Final report

1. Project details

Project title	El Upgraded Biogas II
File no.	64017-05164
Name of the funding scheme	EUDP 2017 II
Project managing company / institution	Haldor Topsøe A/S
CVR number (central business register)	
Project partners	Haldor Topsøe A/S – Aarhus University
Submission date	15 August 2021

2. Summary

The purpose of the present project was to bring the technology readiness level from TRL 6 to TRL 8 for upgrading biogas by means of Solid Oxide electrolysis and catalytic methanation by implementing preventive maintenance on BOP components, optimization of the control system, incorporation of a final steam clean-up mass and finally introducing a more cost effective biological sulfur removal unit using enriched air from the SOEC.

The original milestones have not all been met due to unforeseen problems with especially the balance of plant components. Stable electrolysis has, however, been demonstrated for more than 2000 hours and important learnings for optimizing the system design and operation has been acquired. The steam clean-up mass has with the applied implementation not improved degradation rates and will need a new design, which is in progress. Attention has also been drawn toward degradation caused by the humidity and sulfur in the air feed for the SOEC and mitigation strategies have been developed.

Experiments with the methanation section have demonstrated that the original design was overly conservatives so that significant savings can be obtained due to the excellent thermal stability of the catalyst and a good performance of the biogas desulfurization system.

A novel biological bulk desulfurization of the biogas using oxygen enriched air from the electrolyzer has been developed and tested successfully in semi industrial scale. This cost-effective technology gives better performance than using ambient air and will reduce the nitrogen content in the upgraded biogas. A final sulfur polishing will nevertheless still be needed.

Formålet med projektet var at bringe TRL fra 6 til 8 for opgradering af biogas ved hjælp af faststof oxid elektrolyse (SOEC) og katalytisk metanisering ved optimering af kontrolsystemer, forebyggende vedligeholdelse og brug af en rense-masse til damp. Endelig skulle en mere driftsøkonomisk biologisk afsvovling med brug af beriget luft afprøves.

Ikke alle af de fastsatte milepæle blev mødt på grund af uforudsete problemer med især system hjælpe komponenter. På trods af disse udfordringer blev en stabil elektrolyse drift i mere end 2000 timer demonstreret og vigtige erkendelser vedrørende optimalt system design og komponenter tilvejebragt. Damp rense massen havde ringe effekt med hensyn til degraderingshastigheden med den implementerede placering og et revideret design er blevet udarbejdet. Opmærksomheden er blevet henledt på degradering foranlediget af fugtighed og svovl indhold I procesluft og afbødnings metoder udviklet.

Eksperimenter med metaniserings sektionen har demonstreret at det oprindelig design var yderst konservativt således at betydelige besparelser kan opnås på grund af katalysatorens exceptionelle termiske stabilitet koblet med et velfungerende afsvovlingssystem.

Et nyudviklet biologisk grovafsvovlings system, der bruger beriget luft fra elektrolysen er blevet udviklet og afprøvet med succes i semi-industriel skala. Denne drift-økonomiske løsning giver bedre svovl omsætning og reducerer kvælstof indholdet i den opgraderede biogas. Der vil dog stadig være behov for en slut fin afsvovling.

3. Project objectives

In the EUDP project “El upgraded biogas” a 10 Nm^3/h pipeline quality methane demonstration plant was designed, built and operated based on Solid Oxide Electrolysis, biogas desulphurization and catalytic methanation. Very high energy conversion efficiency and better than pipeline quality gas production has been demonstrated. Problems with balance of plant components (compressors, pumps and power supply) has, however, limited the operating hours of the SOEC stacks. Residual contaminant traces in the feed steam are also suspected of being the cause of accelerated degradation of the stacks.

The purpose of the present project was to bring the technology readiness level from TRL 6 to TRL 8 by implementing preventive maintenance on BOP components, optimize the control system, incorporate a final steam clean-up mass and finally introduce a more cost-effective biological sulfur removal unit using enriched air from the SOEC. The goal was to operate the demonstration plant for at least 4000 hours including transient operation to adapt to the anticipated future electricity market.

4. Project implementation

4.1 Brief description of the main components in the demo plant

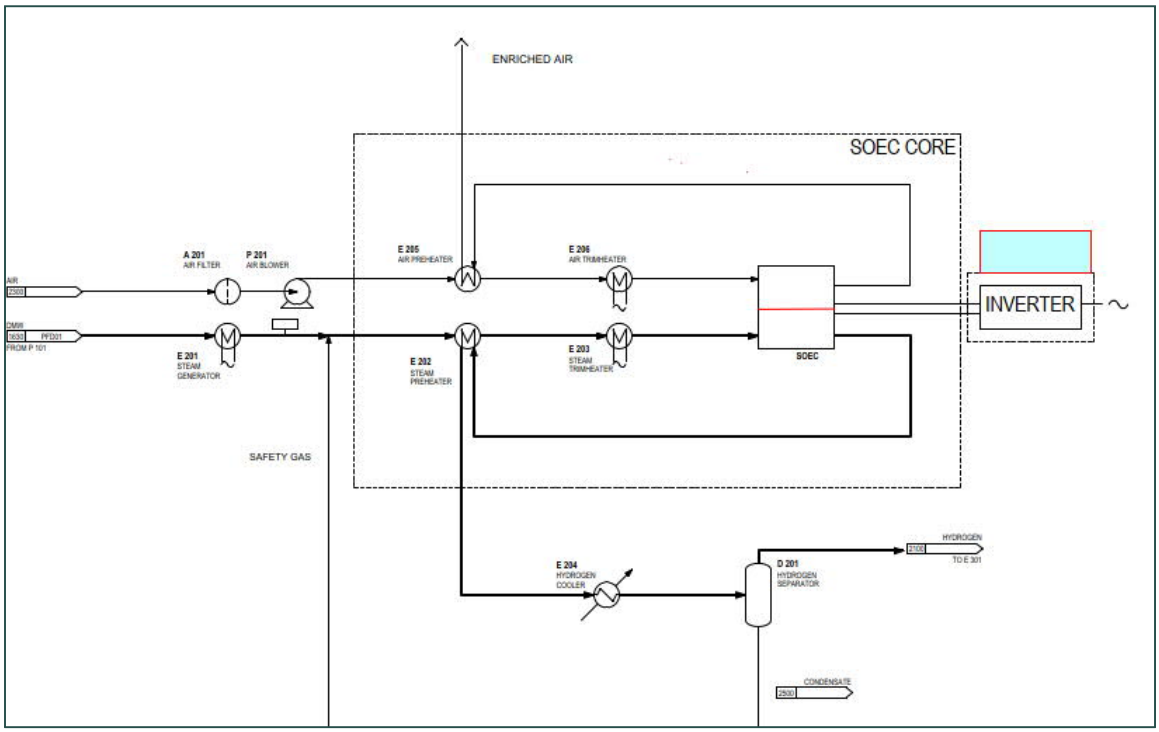

Fig 1: Sketch of the SOEC section

A detailed description of the total demonstration plant can be found in the final report on the EUDP project "Elopgraderet Biogas" and here the focus will be on a description of the focus of the present, new project namely the SOEC section. A basic sketch is shown on Fig. 1. The plant consists of two independent sections A and B, which in the new project was housed in one hot box. Each section has a separate supply of air from a blower, water from a high-precision HPLC pump, pure hydrogen or safety gas (5 % H_2 in N_2) from bottles.

Steam is generated in an electrical heated evaporator and is further heated in a feed/effluent heat exchanger before the final temperature inlet the cathodes to the SOEC stacks is achieved using an electrical heater.

The air is likewise heated first in a feed/effluent exchanger and then an electrical heater before entering the anode side of the SOEC stacks. The outlet from the SOEC anodes consisting of a steam+hydrogen mixture is cooled in the feed/effluent exchanger and further cooled ambient temperature in a cooler. The unconverted steam is condensed out.

During operation 3- 10 % H_2 is added to the steam to ensure that the nickel containing cathodes are kept reduced. For safety reasons during start up and shut downs safety gas is sent to the SOEC until the stacks are above/below the self-ignition temperature of hydrogen. The oxygen enriched air leaving the anodes is just cooled in the feed/effluent exchanger before being discharged to vent.

Each of the two cores consists of 4 stacks of 75 cell each. They are electrically paired two and two and supplied with DC power from Power Supply Units (PSU) capable of controlling the maximum current and/or voltage. In total there is thus 8 stacks with a total nominal capacity of 50 kW corresponding to approx. 16 Nm^3/h of pure hydrogen.

In the project a reactor was designed and constructed to hold a proprietary cleaning mass which was installed after the steam generation and hydrogen addition at around 180 °C. Only one cleaning mass was installed in front of section A. In this way the two production lines could be operated in parallel and any change in observed degradation of the SOEC stacks could be ascribed to the extra gas cleaning step.

4.2 Timeline

During 2018 the overall design of the demonstration unit was updated and changes to the control system verified by experiments. A new design of a core box with 8 stacks have been carried out and manufacturing was started. A redesign of the core containing the SOEC stacks and hot components was carried out for two reasons: The supplier of the previous heat-exchangers was unable to deliver, and the assembly of the previous design was very labor intensive and difficult. The new design makes it possible to house 8 stacks in one hot box instead of 2 cores with 4 stacks in each. The new design should also make maintenance simpler. The redesign, however, caused a delay of approx. 4 months compared to the original time schedule

The manufacture of the new Core Box became, however, further delayed by several months at the sub-supplier workshop due to heavy work load and problems with availability of skilled craftsmen and sub components.

It was agreed that NatureEnergy left the project, but small-scale tests on biological desulphurization was carried out and equipment suitable for upscaling identified at the site.

The vessel containing the water purification unit ruptured and it took three months to obtaining relevant spare parts. Extra spare parts have been bought.

