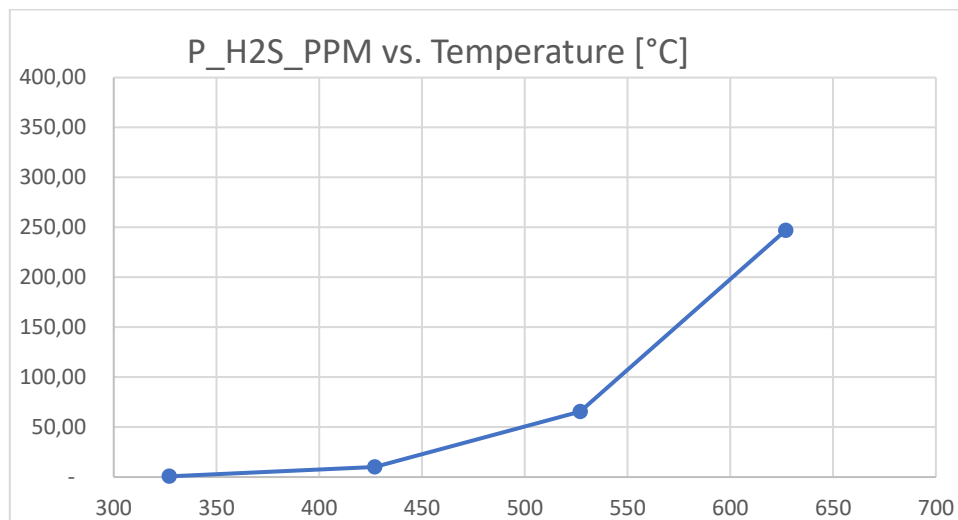


Figure 6. H₂S-equilibrium pressure for reaction equation (1) using $p_{\text{water}}=0.5$ bar absolute, based on data from CRC and NIST

Figure 6 shows the equilibrium pressure of H₂S of equation (3) vs. temperature for a water pressure of 0.5 bar. The dots represent data-values, and there are no extrapolated or fitted values. The H₂S-pressure at 626°C is only P_H₂S=247 PPM, which is very low. And since this is the equilibrium pressure, this is by definition the highest possible H₂S-pressure possible at these conditions at this temperature.

Using this data, we can roughly estimate the time it will take to regenerate the absorbent, assuming that equation (1) is at equilibrium and that the desorption of H₂S only occurs by the chemi-desorption process. Table 3 shows a result of this calculation, using reaction temperature of 600°C, $p_{\text{water}}=0.5$ bar and a total flow of 337 ml/min, which was the flow used during regeneration in most of the laboratory regeneration experiments, and a Sulphur concentration of 3.7% w/w, as also measured after sulfidation.

The calculations show that it takes 72.3 hours to regenerate the absorbent at 600°C, which is approximately the same time as seen by the experimental studies.

Absorbent mass	10	g
s_conc	3.7	% w/w
s_g	0.37	gram
GHSV	2022	
Temperature	600	°C
flow	337	ml/min
H2S pres	177	ppm
H2S flow	0.059649	ml/min
S_mass flow	8.52E-05	gram/min
Time to remove Sulphur	72.3678	hours

Table 3. Desorbtion calculation based on thermodynamic data applied to desorbtions experiment, 2.2.R.

WP2: Pilot test with metal absorbers on gasification gas from Skive Fjernvarme low pressure

In this workpackage the absorbents are to be exposed in a slip-stream reactor situated at Skive Fjernvarme. The gas that passed through the reactor is made from biomass gasification.

