

Final report

1.1 Project details

Project title	BoP-OP
Project identification (program abbrev. and file)	64014-0559
Name of the programme which has funded the project	EUDP
Project managing company/institution (name and address)	Ballard Power Systems Europe A/S (former Dantherm Power) Majsmarken 1, 9500 Hobro, Denmark
Project partners	Aalborg University Aarhus University DGC VAIREX Air System Nissens A/S
CVR (central business register)	30804996
Date for submission	31/05/2018

1.2 Short description of project objective and results

Ballard Power Systems Europe A/S (formerly Dantherm Power) performed a number of eight work packages with the aim of reducing the cost of ownership, maintaining level of performance and improving lifetime, and improving the system availability by optimizing the Balance of Plant (BoP) of a 2,5 kW platform targeting micro CHP and supplemental market. The work packages led to an understanding of existing solutions and standards, and therefore providing a thorough comprehension of the future potential system BOP improvements.

1.3 Executive summary

A micro CHP system comprises many sub-modules and components. An optimization is possible but require working on a complete optimization scheme due to extreme interaction of the components. Serviceability as well as capital cost has been optimized by simplifying the balance of plant components. A system cost of 15000 USD has been achieved a little bit higher than the BOP-op objective but 50% cheaper than the previous generation. The work breakdown has been thoroughly executed leading to the identification of major improvements. While some of those improvements have been implemented to adjacent existing project (US DAN, SIMBA), others will be implemented on the generation of mCHP and other types of fuel cell power products.

1.4 Project objectives

1.4.1 WP1 Fuel treatment

Commercial Natural Gas and Liquefied petroleum gas (LPG) contain a certain amount of sulphur compounds. Sulphur leads to reformer catalyst poisoning via direct adsorption and blocking of the active catalyst. The fuel needs to be desulphurized prior to enter the fuel processor. For PEM fuel cell application, the required level of desulphurization need to be reduced down to 1-3 ppb. Without desulphurisation the fuel will deactivate the catalyst bed within less than 40 hours of operation and lead to a system failure and unrecoverable performance loss. System will need major repair like exchange of fuel processor and fuel cell stack to be operative again. The main objective of this work package comprises the following two sub work packages:

WP 1.1 Improvements of sulphur measurement analytical tools

Improve and develop tools for ultra-low-level detection (1-3 ppb) of gaseous sulphur compounds contained in natural gas and liquefied petroleum gas.

WP 1.2 Hydrodesulphurization

Perform a feasibility study on low cost micro hydrodesulphurization sulphur removal device.

1.4.2 WP2 Polymeric tubing

Piping material is a rather important part of the BOP of reformate fuel cell system. Cost reduction can be achieved by using polymeric material. The objective is to benchmarked existing material piping against requirements and existing standards.

1.4.3 WP3 Air supply

The 2.5 kW reformate platform is using a centrifugal pump with an adiabatic efficiency flooring at 25% at nominal BOL/EOL operating regime. The goal of the WP is to evaluate if this technology can be improved further in terms of performance and cost reduction. The objective is to increase adiabatic efficiency by 10 to 15 points while maintaining life (40 k hours) and reducing the part cost by 25%.

1.4.4. WP4 Cost reduction and optimisation of the water treatment module

The reformer of the system is supplied with an Ion-exchange water treatment where conductivity is lowered below 1 micro siemens/cm at all time. Maintaining such conductivity costs around 25% of the service consumable and leads to some other challenges related to biofilm formation. The objective of this WP is to reduce capital costs and operating costs of this sub assembly by performing an in-depth investigation of the failure mode.

1.4.5 WP5 Aluminium heat exchanger

The long-term stability of aluminium heat exchangers in the system needs to be established. Aluminium has many advantages over stainless steel but corrosion resistance in acidic conditions is not one of them. Aluminium is the most versatile and economical material for heat exchanger applications due to its unique combinations of properties like low cost, light weight, high specific strength, high thermal conductivity, ease of fabrication and high resistance to atmospheric corrosion. The corrosion resistance of aluminium heat exchangers depends on the type of environment to which they are exposed. The quality of the electrolyte, pH, oxygen concentration, alloy composition and microstructure and temperature and flow rate are the parameters that come into play as the environment changes. The available literature covers condensate from boilers and exhaust systems in the automobile industry. Since the fuel to the fuel cell system is free from odorant and sulphur content it is believed that aluminium could be a viable alternative to stainless steel.