The first half year of 2019 was used to install the modified equipment at the pilot site. Due to size and space restrictions the rebuild ended up requiring new piping, new tracing and new instrumentation of the SOEC front-end as well as the new gas cleaning step of Core B.

Execution of the test plan was planned for the remainder of the project (1/7-2019 – 31/12-2020). As COVID resulted in restricted access to the pilot plant most of 2020, additional 6 months project extension was granted to cope with the delays and limitations caused by the pandemic.

Pilot plant rebuild	1/1-2018 to 30/6-2019
Testplan period 1	1/7-2019 to 31/12-2019
Testplan period 2	1/1-2020 to 30/6-2020
Testplan period 3	1/7-2020 to 31/12-2020
Testplan period 4 (COVID extension)	1/1-2021 to 1/6-2021

A pie-chart has been made to visualize how the pilot plant was utilized in each period. The pie-chart consists of three items:

- Pilot Plant Operation
- Pilot Plant Repair
- Pilot Plant Idle

Plant operation is defined as time were the plant is available and part of a heat-up process, actual electrolysis but also controlled shutdown. The repair category covers all service activities (planned and unplanned) were the corebox is removed or when parts are inspected, tested or replaced. The idle category is time with a functional pilot plant but were operation has not been possible due to access restrictions (covid, weekend access etc.).

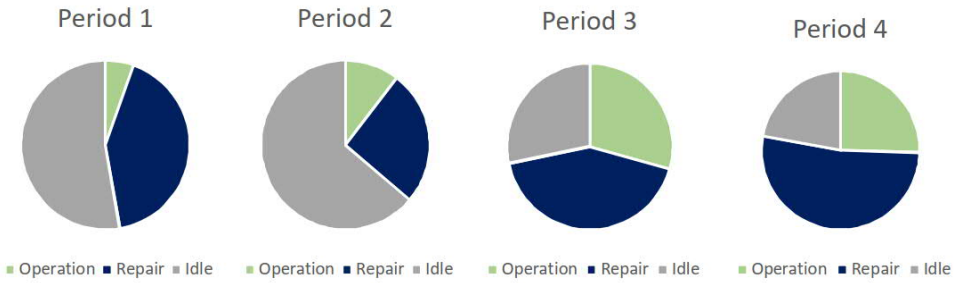

Figure 1: Four half-year periods split into categories of operation, repair and idle time. Extended timelines for each of these periods are available in appendix.

4.2.1 Covid-19 Pandemic

As the pilot plant is located at the campus of Aarhus University in Foulum, severe access restrictions were enforced as the impact of the Covid-19 pandemic became clear. Employees were asked to work from home, no access to laboratory facilities could be granted, and physical meetings were strictly forbidden. Although remote monitoring of the pilot plant is possible, it was impossible to maintain operation, as several of the pilot plant safety checks require inspection on site (checking availability of protection gas, manual flow gauges, replacing filters etc.). As site access was later granted, still restrictions were enforced:

- Only one 4-hour access timeslot could be granted per day
- No operator overlaps when operating the pilot plant
- All activities to be preapproved one week in advance

By end of 2020 the restrictions were relaxed to allow more people on site, and manageable safeguards replaced the previous restrictions. The use of facemasks, distance requirements and quick-tests were enforced for the rest of the project period.

Besides the troubles of COVID, there has been several challenges hindering or restricting smooth execution of the test plan.

- Reliability of building utilities
- Operation of the SOEC preheaters
- Incorrect wiring of probes and cells
- IT issues
- Unplanned maintenance

4.2.2 Building utilities

When testing the effect of the new gas-cleaning step, plant operation for several weeks is required to observe a clear difference. In this aspect the surrounding utilities (power supply, instrument air, water purification unit ect.) need to be reliable. Whenever these components have failed, it has been necessary not only to repair, but also to mitigate the issue, to improve the overall robustness of the plant. Often this involves sourcing new parts, testing new operational procedures and modifying part of the pilot plant.

In the previous project, external power failures were quite frequent, but grid supply from the nearby transformer station has since improved. Only once in this project the pilot plant was shut down due to a planned transformer inspection. The electrolysis power supplies (PSU) had also caused significant delays in the first project. Therefore, a spare PSU were in stock and could replace PSU3 when it failed and had to go for a two-month repair.

The pilot facility has bottled gas supply of safety gas, hydrogen and nitrogen. The supplier provides day-to-day delivery, but for protection gas this quality can only be produced at a single filling station. At one start-up in project period 2, the supplier experienced compressor failure and were suddenly unable to deliver. New start-up procedures were being tested and a simple unit trip ended up without safety gas for purging. As a result, some cells suffered oxidation and the stack had to be replaced. The damage was not clear until the next start-up attempt.

The problem child number one in this project has been the water treatment unit by Purite (DMW). The DMW unit removes calcium from the raw water by reverse osmosis. This is required to avoid deposit to build up in the steam generator and avoid poisoning of the stacks. This unit cannot be serviced during operation so replacing the microbial prefilter every 3 months has been the current hard-limit preventing extended operation. Also replacing the UV lamp every 6000 hours and replacing the osmosis membrane once a year, made this unit heavy on maintenance. As this DMW unit is no longer sold with the same components only refurbished spare parts could be sourced. Gaskets and O-rings from alternative suppliers were tested with some success. The continued issues with leaks and several plant shut-downs finally resulted in the decision to replace the unit. The DMW unit was replaced with a unit from Best Water Technology. This new unit removes calcium but also includes a degasser, able to remove dissolved gasses like carbon dioxide and hydrogen sulfide.

The initial rebuilding of the pilot plant allowed an extra gas cleaning step to be implemented on one of the two parallel production lines. The underlying theory is, that impurities like sulfur, would end up in the steam and poison the solid oxide electrolysis cells. The DMW unit was replaced end of period 3. A successful long operational period of 72 days was accomplished shortly hereafter.

4.2.3 Operation of SOEC preheaters

Unfortunately, the new SOEC corebox were by mistake equipped with more powerful heaters (10 kW) designed for another SOEC application. Initial start-up failed as the powerful heaters blew the fuses and damaged one of the heater controllers. Several start-up attempts were made with the powerful heaters, but managing control using the existing power regulators was difficult, and ultimately the heaters were replaced with the previous 4 kW type. All the start-up attempts are marked as Startup #1 (SU#1) in the extended timeline (available in appendix).

Not all the SOEC start-up procedures from the previous project could be directly translated to the new corebox design. The temperature probes used to control heater duty were moved closer to the stacks. This allowed better control of the stack inlet temperature, but also introduced a delay in the response. Using the previous control parameters resulted in temperature oscillation and the control parameters had to be reconfigured. The system became especially unstable when ramping up steam flow, resulting in several failed startup attempts. The startup attempts are marked as SU#2 in the extended timeline.

The issues with the preheaters did not end after project period 2. Due to incorrect flow distribution between production line A and B, one heater got damaged due to low flow. The incorrect flow distribution was believed to be caused by the changes with a new gas cleaning step, causing one production line to include more equipment and thus a higher pressure drop. Individual flow meters on production line A and B solved the issue.

4.2.4 Incorrect wiring

The pilot plant is equipped with more than 100 temperature and voltage sensors. This allows monitoring of smaller sections of electrolysis cells as well as temperature profiles of all streams. As all sensors are manually connected, the risk of human error was high, and swapped signals made data reconciliation difficult. Damage to sensor connectors during transport was also a frequent issue. A particularly severe human error was the swap of + and – from two of the power supplies, resulting in damage to stacks.

4.2.5 IT issues

The project has encountered two hard drive crashes. Although these issues can potentially lead to loss of data, it is always a setback as reinstalling and recovering from recent backup takes time and focus.

4.2.6 Unplanned maintenance

To allow safe operation, selected components like gas sensors, pressure safety valves, ventilation fans etc. are continuously maintained. During inspection of the pressure safety valves, it was found than one valve was leaking. It was identified to be due to higher pressure of the Core B feed line. The

pressure increase was due to the new cleaning step and downstream dust filter. The valve had to be replaced and the pressure rating of the new valve was increased. A larger dust filter was also installed to allow similar pressure profiles on the two production lines.
During functional testing (period 3) of the heated hoses in the electrolysis frontend, it was found that the tracing was damaged, and the hoses were struggling to keep the steam above condensation temperature. The heated hoses had to be replaced.

4.2.7 Timeline summary for the SOEC part

Surely the Covid pandemic has had the most direct impact on how operation as well as repair could be executed. This put a constant restriction on all activities. In hindsight we were quite "lucky" to face one of our major issues with operation and replacement of preheaters just before the national lockdown. Despite the many setbacks and challenges with reliability of utilities, the plant design has proven its ability to operate a full scale SOEC corebox for months. The milestone of 4000 hours was not reached but the learnings acquired during the project concerning reliability of balance of plant components, control procedures etc. are invaluable for further developments. This know-how will be implemented in Haldor Topsøe SOEC platforms and in the subsequent and parallel EUDP project SOC4NH3 where the purpose is to generate synthesis gas suitable for ammonia synthesis.

4.3 Utilization of enriched air for H_2S removal

During the previous EI Upgraded Biogas project, removal of hydrogen sulphide as a necessary step of biogas treatment in the chemical methanation process were demonstrated. We suggested to study the utilization of enriched air by-product of SOEC for bulk removal of H_2S from biogas. In the original project a design a custom reactor for biological H_2S removal was included. The reactor was significantly above laboratory scale, but still small when compared to current industrial solutions. Construction of this custom reactor for this project was planned to be done by a vendor in Germany. However, the vendor faced considerable constraints when designing a small version of their current industrial solution. With limited market potential for this reactor, so they decided to withdraw their offer. Alternate vendors for this intermediate reactor size was investigated, but to ensure progress it was decided to perform some of the studies at laboratory scale. As no vendors could be found, the university ended up completely constructing the desired reactor "in house". The reactor was available in the final months of the project, meaning only part of the findings from the laboratory experiments could be verified at larger scale.