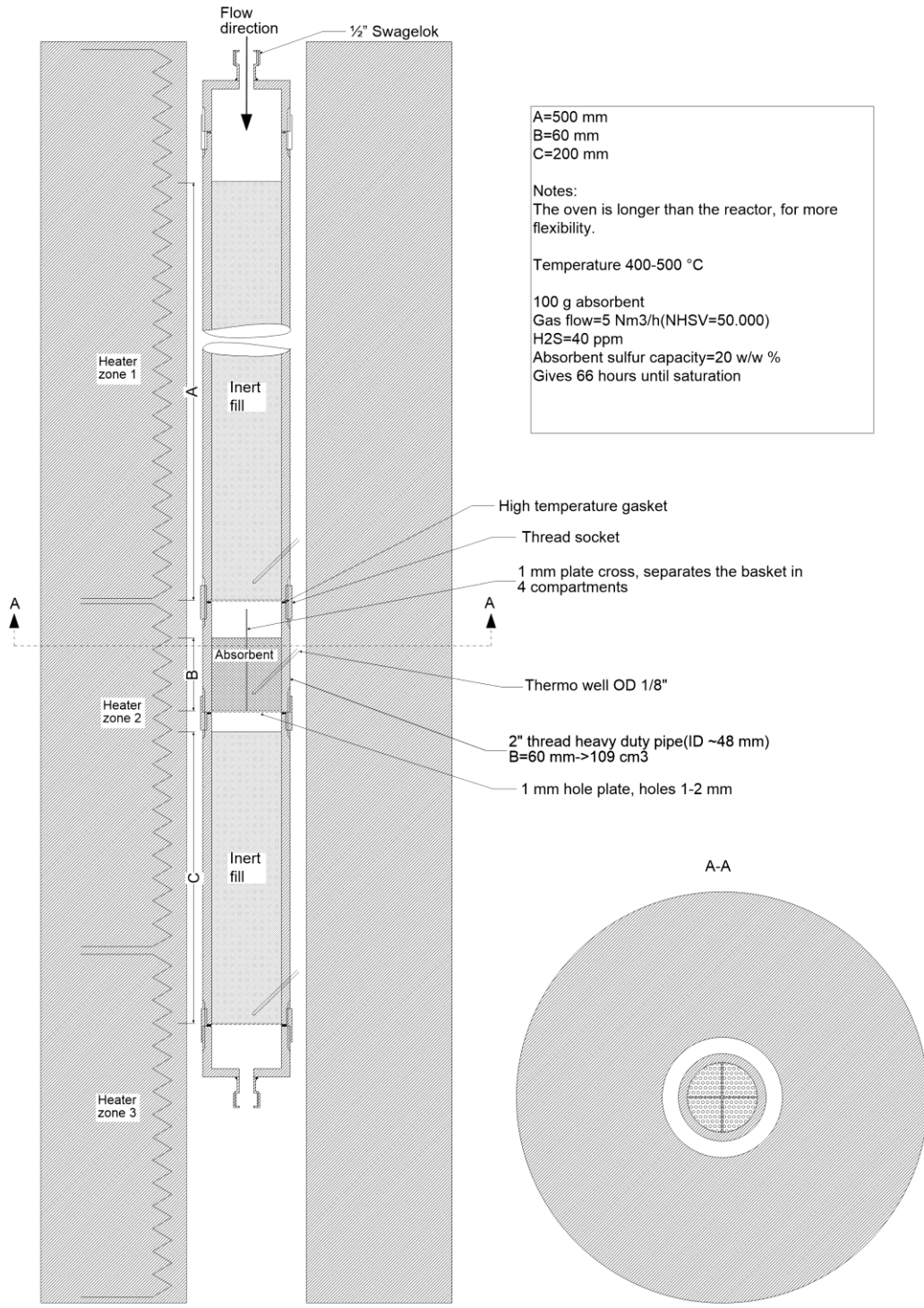
A reactor is constructed, that comprises of a tube consisting of 4 compartments. In each compartment around 150-200 grams of absorbent can be placed. The gas inlet is from the top. The reactor is surrounded by a 2 meter long oven, that enables precise temperature control during exposure. The reactor design is shown in Figure 7. Pictures of the reactor and the oven, placed at Skive Fjernvarme is shown in Figure 8.

A hot gas outlet is taken from the main gas flow from Skive Fjernvarmes gasification gas. The gas is taken from the section between the tar reformer and the dust bag filters. This means that the gas contains dust. This means that the gas has to be cleaned from dust and char-particles before it enters the exposure reactor. To clean the gas, a gas filter unit is installed before the exposure reactor. This filter unit can be seen behind the reactor oven in one of the pictures.