1.4.6 WP6 Humidification

Proton Exchange Membrane (PEM) Fuel Cell Stacks efficiently convert the chemical energy in hydrogen to electricity through electrochemical reactions occurring on either side of a proton conducting electrolyte. This is a promising and very robust energy conversion process which can be used in many applications. Humidification of the inlet air of PEM fuel cell stacks is essential to obtain optimum proton conductivity. Operational humidification of the anode and cathode streams with a dew points close to the fuel cell operating temperature are required. These conditions must be met at the Beginning-Of-Life (BOL) as well as at the End-Of-Life (EOL) of the fuel cell system.

1.4.7 WP7 System reliability

The system needs to reach a B10-10 reliability target (10% failure after 10 years of operation). Most suppliers cannot provide any data and it is nearly impossible to prove the reliability. Therefore, the scope of this WP is to perform a detailed Failure Mode and Effect Analysis (FMEA) of the micro CHP system and determine which components are susceptible to fail first. This work package used the reliability tools developed with the EUDP-funded REST project.

1.5 Project results and dissemination of results

1.5.1 WP 1.1 Improvements of sulphur measurement analytical tools

The state in which sulphur is found differs between the two types of gases. In natural gas, H₂S and tetrahydrothiophene (THT) are the two major compounds, accounting for over 99 % of total S content. In LPG, ethanethiol (or ethyl mercaptan, C₂H₅SH) is the major compound, accounting for over 94% of total S content. An ideal portable equipment to detect online sulphur breakthrough must be able to measure naturally present sulphur compounds as well as sulphur compounds from added odorants.

There are various specific detectors that are available for measuring sulphur compounds, such as hydrogen sulphide H₂S, methanethiol CH₄S, dimethyl sulphide (CH₃)₂S, carbon disulphide CS₂, and dimethyl disulphide (CH₃)₂S₂ in the atmosphere. Examples of detectors are electron capture detector (ECD), flame photometric detector (FPD), pulsed flame pho-

tometric detector (PFPD), sulphur chemiluminescence detector (SCD), atomic emission detection (AED), Hall electrical conductivity detector (HECD), and photo-ionization detector (PID). Most detectors are however coupled with Gas Chromatography (GC), which is not portable or cost-effective.

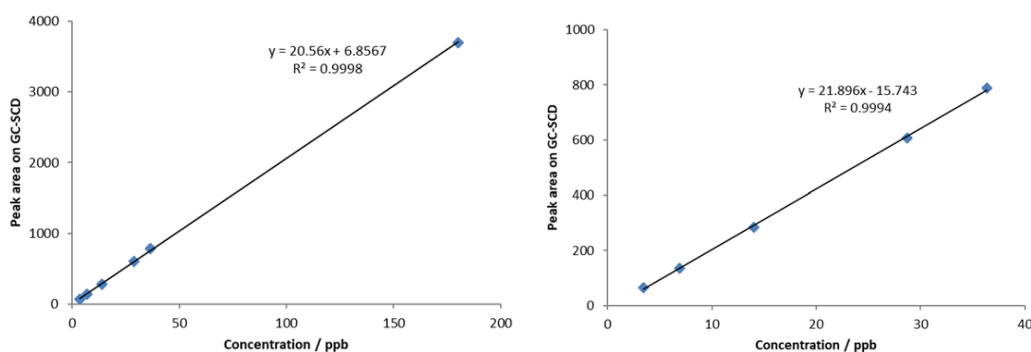
The relevant Sulphur detection methods are found to be:

- Gas Chromatography – Sulphur Chemiluminescence Detection (GC-SCD), an offline method for S measurements;
- Proton- Transfer-Reaction Mass Spectrometer (PTR-MS);
- Single-column trapping/desorption combined with chemiluminescence;
- Microchannel collection and micro-fluorescence detection (μ GAS).

For developing a portable sulphur analyser based on low cost colour sensitive absorbents, two popular brands of portable sulphur analysers were investigated, including Dräger (Lübeck, Germany) and Gastec (Kanagawa, Japan). Two corresponding manual tube pumps, Dräger Accuro from Dräger and Gastec Detector Tube Pump (model GV100) from Gastec, were used. A common tube opener (model Dräger TO 7000) was used to open all detector tubes.