5. Project results

5.1 SOEC

Despite the numerous mechanical, electrical and logistic problems described above we managed to operate some of the stacks more than 2000 hours due to the different mitigation efforts.

The operating strategy has been to gradually increase the operating temperature to counteract ageing of the stacks. The voltage has been kept close to the thermoneutral, e.g. the voltage per cell has been close to 1.29 V/cell. At this operating point there are no thermal gradients in the stack and the inlet and outlet

temperatures are close to equal. The metrics used to assess the performance of the stacks are thus simply the operating temperature and current drawn. This is a unique feature of SOEC technology which allows for a wide operating temperature window from 700 – 825 °C as opposed to low temperature electrolysers, which has a rather narrow temperature operating range.

All the data from the SOEC demo, including temperature, flows, pressures, voltage and current have been logged on a second to second basis but here are only presented the most pertinent ones for each stack pair.

For the stack pair 1&2 in the A core box the results are shown on Fig.2. The first unsuccessful run caused by malfunctioning PSU is not included. It is seen that the degradation is relatively fast for the first 600 hours as reflected in the ramping up of the inlet temperature required for a stable current = production of hydrogen. After 1000 hours the performance, however, becomes very stable. After 1500 hours a mishap unfortunately forced us to change out all the stacks in Core A and the good performance of the fresh stacks but also the rapid initial decline can be observed from the temperature development.

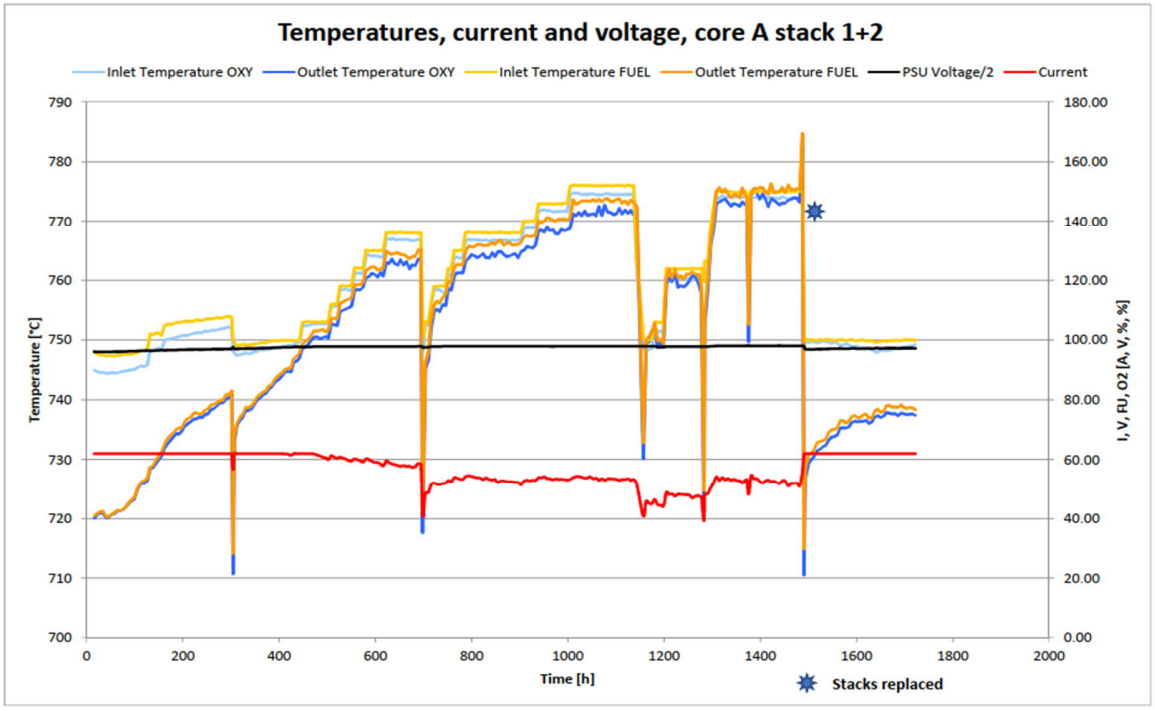

Fig. 2 Performance of Stack Pair A 1&2

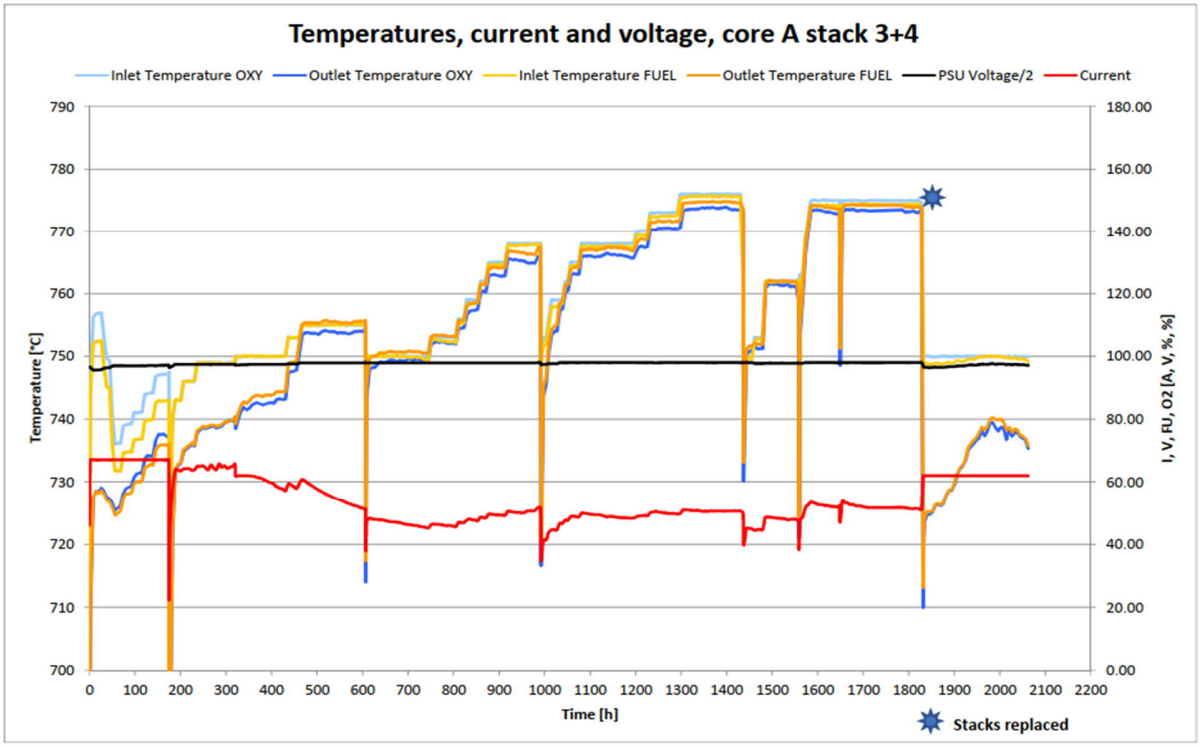

Fig. 3 Performance of Stack Pair A 3&4

The same pattern can be observed for stack pair 3&4 in Core A. In fact, it is remarkable how similar the performances are. The freshly replaced stacks here also displays good performance and is in fact available for further experiments with improved air quality (see later on that issue)

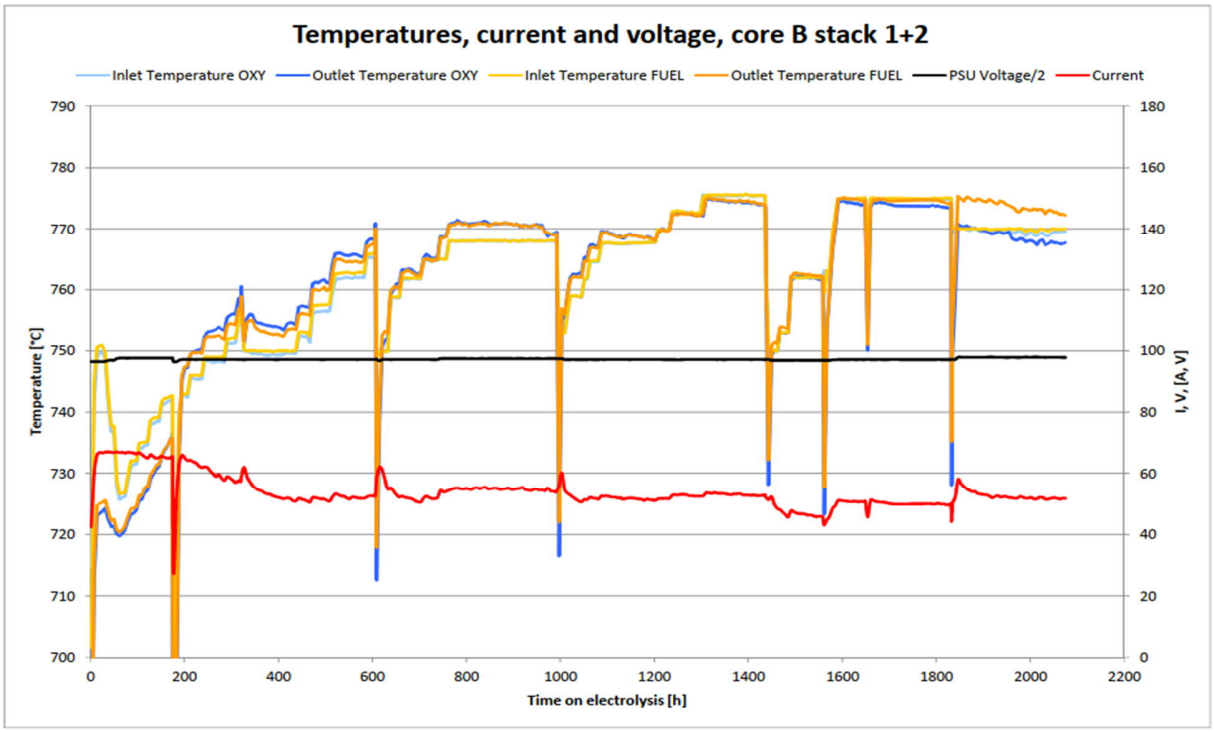

Fig. 4 Performance of Stack Pair B 1&2

The stacks pairs in Core B have been operating for more than 2100 hours and do also show the same initial degradation for the first 600 – 800 hours before the performance becomes very stable. It is noteworthy that the performance improves after each trip (indicated by lower operating temperatures) for the stack pair B 1&2 as shown on Fig. 4. This behaviour and improved long term stability can be ascribed to the fact this this stack pair is using a new, experimental manufacturing process.