The gas leaving the reactor is sent to a small flaring unit, that is situated in the same room as the main flarer at Skive Fjernvarme.

The construction of the side stream reactor at Skive Fjernvarme had to be approved by Skive Kommune. The permission was given with reference to a note made by "Miljøstyrelsen" regarding "Miljøgodkendelser og Forsøgsanlæg" Nr 4 1987, ISSN nr 0107-2722. Following the guidelines outlined in this note, an experimental facility can be approved if e.g. the production, or emissions from the setup are below 2% of the annual production from the main facility. The sidestream setup in this EUDP-projects are well below the 2% and Skive Kommune approved the sidestream setup.

We can also mention, that the exposure tests at Skive Fjernvarme was delayed due to a fire that occurred at Chimneylab-Europe in Hadsten in September 2018, where most of the Chimneylab-company was lost, including the exposure reactor. This reactor was rebuild in beginning of 2019, and a last exposure experiment was performed in June 2019.



A=500 mm
 B=60 mm
 C=200 mm

Notes:
 The oven is longer than the reactor, for more flexibility.

Temperature 400-500 °C

100 g absorbent
 Gas flow=5 Nm³/h (NHSV=50.000)
 H₂S=40 ppm
 Absorbent sulfur capacity=20 w/w %
 Gives 66 hours until saturation

Title: Absorption reactor	
Material: 1.4404	Date: 20-11-2015
Project: Regenerative Sulfur Removal from Biomass Gasifiers	
Filename: Absorption reactor ver.2.vsd	Order-no.: 0544
Supplier: Chimneylab Europe ApS tel. +45 8691 5542, mobile +45 2096 8598	
Constructor: Finn Petersen	Page: 1 of 1

Figure 7. Drawing of absorptions reactor used for absorptions experiments in Skive