Three sulphur standards were selected to represent the major sulphur compounds in Danish NG (hydrogen sulfide (H₂S) in methane, 0.18 ± 0.03 ppm, EffecTech, UK and tetrahydrothiophene (THT) in methane, 0.21 ± 0.03 ppm, EffecTech, UK) and Danish LPG (ethyl mercaptan (C₂H₅SH) in propane, 5.54 ppm, BOC, UK). Due to the targeted low ppb concentrations of sulphur to be measured in NG and LPG, colour detector tubes with the lowest detection limit range were selected to use with the portable Dräger and Gastec pumps. In order to evaluate the commercial colour detector tubes in ppb concentrations of sulphurs, three tests were carried where extra gas was sample to achieve the colour sensitive level. Correlation was then established between a Draeger tube and actual low ppb content

H₂S correlation – manual pump:



Measurement of H₂S by GC-SCD over lower concentration range (right) and broader concentration range (left).

The calibration was then used to correlates with colour sensitivity for 3 different compounds.

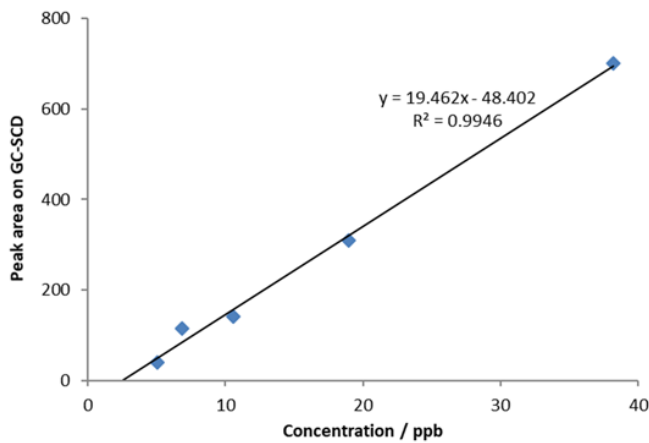
H₂S concentration

strokes



Demonstration of colour change from measuring H₂S using Dräger detector tubes (Dräger Hydrogen sulphide 0.2/b).

C₂H₅SH correlation – manual pump:



Measurement of C₂H₅SH by GC-SCD

C₂H₅SH concentration

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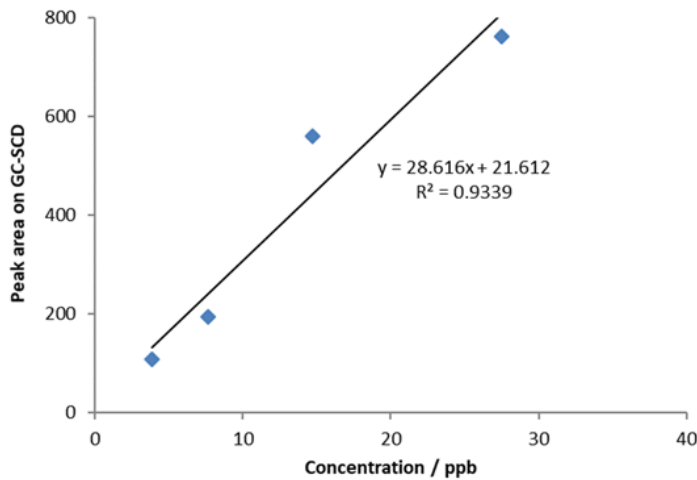


Demonstration of colour change from measuring C₂H₅SH using Dräger detector tubes (Dräger Mercaptan 0.1/a).

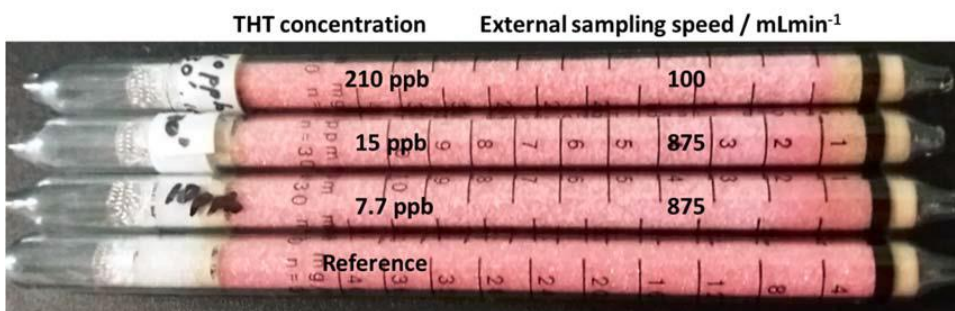


Demonstration of colour change from yellow to light pink from measurement of C₂H₅SH by Gastec detector tubes (mercaptan N70L).