The results for stack pair 3&4 in Core B is shown on Fig. 5. The end performance is somewhat lower than for stack pair B 1&2.

For all the stacks the operation at the thermoneutral voltage and the degradation mitigation strategy by slowly increasing temperature proved to work well. This operation mode also allows for changes between idling at 2-3 % capacity and 100 % load without significant effect on the operating temperatures which is useful for transient operation modes. The very high efficiency close to 100 % on a LHV basis was again verified by having a stack DC electricity consumption of 3.07 kWh/Nm^3 of hydrogen produced.

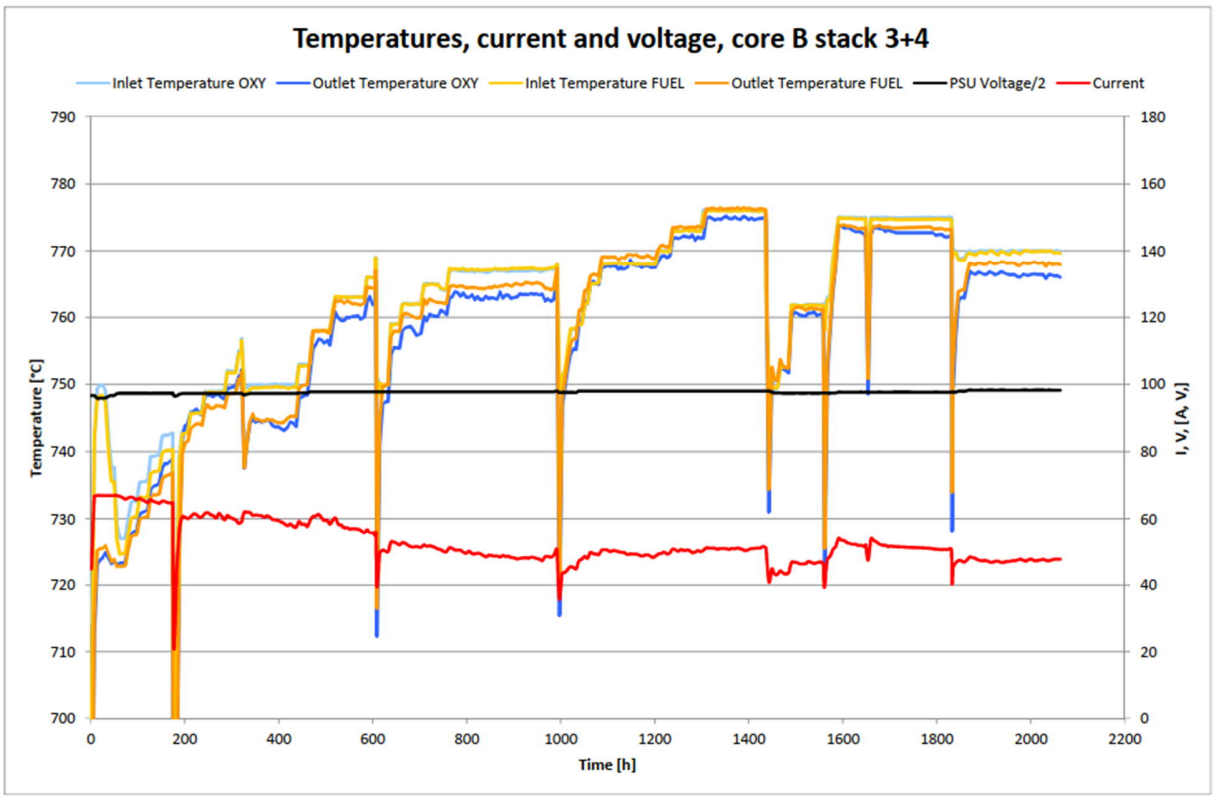

Fig. 5 Performance of Stack Pair B 3&4

Haldor Topsøe has developed a proprietary, mathematical model for SOEC stack which calculate a performance factor correcting for differences in flow, temperatures, pressures, voltage and current. This model is also used for system designs.

The model has been used to calculate the performance factors, Pf, for all the experiments described above and the results are shown on Fig. 6. It can be seen that the stacks display slightly different deactivation patterns in the beginning but are remarkably similar except for stack pair B 1&2 in core B, which also shows a reactivation after each trip and thermocycle.

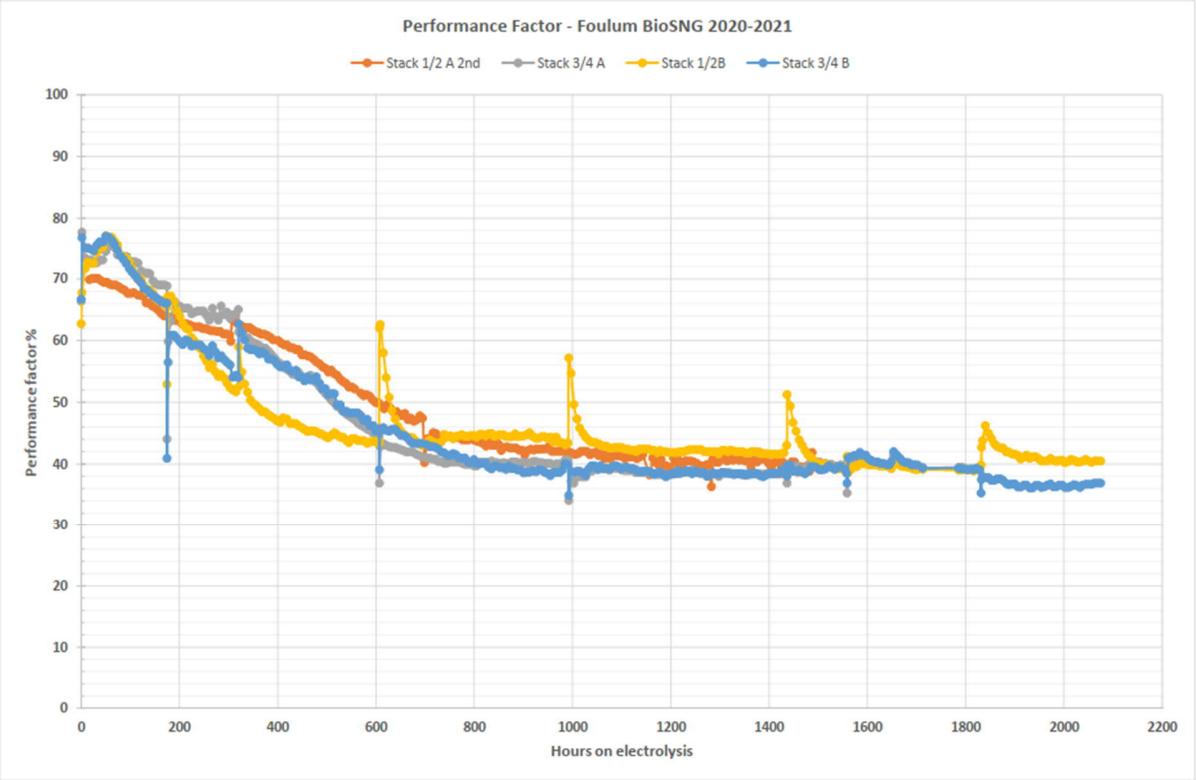

Fig. 6. Calculated performance factors

Unfortunately, there is not a clear difference between the stacks protected by the cleaning mass and the one without. The explanation is either that the amount of poisons on the cathode are negligible or that the cleaning mass is operated at to low temperature. It would have been more optimal to place the cleaning mass reactor just in front of stacks after the electrical preheater at the elevated temperature, but this would have required a major mechanical redesign of the core box. Such designs are nevertheless under development.

The overall performance is somewhat inferior to the performance of the stacks in EI Upgraded Biogas I project. A lot of thoughts and investigations have gone into in finding an explanation for that. The stacks used in this project should in fact be better than the ones used previously and the equipment is-mostly unchanged and in fact optimised. One tentative, but likely explanation should probably be found on the air side. It is known from the literature and own experience that humidity in the air can promote evaporation of hexavalent chromium from balance of plant components like heat exchangers, piping etc. Attention was thus directed at the air supply.

5.1.1 Air quality

As process air is used both to operate valves, as heat carrier during heat-up and as sweep air during electrolysis, the quality of the process air may critically affect pilot plant operation.
The process hall at Aarhus University has two air compressors to provide process air to all pilot plants. The compressors operate in parallel and the compressed air from both is mixed before it is send to

downstream plants. One compressor can be taken out to allow service, but this reduces the total capacity available.
Although the compressors both deliver the same quality of compressed air, they are quite different in design. Both are delivered from the vendor Reno.
Compressor #1 is an oil free screw compressor. The compressed air and the resulting condensate is stored in an intermediate “wet” buffer tank. At the discharge of the buffer tank, the wet compressed air is passed through a refrigerated plate heat exchanger to dry the air. The resulting dry compressed air is oil-free according to ISO 8573-1 and commercially known as “dentist grade”.
Compressor #2 is an oil lubricated screw compressor. To avoid oil droplets in the downstream equipment, both an oil separator and an oil filter is installed before the compressed air is send to a molar sieve unit (pressure swing adsorption dryer). Dry compressed air is send to the compressors buffer tank.