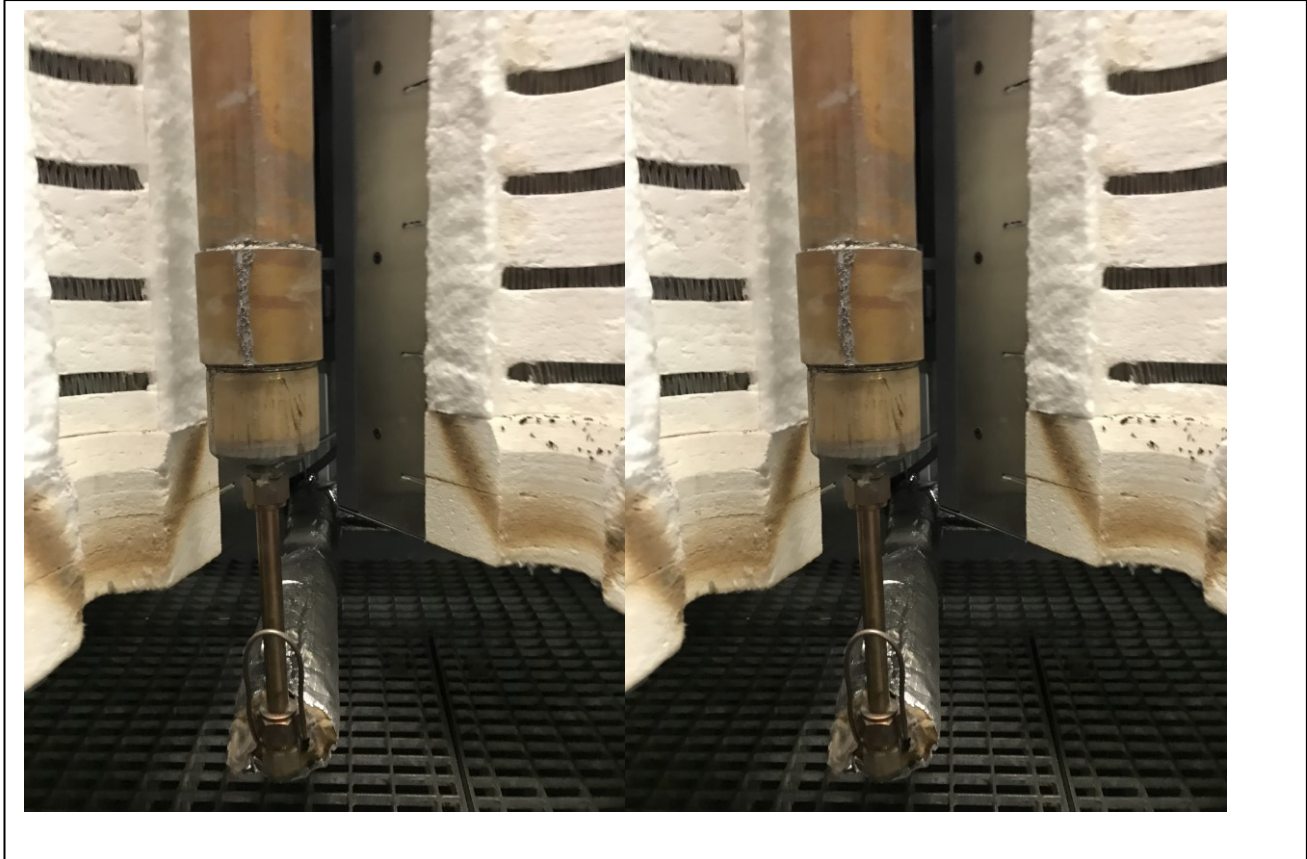


Figure 8. Pictures of the setup used at Skive Fjernvarme

Figure 9 shows the Piping and Instrumentation Diagram (PI-diagram) of the sidestream setup at Skive Fjernvarme. The red line shown the Battery limit between the Skive Fjernvarme-plant and tubings, and the sidestream setup and tubings.