THT correlation external pump

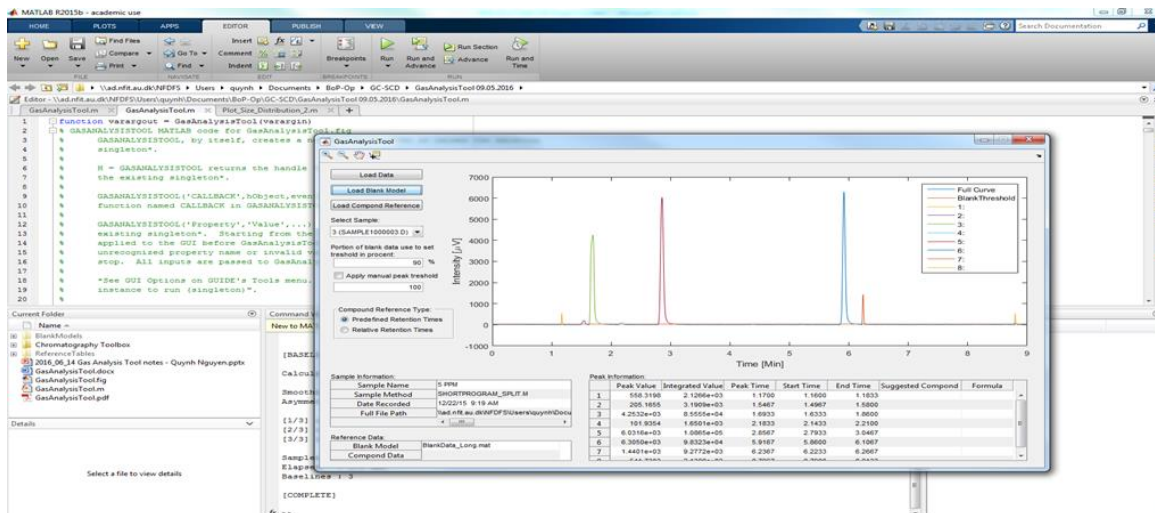


Measurement of THT by GC-SCD



Demonstration of colour change from measurement of THT using the Dräger detector tubes (Dräger tetrahydrothiophene 1/b).

A Sulphur Analysis Tool (SAT) was developed in Matlab, which has the capability of identifying and quantifying gas compounds and samples run using an Agilent GC system, with known standards.



Conclusions

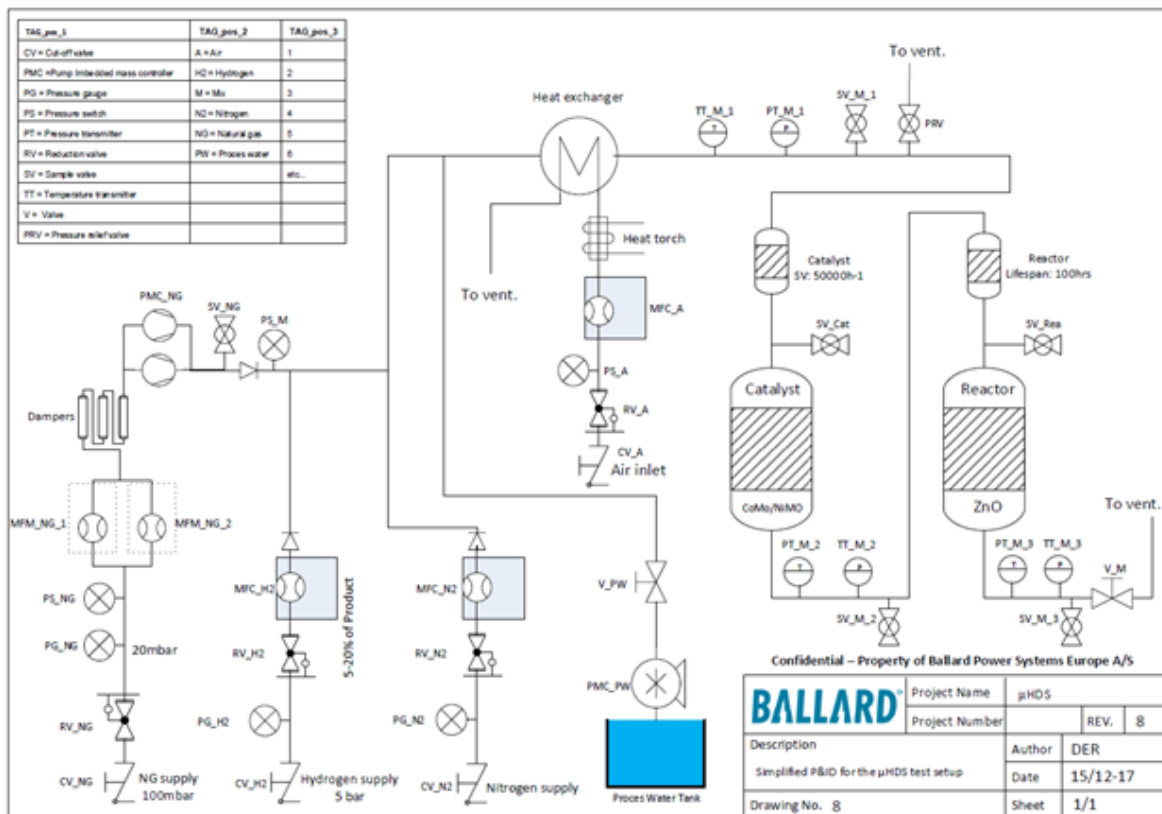
In general, the commercial colour absorbent detector tubes from Dräger are preferred over those from Gastec. The Dräger detector tubes could be recommended for fast qualitative measurements of sulphur contents for all major sulphur gases including H₂S and THT in NG and C₂H₅SH in LPG, both using the manual pumps or by applying an external pump. With the first option, a minimum of 45 minutes sampling time would be required for H₂S, while a minimum of 25 minutes sampling time would be required for C₂H₅SH to measure corresponding concentrations in the low ppb range. The second option using an external pump would be easier to operate but requires extra effort to setup. This second option would be required to measure sulphur compounds that require many strokes for sampling into the “readable” window, such as THT. It should also be noted that cross sensitivity of the detector tubes is also possible. For example, the mercaptan tubes would react to both methyl and ethyl mercaptan, without a clear known contribution from each. However, this should be acceptable if only qualitative evaluation is required. In both cases of using either the manual pump or external pump, the change of colour should be used to qualitatively indicate the presence of ppb concentrations of H₂S, C₂H₅SH and THT. At the same time, concentration indication (from the column length reading) of the colour change on the detector tube did show any correct concentration. No discernible effect of the drying sections/tubes was found retaining unwanted sulphur compounds, as indicated by PTR-MS measurements.