To operate pneumatic equipment like valves and pumps, the air must be oil and water free to ensure condensate does not built up in the pneumatic equipment. We realized that residual moisture in one of the electro-pneumatic positioners (flow control valve) had damaged the valve resulted in repair in the range of 2000 €. The issue was believed to be due to inadequate cooling of the refrigerated heat exchanger of compressor #1.. This also raised a general awareness on the quality of the compressed air, as this issue potentially had been present for a long time and could lead to problems with chromia evaporation and poison the anodes. A pair of dew point measurement devices were purchased and used to diagnose the problems. The issue was believed to be due to inadequate cooling of the refrigerated heat exchanger of compressor #1. The cooling unit has now been replaced. For Compressor #2 it was found that one of the PSA vessels were not operating correctly so the gas was wet half of the time. This has also been corrected now.

Another air contaminant of concern are sulfur compounds. Cr evaporation from balance of plant components and sulfur in combination is especially harmful.

Using the sulfur analysis method described in the article by Dannesboe, Hansen et al. (2019) the background level of sulfur in the compressed air was measured. Results show hydrogen sulfide to be present at a level of 6-12 ppb, but also a small trace of CS_2 was within the detection limit. On top of that there is always traces of SO_2 in ambient air. The background level of sulfur compounds in Foulum is expected to be above national average as the pilot plant is in close proximity to on site biogas activities. How control of this level of sulfur affects the air side of the SOEC stack will be investigated in the SOC4NH3 project.

References

Dannesboe, C., Hansen et al. (2019). "Removal of sulfur contaminants from biogas to enable direct catalytic methanation." Biomass Conversion and Biorefinery.

5.2 Further Studies on Methanation Process

During the first phase of the project, the methanation process was tested at the nominal design conditions. The experiments showed that the process is very successful in converting almost all CO_2 in biogas to methane only limited by the chemical equilibrium. The outlet gas has more than 97-98 % CH_4 without any trace of CO_2. Besides, it was concluded that the reactor volume is overdesigned for the nominal operating condition, while the catalyst showed very high activity, resulting in the production of hpeak temperature at the first 10 cm of the reactor. The position of the peak temperature did not move either during

more than 1000 hours of operation, which shows that catalyst deactivation is non-detectable. The over-design was done in the original design, to include a certain buffer to account for thermal aging as well as for poisoning, neither was to be seen To investigate the sensitivity of methanator section to the operational condition a study a wider operational range was undertaken. For reference the design, nominal condition is a production of 10 Nm^3/h of methane.

Four operational parameters including pressure, boiling water reactor temperature, feed flow rate, and H_2:CO_2 ratio, was selected for further study. A statistical design of an experiment based on the response surface method is used to minimize the number of experiments. The main goal of a response surface experiment is to develop a predictive model of the relationship between the factors and the response. This model is sometimes used to find the optimum operating condition in the complex system. Table 1 shows the design margin for each parameter, while table 2 presents the experiment design.

Table 1. Selected parameters and ranges

Parameter	Lower margin	Upper margin
Pressure, bar	10	20
BWR Temperature, °C	250	300
Feed Flow rate, Nm^3/h	6	20
H_2:CO_2 ratio	3.9	4.1

Table 2. Experimental Matrix

Exp. No	T (°C)	P (bar)	Flow rate (Nm^3/h)	H_2:CO_2 ratio	Exp. No	T (°C)	P (bar)	Flow rate (Nm^3/h)	H_2:CO_2 ratio
1	250	10	8	3.9	15	260	20	12	4.05
2	250	10	8	4	16	270	10	12	3.95
3	250	15	12	4	17	270	15	16	3.9
4	250	15	16	4.1	18	270	20	12	4
5	250	20	12	4.1	19	285	10	12	4.1
6	250	20	16	4.1	20	280	20	16	4
7	250	20	16	4.05	21	290	15	12	4.1
8	250	15	12	4.05	22	290	20	16	3.95
9	280	20	20	4	23	290	20	12	4
10	285	15	16	4	24	290	20	16	4.05
11	260	15	8	4.1	25	300	15	12	4.1
12	260	15	12	3.9	26	300	20	12	4
13	260	20	8	3.9	27	300	20	12	3.9
14	260	20	8	4.1					

The new results confirmed that the main reactor was overdesigned for all operating conditions when taking into considerations the excellent thermal stability and perfect behavior of the desulfurization. Figure 7 shows the temperature profile in the first stage of BWR during four different tests at 20 bar and various feed flow rates. As shown in this figure, increasing the flow rate pushes the temperature peak slightly down in the reactor, however, in all cases, the reaction in the first stage reaches the maximum conversion after passing only 40% of the reactor bed judged by the temperature profile.

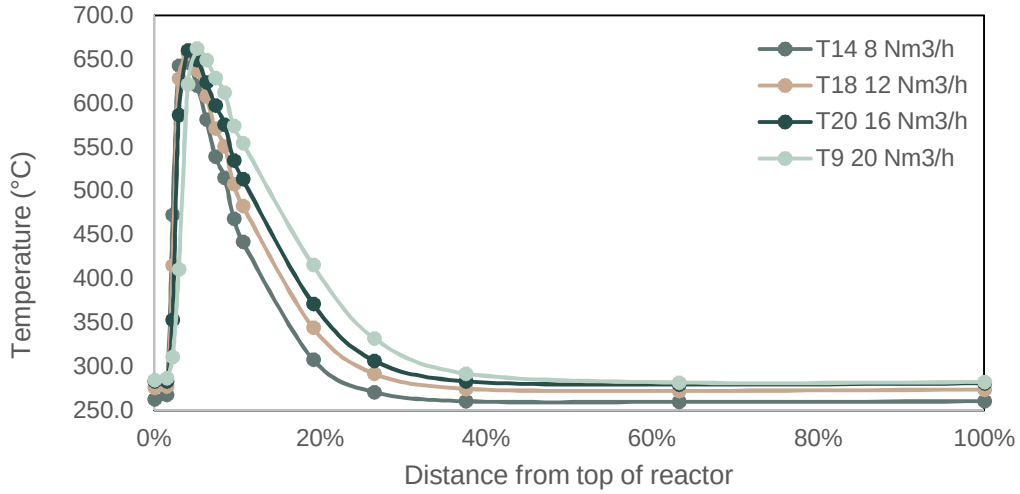

Figure 7. The temperature profile of the 1st reactor tube at various feed flow rates and 20 bar.

The methanator consists of two tubes immersed in boiling water and there is a cooling and condensation step in between so that the equilibrium is pushed to become more favorable in the second tube due to the removal of water. The temperature profiles in the second reactor is shown on Fig. 8. As illustrated in the figure, the hot spot location in the second stage depends on the flow rate. The shape and location of the peak temperature is a balance between the heat generated e.g. reaction rate per volume and the heat removal by heat transfer to the boiling water. The exit gas from the methanator is, however, still in equilibrium in all cases. The complete analysis of experimental results will be presented in scientific publications. However, the new series of experimental work provide guidelines for savings in full scale commercial, industrial scales compared to the original design.

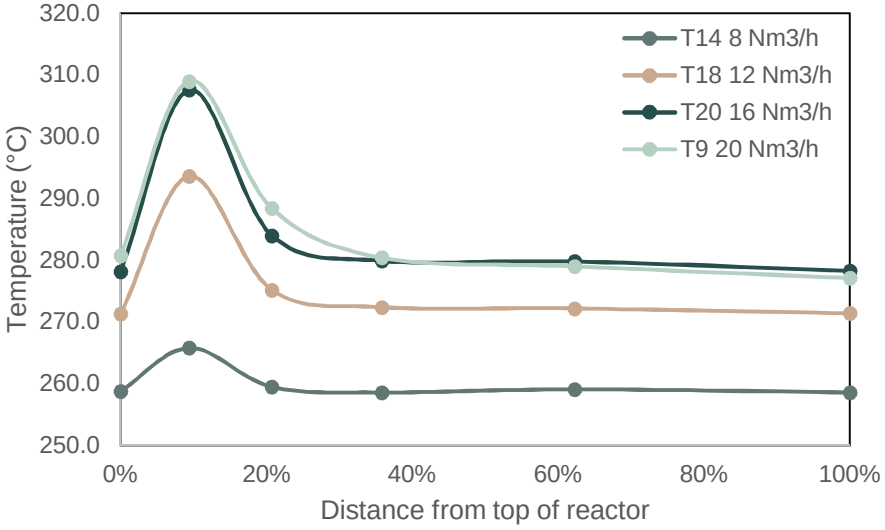

Figure 8. The temperature profile of the 2nd reactor tube at various feed flow rates and 20 bar.

5.3 Biological sulfur removal

5.3.1 Theory and background

A common large-scale removal solution for hydrogen sulphide is biological oxidation in a biotrickling filter (BTF), using conditions favouring conversion by acidithiobacillus thiooxidans (Smet et al. 1998, Ryckebosch et al. 2011). This technique involves oxidation of hydrogen sulphide (H_2S (g)) to sulphur (S(s)) or an even higher oxidation state of sulphur (e.g. sulphuric acid, H_2SO_4) as per the following reactions.

$$H_2S_{(aq)} \rightleftarrows H^+_{(aq)} + HS^-_{(aq)} \qquad pK_a = 6.9 \qquad \text{(eq. 1)}$$

$$HS^-_{(aq)} + 0.5\, O_{2\,(aq)} \rightleftarrows S_{(aq)} + OH^-_{(aq)} \qquad \Delta G^{\circ\prime} = -209.4\, \frac{kJ}{mol} \qquad \text{(eq. 2)}$$

$$S_{(aq)} + 1.5\, O_{2\,(aq)} + H_2O_{(l)} \rightleftarrows SO^{2-}_{4\,(aq)} + H^+_{(aq)} \qquad \Delta G^{\circ\prime} = -796.5\, \frac{kJ}{mol} \qquad \text{(eq. 3)}$$

The production of sulphuric acid, results in a low pH of 1-2 and this environment is intolerable to most other organisms, resulting in a selective removal of H_2S (Devinny 1998).