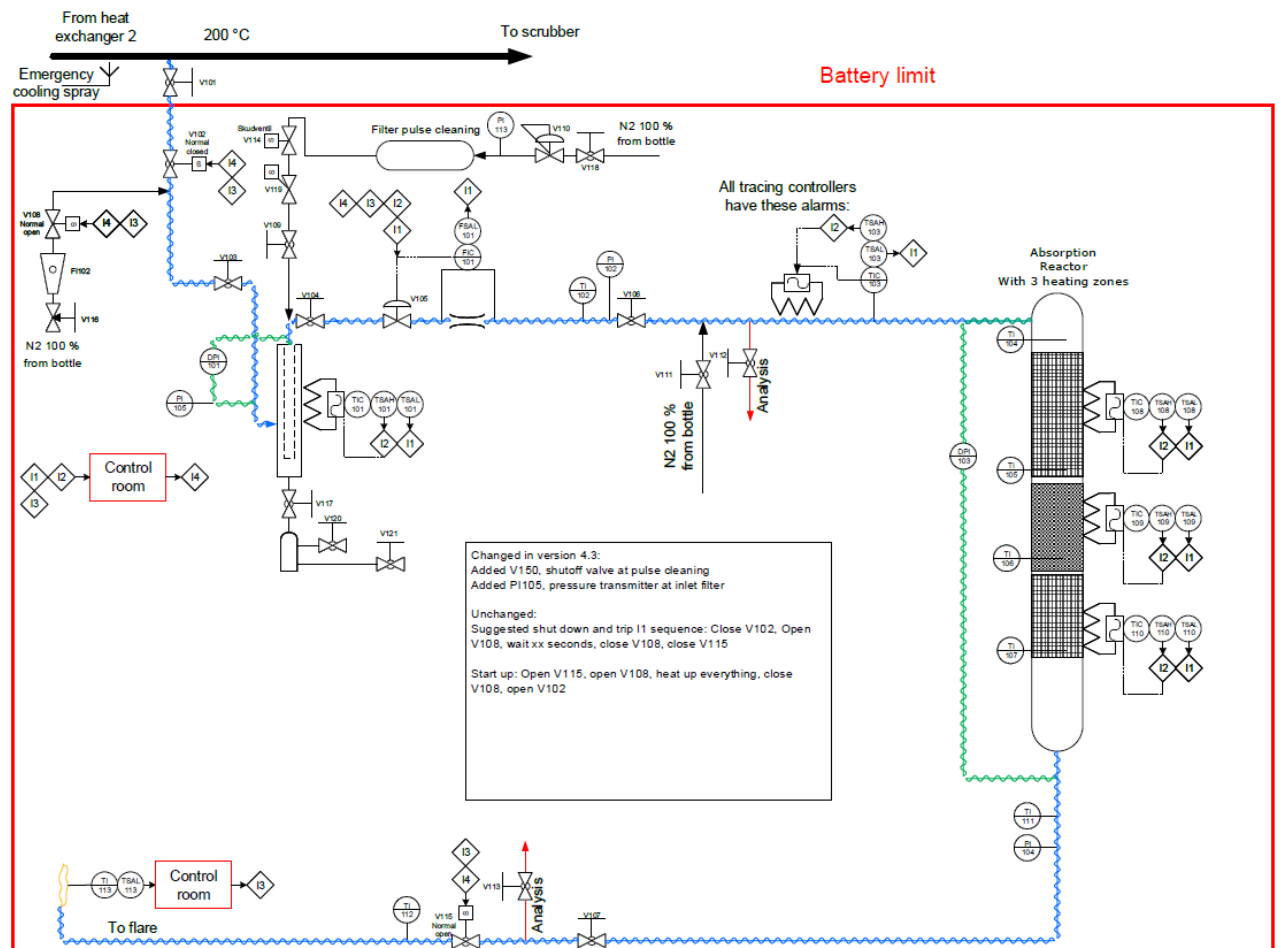


Figure 9. Piping- and instrumentation diagram of the regeneration facility at Skive Fjernvarme

Experiments in the project:

Two exposure experiments were performed in on the sidestream setup in at Skive Fjernvarme.

Exposure experiments, May 2017

The test conducted in May 2017 was performed on the absorbent for 19.7 hours. It was expected from this experiment to observe a gradient throughout the reactor, in order to see a break-through of sulphur, that is, a significant difference between the Sulphur concentration in the top basket and the bottom basket.

The conditions of the test are shown below:

Conditions of test:

Flow rate, nM3/h	6 nM3/h
Temperature in bed	400°C
Hours of exposure	19.7 hours
Amount of absorbent	168,7 grams

During the test, the exit and inlet concentration of H₂S is measured using Dräger tubes and pumps. The measured H₂S concentrations are listed below:

Measurements during test:

Exposure time [h]	1	17
H ₂ S conc, in inlet [ppm]	10.4	13.0
H ₂ S conc, in exit [ppm]	3.2	8.2

The samples were subsequently analyzed for Sulphur- and Carbon content. The results for Sulphur are given below:

Concentration of sulfur in zones of the reactor:

Zone	Sulphur content as % of saturation full
1, Top	13.56
2, Middel	10.90
3, Buttom	9.57

The absorbant pellets from the top basket was placed in the regeneration reactor at DTI and regenerated with a combination of water and oxygen.

The result is given in the table below:

Zone	Sulphur content as % of saturation full
Before regeneration, Basket 1, top	13.56
After regeneration with water and oxygen	8.51

Exposure experiments, June 2019

A second exposure experiemt was performed in June of 2019. In this exposure, the flowrate was reduced. The aim was to investigate if a concentration front could be established, and thereby determine the breakthrough time of a large scale absorption reactor. Before exposing the absorbent pellets, the carbon-content in the pellets was removed by slowly heating the pellets to 700°C and thereby oxidizing the carbon to CO₂. This process was confirmed by measuring the carbon-content that indeed was reduced to around 0.1 w/w% carbon.

The flow rate of 1.1 Nm³/h was the lowest rate that could be achieved, otherwise the gas flare at the exit could not ignite.