1.5.2 WP1.2 Hydrodesulphurization

The maximum allowable Sulphur on the C3 reformer is specified by WS to be around 1,66ppb (molar based) for an expected lifetime of 40000 hours. Regarding the stack a document from Ebara Ballard specifies sulphur level of 1 ppb for an expected lifetime of 40000 hours for the 1310 Stack. The requirement has been summarized in the table below.

Maximum allowable Sulphur		
	Reformer	Stack
Life time (h)	40 000	40 000
Allowable absorbed sulphur weight (mg)	< 70	< 42,2
Sulphur content (ppb)	< 1,66	< 1
Sulphur content ($\mu\text{g}/\text{Nm}^3$)	2,4	1,4

A test bench was constructed to test the μHDS desulphurization method. The Test bench is designed to provide a proof of concept of the μHDS method but also to mimic the expected operating conditions when implemented in the FCgen-HC2-mCHP system. Furthermore, it is designed for accelerated testing of the catalyst and adsorption material. PID of the test setup are shown in the illustration below.



To document a proof of concept a test matrix was defined. The test plan below covers 20 of the possible 206 tests defined in the test matrix. These tests were specifically chosen to document the μHDS method.

Index/ID	Fuel		Operation		Catalyst		Gas composition				Temperature		%H2 recirkulation				Fuel Sulfur concentration [ppm]	Gas komp ok? [Yes/No]	Catalyst conversion ok? [Yes/No]	Fluegas sulfur concentration [ppm]
	NG	LPG	Startup	Operation	A	B	Pure Hydrogen	Shift Outlet	Ref. Pre cool	Ref. Post cool	AWG	Cat: 380°C - Rea: 225°C	Cat: 20°C - Rea: 20°C	5%	10%	15%				
1	x			x	x		x				x			x						
2	x			x	x		x				x				x					
3	x			x	x		x				x					x				
4	x			x	x		x				x						x			
5	x			x	x		x					x	x							
6	x			x	x		x					x	x							
17	x			x	x			x			x			x						
18	x			x	x			x			x				x					
21	x			x	x			x				x	x							
22	x			x	x			x				x	x							
41	x			x	x		x				x			x						
42	x			x	x		x				x				x					
43	x			x	x		x				x					x				
44	x			x	x		x				x						x			
45	x			x	x		x					x	x							
46	x			x	x		x					x	x							
57	x			x	x			x			x			x						
58	x			x	x			x			x				x					
61	x			x	x			x				x	x							
62	x			x	x			x			x			x						