The BTF is robust and requires low maintenance, providing a cheap removal of bulk hydrogen sulphide (from ~1500 ppm to ~30 ppm levels) (Devinny 1998, Ryckebosch et al. 2011). The only additional reactant for the process is oxygen. The cheapest O_2 source is air, and injecting air both in the BTF and carbon filter is common practice (Ryckebosch et al. 2011). As a result of H_2S removal by the BTF, new contaminants, N_2 and O_2, are introduced. As N_2 is non-flammable, it is undesired in the final product, and air injection is normally kept at a minimum requirement. Addition of O_2 at only the stoichiometric requirement would in principle ensure complete conversion of O_2 and minimal N_2 contamination, but in all practical applications, a surplus of O_2 is required to ensure sufficient driving force and to avoid equilibrium restrictions (Devinny 1998). Providing O_2 enriched air or pure O_2, will indeed improve the conversion of H_2S, but this is not practiced in industrial filters, as it is currently economically infeasible to source the O_2 (Devinny 1998, Díaz et al. 2015).

With an SOEC on site, it is possible to provide oxygen enriched air both to the BTF and carbon filter, thereby significantly reducing the N_2 contamination. Further, as oxygen enriched air has a higher O_2 partial pressure, the transfer of O_2 to the aqueous phase will increase; this is a known restriction of the BTF. The waste stream of enriched oxygen will allow integrated treatment of biogas as shown in Fig 9.

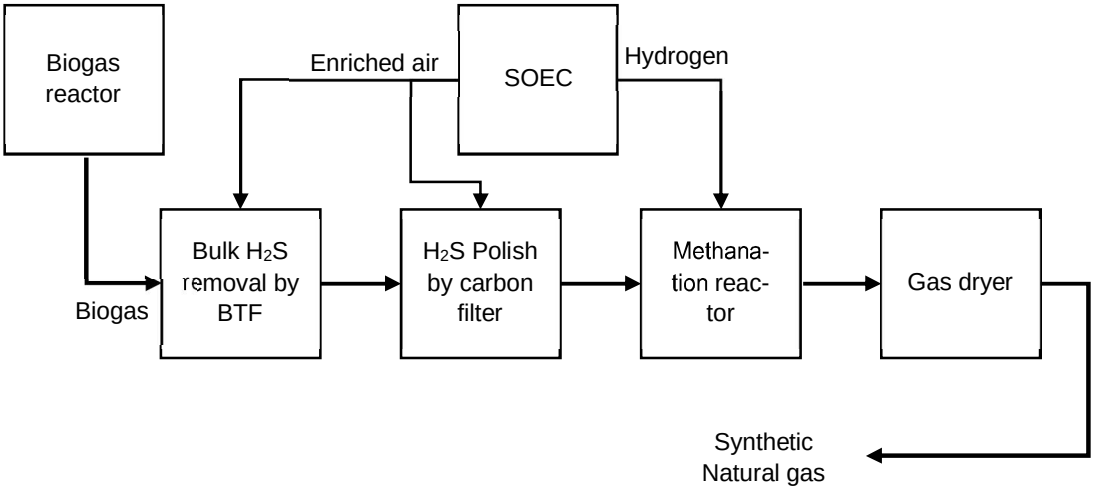

Fig. 9. Block diagram of proposed integrated treatment of biogas before methanation and export.

As most of the hydrogen sulphide is removed in the BTF, only this reactor type is the focus of the studies.

- The minimum oxygen requirement was determined for a bench-scale bio-trickling filter operated on raw biogas. The biotrickling filter was tested both with air injection and pure oxygen injection.
- Hydrogen sulphide removal was confirmed in a pilot-scale bio-trickling filter. The bio-trickling filter was tested both with air injection, enriched air injection and pure oxygen injection.

5.3.2 Bench-scale BTF

Basic system parameters of the bench scale BTF were obtained from a full scale BTF in use at the biogas site at Aarhus University, Foulum, Denmark. This provided a ratio H/D = 3 of the filter medium and a reactor residence time of one minute. The bench scale BTF was constructed from PVC pipe. The pipe had a diameter of 11 cm, a height of 116 cm and allowed treatment of 165 NL/h biogas. A gas dispersion layer of lightweight expanded clay aggregate (Leca) was placed before the filter medium (Fig 10). The filter medium consisted of Leca with immobilized a. thiooxidans. The filter medium was kindly donated from a full scale BTF in operation at Madsen Bioenergi I/S, Spøttrup, Denmark, ensuring a healthy biofilm had already been established (pH 1.5). The filter medium was kept wet by purging water and nutrients (Rabasol Chemie, NPK 886, diluted 1:100) at a flow of 30 mL/h. The reactor was wrapped with a heating mat and kept at 28 °C. Small pumps delivered the flow of biogas and air. A constant gas flow was verified by flowmeter. The O_2 and H_2S levels in the biogas were measured using a portable analyzer.

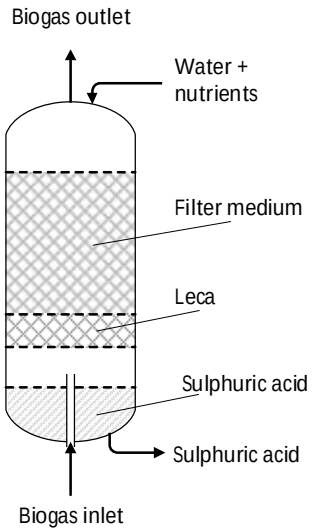

Fig. 10. Bench scale bio trickling filter used for bulk H_2S removal

Biogas was provided from the main biogas reactor at Aarhus University, Foulum. The H_2S content was in the range of 800-1200 ppm in the period of testing. Oxygen was provided in cylinders by AirLiquide (O_2, 99.995%). The reactor was operated for three days with no changes. After this stabilizing period, changes with air injection and injection of pure O_2 were made. The results are presented in Fig 11 Oxygen injection was varied in the range 0.5% - 5%. Conversion of H_2S was calculated from a simple input/output comparison. In the case of air, the results show a conversion drop as the oxygen level goes below 1.0 %. If pure oxygen is used, a. thiooxidans will tolerate a lower oxygen content of 0.5 %. To obtain a reasonable conversion, an oxygen content of 2.0 % is required.

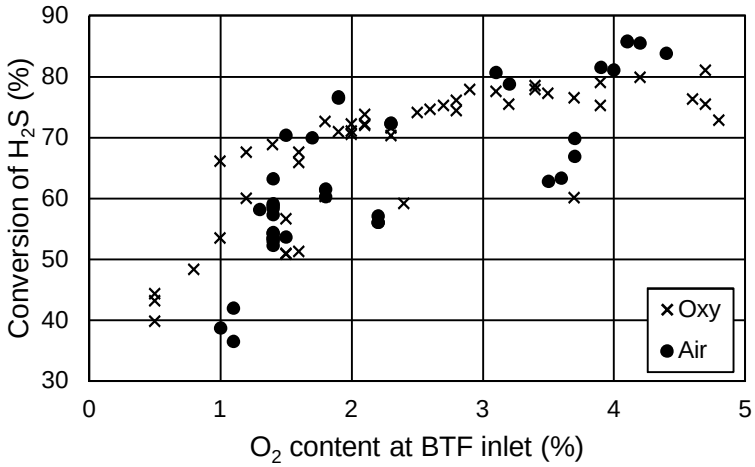

Fig. 11. Conversion of H_2S using a bench scale BTF. Oxygen was provided by air injection or by pure oxygen

5.3.3 Pilot-scale BTF

A pilot-scale BTF located at the biogas site of Aarhus University, at Foulum is used for this part of study. The fixed bed with an approximate volume of 790 L (D = 85 cm, H = 140 cm) is filled with plastic pall ring packing where the microorganisms are immobilised on the surface of packing material. The setup configuration is shown in Fig. 12.

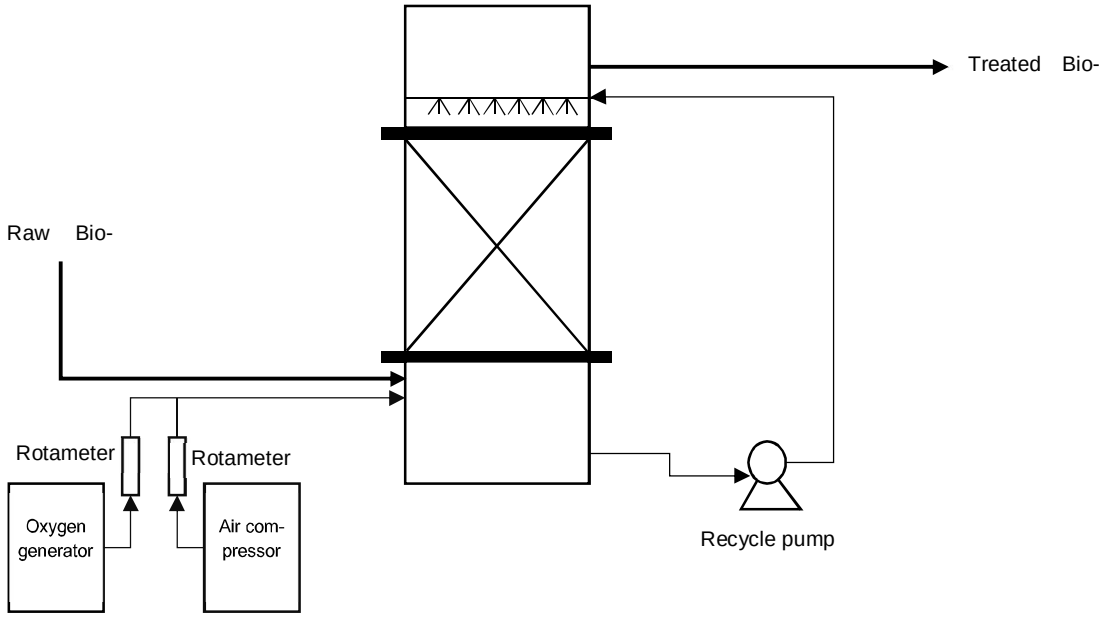

Fig. 12. Schematic of BTF setup at AU Foulum site

The raw biogas with a flow rate of 250 L/h and an H_2S concentration of 1600 ppm entered the BTF below the fixed bed section. The oxygen was produced by an oxygen concentrator OXYVET IV which can produce a continuous flow of oxygen from 0.5 to 5 L / min with a purity of 93%. This stream was mixed with a stream of air to produce a mixture of 49 % O_2 and 51% N_2. The experiments were performed at two different flow rates of 3 and 6.6 L/h for approximately 1200 hours. In addition, one experimental work was performed with only the stream from oxygen generator (93% O_2) and a flow rate of 6.6 L/h for comparison. The results of these experiments are presented in Fig. 13