Conditions of test:

Flow rate, nM3/h	1.1 Nm3/h
Temperature in bed	400°C
Hours of exposure	62 hours
Amount of absorbent	168,7 grams

Measurements during test:

Exposure time [h]	0.5	14	36	62
H2S conc, in inlet	6	15	15.5	15.5
H2S conc, in exit	0	1.0	2.2	3.0

Note: The low initial inlet H2S conc. could be because the carbon dust in the filter and the inlet tubing were not saturated with H2S

Concentration of sulfur in zones of the reactor:

Zone	Sulphur content as % of saturation full
1, Top	26.06
2	17.82
3, Middle	27.66
4, Middle	18.09
5	15.96
6, Bottom	8.24

The absorbent pellets from the top basket was placed in the regeneration reactor at DTI and regenerated with a combination of water and oxygen.

The result is given in the table below:

Zone	Sulphur content as % of saturation full
Before regeneration, Basket 1, top	26.06
After regeneration with water and oxygen	13.56

In the regeneration experiment, very little SO₂ or H₂S could be measured in exit gas. It was expected that the concentrations of H₂S and SO₂ were below the detection limit.

In order to investigate the extent of regeneration, this last regeneration experiment was run for an extended time, which was more than seven days, 172 hours. During this time the temperature was increased gradually from 700°C, up to 840°C. The regeneration was also run with addition of air, up to 10%, which is very high, in order to speed up the regeneration process.

Considering the very high temperature and the extended regeneration time, the results in the above table can be considered the best possible regeneration of this particular Sulphur absorbent. As can be seen, the Sulphur concentration is reduced, from 26.06 % to 13.56%.

WP3: Pilot test with metal absorbers on gasification gas from the Luleå University gasification facility, high pressure operation

The status of this work package changed in 2017, since Piteå/Lulea University announced that the gasifier in Piteå would be closed down.

Instead of the work in this WP, the regeneration-setup at DTI was expanded, so that sulfidation could also be performed, since this was not originally part of the project description. Furthermore, the setup at DTI was re-designed in order to be able to perform automated cycles of regeneration- and sulfidations experiments.

WP4: Regarding market evaluation and commercialization, Utilization of project results, conclusion and perspective

The political consensus in Denmark calls for a reduction of fossil CO₂ emissions of 70 % before 2030 and complete decarbonization of all sectors before 2050. It is envisaged that this trend will pick up also elsewhere in the EU and abroad.

This will require massive deployment of especially wind and solar based power generation but in order to supply especially heavy duty transport and industry with energy dense, hydrocarbon based fuels there will also be a need for biomass gasification based fuel synthesis plants.

Haldor Topsøe has been active in development of downstream gas conditioning technology and catalysts for gasification plants as exemplified in the revamp of the combined heat and power plant in Skive, the black liquor to DME plant in Piteå, the wood to gasoline demo plant in Chicago and the woodchips to substitute natural gas (SNG) in Gothenburg.

Topsøe has studied the design of a conceptual SNG, which is a more advanced design than the GoBiGas plant in Gothenburg. The design is shown on Fig. 10.

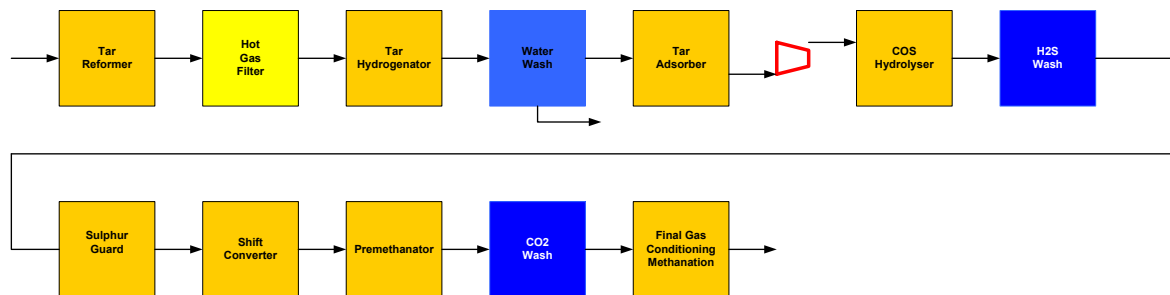


Fig. 10

After the gasifier a dusty tar reformer, like the one successfully employed at Skive Fjernvarme, would convert most of the tars to more synthesis gas. Dust will then be removed in the hot gas filter followed by a hydrogenation of the remaining unsaturated tars. The gas is cooled down and washed with water, which will remove also chlorine from the gas. The residual tars is then removed in adsorption beds. After compression carbonyl sulphide is converted to hydrogen sulphide. The H₂S is then removed in a MDEA wash. The last traces of Sulphur is removed in a guards and the gas is converted in a water gas shift reactor producing more hydrogen. The premethanator converts parts of the carbon oxides to methane reducing the heat removal load for the final methanation step. Finally the gas stoichiometry is adjusted by removing most of the CO₂ in a second MDEA wash before being converted to pipeline quality SNG in the final methanation steps.

The H₂S wash is a very costly item with respect to capital investment contributing to approx. 25 % of the total cost. Furthermore this layout is not very amenable to coupling with an electrolysis unit because the approx. 2/3 the CO₂ is removed in this wash and is contaminated with Sulphur. Coupling with an electrolysis providing extra hydrogen to match the overall methane stoichiometry could increase the methane output by a factor of almost three.

The idea behind the present project on regenerative Sulphur removal from biomass gasifier was accordingly a flow scheme as presented in Fig. 11.

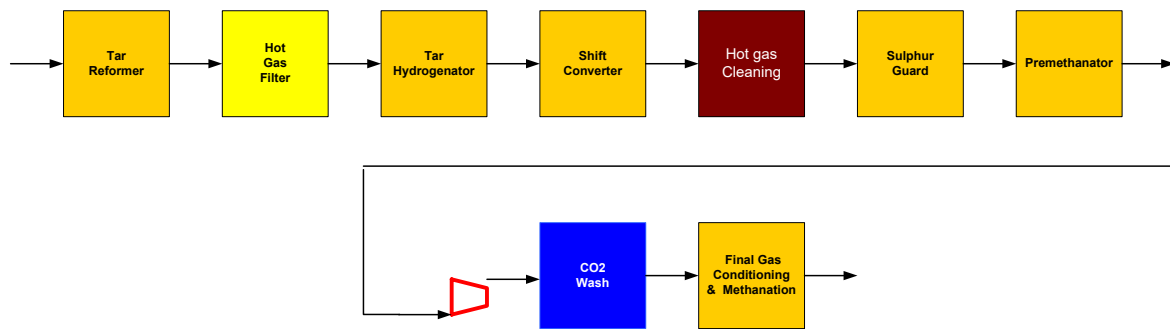


Fig. 11

Instead of cooling down the synthesis gas from the tar hydrogenator, water washing, COS hydrolysis and the MDEA hydrogen sulphide wash the gas is kept around 400 C and sent to a sulphur tolerant shift reactor followed by the regenerative Sulphur removal reactor marked as red on Fig. 11.

The project results, in combination with results from the previous EUDP-projects with Haldor Topsøe, Skive Fjernvarme has been disseminated and mentioned here:

- "Strategiudspil termisk forgasning", Partnerskabet for Termisk Forgasning, 26-06-2018. Udarbejdet af: Ea Energianalyse
- "Thermal Biomass Gasification in Denmark Task 33 Country Report 2019", af Morten Tony Hansen og Ida Stokkebye Christensen
- Task 33 Workshop meeting on Fluidized bed conversion of biomass and waste, Skive Fjernvarme October 24th 2017. Presentations by Tage Meltofte and John Bøgild
- "Case: Skive Forgasningsanlæg. Baggrund og erfaringer fra etablering af forgasningsanlæg" v/ Tage Meltofte, Skive Fjernvarme, Seminar om termisk forgasning i Danmark, FORCE Technology, 17. November 2015.
- Gastekniske Dage 2017, "Forgasning ved brug af overskudselektricitet", v. Jens Kromann Nielsen, Teknologisk Institut

Jens Kromann Nielsen has additionally been a member of the board in the Partnership for Thermal Gasification "Partnerskab for Termisk Forgasning", and has through this contributed with input to the e.g. the Strategy note (Strategiudspil termisk forgasning) taking the results from the current EUDP-project into consideration, and using the experience from the previous EUDP-projects together with Haldor Topsøe and Skive Fjernvarme.