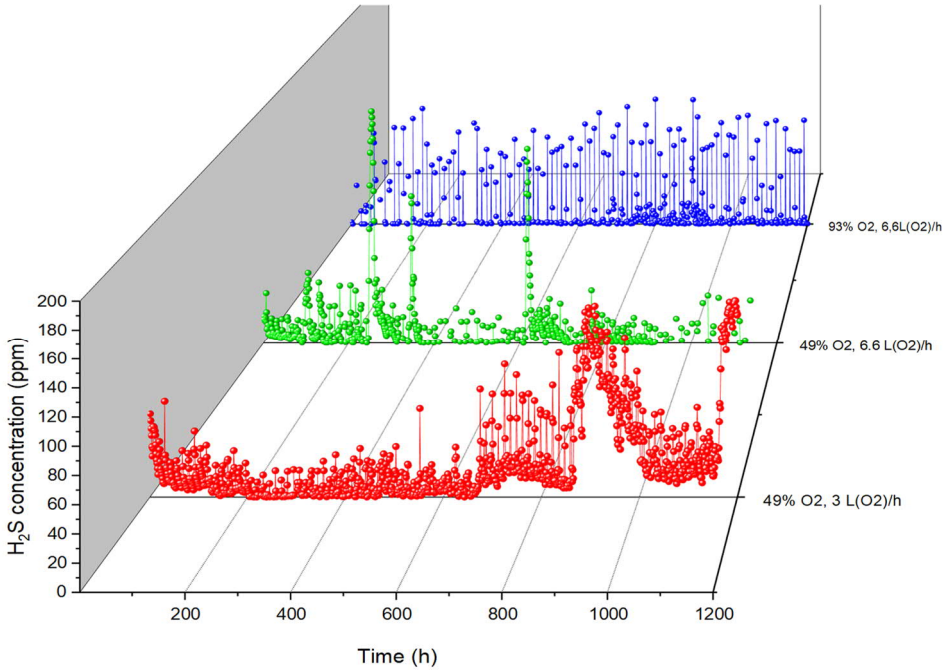

Fig. 13. H_2S concentration at the outlet stream of BTF

As shown in Fig. 13, the outlet concentration of H_2S reduced for all cases. The average concentration of output for 3 L/h of enriched air (49%) experiment was 29 ppm with a maximum of 146 ppm and maximum

standard deviation of 63 ppm. Increasing the flow of enriched air to 6.6 L/h enhanced the conversion rate and the average H_2S content of biogas reduced to 17 ppm. The most interesting observation was for the very pure oxygen experiments (93%), were the average H_2S concentration of 26 ppm was recorded. However, the output concentration showed considerable fluctuation with a maximum of 120 ppm and minimum of 0. Table 3 presents the experimental results summary.

Table 3. Summary of experimental work data

Experiment	1	2	3
Medium	Enriched air	Enriched Air	Purified air
O_2 Concentration	49%	49%	93
O_2 flow rate	3 L/h	6.6 L/h	6.6 L/h
Total flow rate	5.9 L/h	12.9 L/h	7.1 L/h
Average H_2S inlet	1600 ppm	1600 ppm	1600 ppm
Average H_2S outlet	29 ppm	17 ppm	26 ppm
Maximum H_2S outlet	146 ppm	197 ppm	120 ppm
Max Standard deviation	63	62	460
Average Conversion	98%	99%	98%
Min conversion	90%	88%	92.5%
O_2:H_2S feed ratio	7.5	16.5	16.5
Average O_2 inlet	1.17 mol%	2.51 mol%	2.57 mol%
Average output	0.11 mol%	0.89 mol%	0.70 mol%
Maximum O_2 output	0.71 mol%	2.00 mol%	1.49 mol%
Max Standard deviation	8.18	0.77	2.40

5.3.4 Summary

Comparing the result shown in the Fig 13 and tabulated in Table 3, utilizing the enriched air can increase the H_2S conversion to almost 99%. The previous experiments with normal air (not presented here) showed that the average conversion rate is up to 97%. Considering the lower nitrogen content of enriched air, it can be concluded that utilization of enriched air, whenever it existed on site, is recommended. Aarhus University intend to implement this at the Foulum site because it means savings for them in the use of the produced biogas.

However, the fluctuation in the outlet concentration of H_2S indicates that the final polishing step is unavoidable for any application of biogas in catalytic processes.

5.3.5 References

Devinny, J. S., Deshusses, M.A., & Webster, T.S. (1998). Biofiltration for Air Pollution Control CRC Press.

Díaz, I., I. Ramos and M. Fdz-Polanco (2015). "Economic analysis of microaerobic removal of H2S from biogas in full-scale sludge digesters." Bioresource Technology 192: 280-286.

Ryckebosch, E., M. Drouillon and H. Vervaeren (2011). "Techniques for transformation of biogas to biomethane." Biomass and Bioenergy 35(5): 1633-1645.

Smet, E., P. Lens and H. V. Langenhove (1998). "Treatment of Waste Gases Contaminated with Odorous Sulfur Compounds." Critical Reviews in Environmental Science and Technology 28(1): 89-117.

5.4 Commercial results and target groups

The commercial results arising from the experiments are that the lifetime of the stacks can be predicted with better confidence and potential areas for improvement of robustness and degradation have been identified which will make the SOEC technology in general more competitive with respect to capital expenditure. The superior energetic effciency has not been improved as it is already close to the maximum theoretically possible.

The cost savings with respect to the investment in methanation and bulk desulrisation are also very important to strengthen the competitiveness of the technology.

The target group for the technology is biogas system integrators, large biogas producers or operators with large point source CO_2 emissions.

5.5 Dissemination

The project content has been disseminated at:

- ETIP/SNET meeting, Riga, Estonia, December 2017
- European Fuel Cell Conference, Naples, Italy, December 2017
- EUDP programme meeting, IDA, Copenhagen, April ,2018
- Brintbranchens Årsdag, Aalborg, April 2018
- Dansk Bioøkonomi Konference, Sakskøbing, september, 2018
- Nordic Energy Research Strategy Conference, Stockholm, Sweden, October 2018
- Energistyrelsen Gasstrategidag, Copenhagen, March 2018
- Praxisforum Power to X, DECHEMA, Frankfurt, October 2019
- Chemcon, New Delhi, December 2019
- Hydrogen & P2X, Copenhagen, June 2021

- Deadline in DR2, March 2019
- TV2 News, Region Midtjylland, May 2019
- Peer Reviewed paper in Science, 2020
- TV Avisen 2. February, 2021
- SOFC XVII Conference On-Line, July, 2021

6. Utilisation of project results

The technological and commercial results from the project will mainly be used by Haldor Topsøe A/S to further optimize and consolidate their SOEC offerings. Haldor Topsøe A/S has partly based on the results from this and other EUDP projects decided to substantially increase their efforts and investments in the field of SOEC based solutions not only for biogas upgrading/methanation but also for hydrogen, methanol, ammonia and jet fuel plants. The number of employees has increased to close to 100 and substantial investment is foreseen for R&D and production facilities, which will create a substantial number (+100) of new jobs in Denmark.

The electrolysis field in general is expanding at astonishingly speed since the inception of this project and numerous projects have been announced mostly based on the established alkaline or PEM electrolysis technology. It is, however, believed that the SOEC will be a potential long-term winner due to its higher energy efficiency and ability to utilize waste heat from downstream chemical syntheses as exemplified in this project. Specifically, with respect to SOEC for biogas upgrading we are only aware of one large scale project by Sunfire and KIT in Germany which attempted amore a less a close copy of the original El Upgraded Biogas concept. They did, however, only managed to operate for a few hundred hours.

The methanation is in our opinion at TRL 9 and ready for commercial sales, but if the el-upgraded biogas methane has to compete head on with fossil natural gas it is difficult to present a convincing business case until either a subsidy scheme approaching the biologically produced methane is implemented or a substantial CO_2 quota price is politically agreed.

The utilization of renewable electric energy for production of fuels and chemicals from water, air and renewable carbon sources will no doubt be important part of the puzzle to help solve the impending climate crisis, the severity of which is underlined in the latest IPCC AR6 report. It will be important to be able to offer efficient and competitive solution using a combination of electrolysis and catalysis to that end and a broad-based consensus on that conclusion at least in Denmark and the EU has emerged the last couple of years.