1.6 Utilization of project results

The requirements to the regenerative absorption mass is then:

1. High Sulphur absorption capacity
2. Fast absorption kinetics minimizing the absorption front length
3. Retention of the high Sulphur capacity after several regenerations using steam and air
4. Fast desorption kinetics at not excessive temperatures

Based on initial and preliminary small-scale tests these criteria seemed to be met and the economic and technological viability was calculated to be competitive.

The experimental work carried out in Work Package 1 and especially 2 has, however, demonstrated that in particular criteria 2 and 3 were not fulfilled. Calculations of the needed absorber volumes and required regeneration temperatures makes the concept too capital intensive and less attractive than foreseen.

The conclusion is unfortunately therefore that the concept is not viable with the present absorption materials in tar containing gases and until better candidates has been identified, there are not incentives to commercialize the technology.

1.7 Project conclusion and perspective

As describe above, the conclusion is that the concept of high temperature sulphur removal in not commercially viable.

The perspective for removing sulphur from gasification gas currently relies on the technological route described in figure 10, there the Sulphur is removed in am MDEA (Methyl diethanolamine) scrubber.

The current facility at Skive Fjernvarme is currently a world class operational case for fluid bed biomass gasification technology with around 6000 hours of operation a year. A major contributor to this achievement is a result of the aid from the previous EUDP project, "Katalytisk fjernelse af tjære fra biomasse forgassere II" where a completely new design of the tar reformer was performed, installed and operated.

If biomass gasification will become part of the pathway towards a fossil free future, Haldor Topsøe will have a competitive advantage within the field of biomass gasification and especially tar reforming. The current project will help Haldor Topsøe to better estimate the total cost of such a gasification facility, since it is known that the sulphur must be removed by MDEA washing.

2. Annex 1: Thermodynamic data

		$\Delta G_{\text{formation}}$
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Temp, K	Temp C	KJ/mol*K			
		ZnS (s)	ZnO(s), fra CRC	H2O(g)	H2S(g),
298	24.85	-201.24	-320.42	-228.58	-33.33
400	126.85	-198.49	-310.30	-223.90	-37.34
500	226.85	-192.86	-300.39	-219.05	-40.18
600	326.85	-186.28	-290.47	-214.01	-42.40
700	426.85	-178.98	-280.59	-208.81	-44.20
800	526.85	-171.41	-269.76	-203.50	-45.69
900	626.85	-163.71	-258.96	-198.09	-45.87

	$\Delta G_{\text{reaction}}$ for: ZnO + H2S => ZnS + H2O	K_{eq} for: ZnO + H2S => ZnS + H2O
	KJ/mol*K	
Temp C	ZnO(s) + H2S(g) => ZnS(s) + H2O(g)	ZnO(s) + H2S(g) => ZnS(s) + H2O(g)
24.85	-76.08	21629677747666.50
126.85	-74.75	5768136430.51
226.85	-71.35	28391069.02
326.85	-67.42	739716.06
426.85	-62.99	50183.04
526.85	-59.46	7620.72
626.85	-56.97	2025.29

	P_H2O=0.5 bar
Temp C	P_H2S_PPM
24.85	0.00
126.85	0.00
226.85	0.02
326.85	0.68
426.85	9.96
526.85	65.61
626.85	246.88

The data in the tables are a combinations of raw data from the sources refereed below. Other values, for e.g. ZnS at different temperatures, are calculated from the commonly know thermodynamic relations between e.g. ΔH , ΔS , ΔG , C_p and T .

In the last table, the H2S-pressure is calculated as: $P_{\text{H2S}} = P_{\text{H2O}}/K_{\text{eq}}$.

Sources:

- 1) H2S: <http://webbook.nist.gov/cgi/cbook.cgi?ID=C7783064&Mask=1>
- 2) CRC - Handbook of Chemistry and Physics by David R. Lide, 75th edition, 1994-1995