7. Project conclusion and perspective

- *More than 2000 hours of SOEC electrolysis has been demonstrated with high efficiency*
- *The strategy to counteract degradation by increasing temperature and operating at thermoneutral voltage works and can also handle transients*
- *The steam clean-up mass need to be located close to the SOEC stacks*
- *Control of air humidity and sulfur need to be implemented and mitigation solutions designed*
- *Careful selection of balance of plant components and vendors is very important*
- *Some of the solution will be used in the ongoing SOC4NH3 EUDP projects as well as in other Haldor Topsøe SOEC based plants*
- *The catalyst inventory for methanation can be reduced*
- *A new, improved biological desulfurisation technology using enriched air from electrolyzers has been demonstrated*

8. Appendices

Timelines

The project periods are as follows:

Pilot plant rebuild	1/1-2019 to 30/6-2019
Testplan period 1	1/7-2019 to 31/12-2019
Testplan period 2	1/1-2020 to 30/6-2020
Testplan period 3	1/7-2020 to 31/12-2020
Testplan period 4 (COVID extension)	1/1-2021 to 1/6-2021

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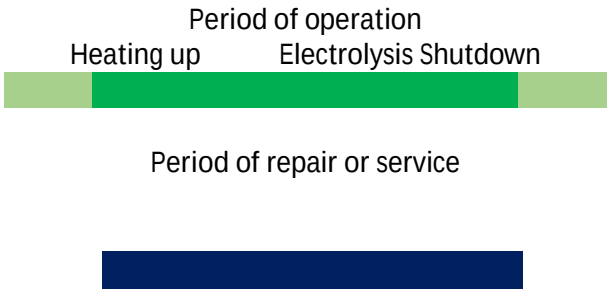

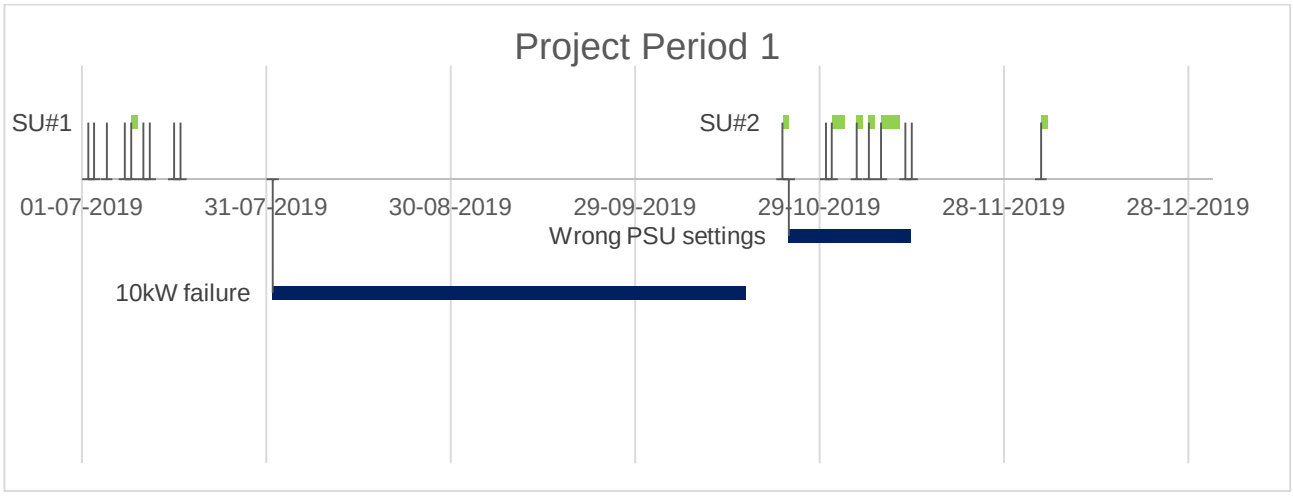

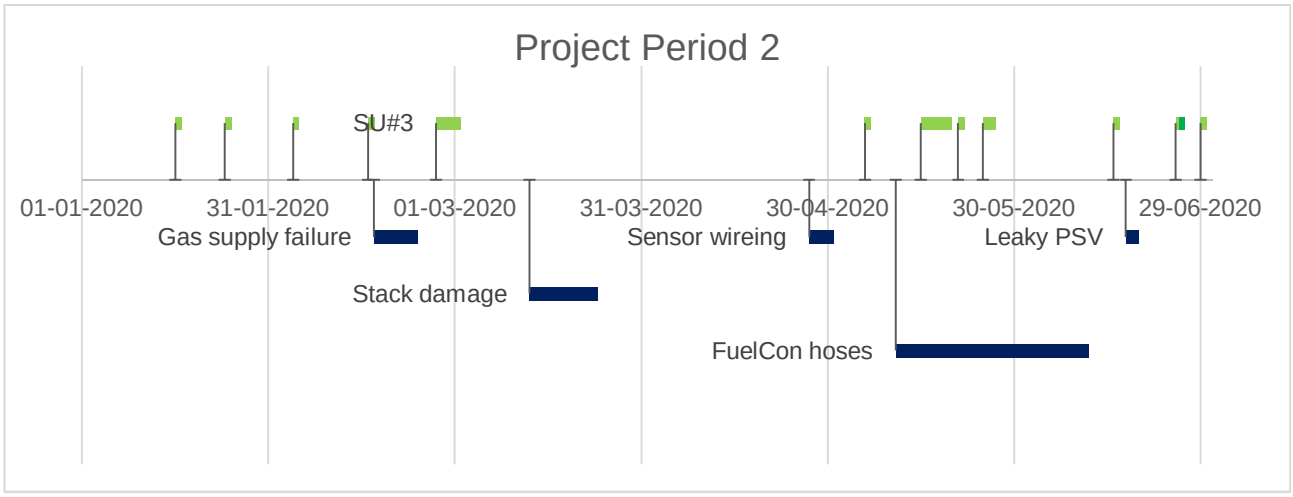

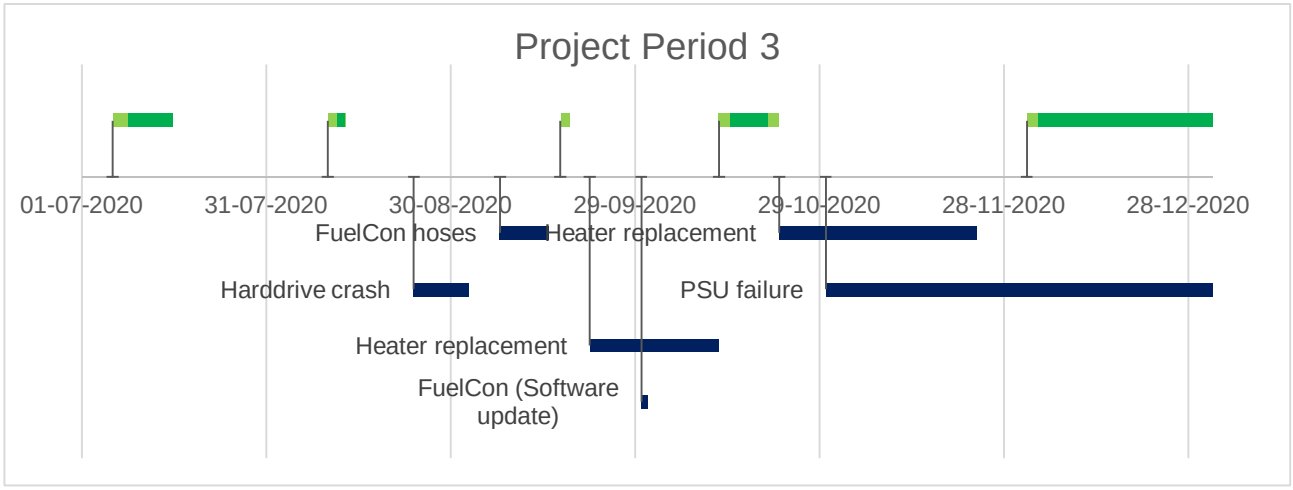

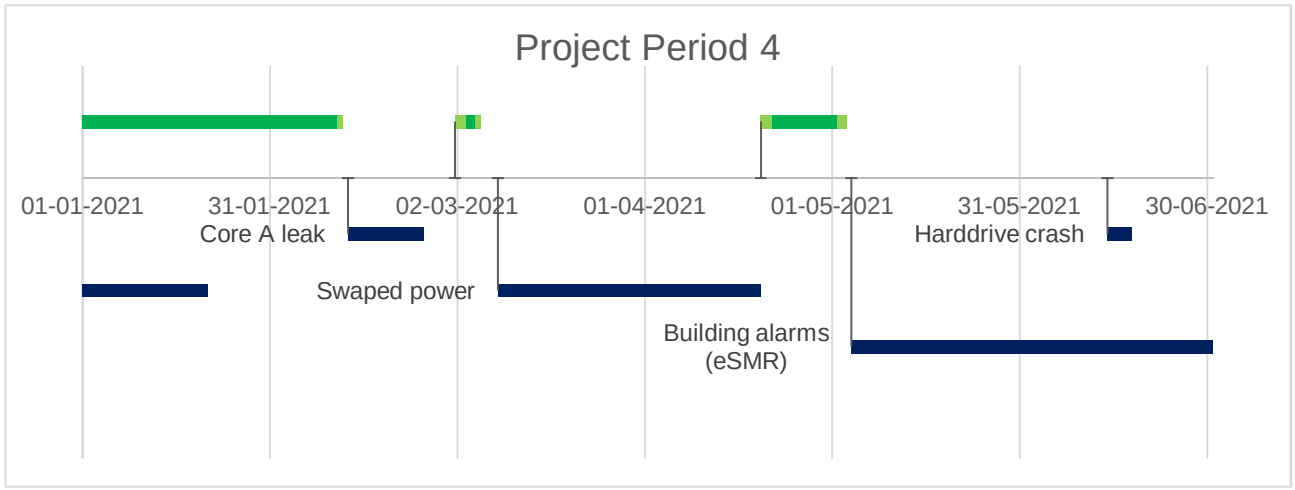

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