The testing was conducted within the premises of BPSE. The system was placed in a ventilated test area inside the laboratory. All samples were taken in the same manner using 3L SKC Tedlar sample bags (Cat. NO. 232-03). All sample bags were flushed 6 times with Air prior to use. After each Test run, all collected sample bags were sent to Aarhus University for GC-SCD analysis. Picture of the μ HDS test bench:



The test samples are named according to the specific Test-ID and sample ID. E.g. "Test 1 – 2A" is a reference for Test ID #1, sample ID 2, Sample A. The table below shows the Sample ID definitions according to the test positions showed in the PID of the test bench, see table below:

Sample ID#	1	2	3	4	5	6
Sample Tag	SV_NG	SV_M_1	SV_Cat	SV_M_2	SV_Rea	SV_M_3

In the first test run, the following Test ID was performed: Test ID 1,2,3 and 4. The table with test results is shown below:

Standards							
	Conc (ppb)	Area	Retention time				
H2S	750	68.472	1,638				
DMS	1080	84.300	2,787				
THT	990	70.260	5,854				
Raw data: Integrated area							
Suggested compound	Unknown	H ₂ S	Unknown	Thiophene	3-methyl-2-butanethiol	Unknown	THT
Retention time	1,4433	1,6300	2,1133	4,3100	5,2400	5,35	5,8533
Test 1-2A		119.880	2.113			1.714	245.100
Test 1-2B		118.540	2.053			1.620	245.580
Test 1-4A	759			1.364			
Test 1-4B	454			1.814			
Test 1-6A	511			1.465	178		
Test 1-6B	185			1.002			
Test 2-2A		129.370	2.068			1.456	240.460
Test 2-2B		127.940	1.819			1.388	243.300
Test 2-4A	720	524		1.076			
Test 2-4B	220	428		484			
Test 2-6A	275						
Test 2-6B	222						
Test 3-2A		115.520	1.060			1.228	203.760
Test 3-2B		103.770	855			1.158	195.670
Test 3-4A	855			935			
Test 3-4B	561			1.106			
Test 3-6A	581			666			
Test 3-6B	567						
Test 4-1A		141.770	2.674			1.011	197.040
Test 4-1B		140.450	3.020			907	197.160
Test 4-2A		111.600	800			1.005	166.630
Test 4-2B		111.390	851			996	165.590
Test 4-4A	878	644		1.800			
Test 4-4B							
Test 4-6A	744						
Test 4-6B	591						

Concentration has been calculated with the use of known retention times and their concentration/area ratio, using calibrated gasses as reference. Example of the calculations is shown below:

$$C_{H_2S \text{ Test 1-2A}} = \frac{C_{stdH_2S}}{A_{H_2S}} * A_{H_2S} \Rightarrow \frac{750}{68472} * 119880 = \mathbf{1313 \text{ ppb}}$$

Suggested compound	Concentration / ppb						
	Unknown	H ₂ S	Unknown	Thiophene	3-methyl-2-butanethiol	Unknown	THT
Retention time	1,4433	1,6300	2,1133	4,3100	5,2400	5,35	5,8533
Test 1-2A		1.313	27			24	3.454
Test 1-2B		1.298	26			23	3.460
Test 1-4A	8			17			0
Test 1-4B	5			23			0
Test 1-6A	6			19	3		0
Test 1-6B	2			13			0
Test 2-2A		1.417	26			21	3.388
Test 2-2B		1.401	23			20	3.428
Test 2-4A	8			14			0
Test 2-4B	2			6			0
Test 2-6A	3						0
Test 2-6B	2						0
Test 3-2A		1.265	14			17	2.871
Test 3-2B		1.137	11			16	2.757
Test 3-4A	9			12			0
Test 3-4B	6			14			0
Test 3-6A	6			9			0
Test 3-6B	6						0
Test 4-1A		1.553	34			14	2.776
Test 4-1B		1.538	39			13	2.778
Test 4-2A		1.222	10			14	2.348
Test 4-2B		1.220	11			14	2.333
Test 4-4A	10	7		23			0
Test 4-4B	0						0
Test 4-6A	8						0
Test 4-6B	6						0

The test results show that the sulphur uptake takes place between the sample positions 2 and 4. This is a result of the sulphur being absorbed in the catalyst bed which corresponds to an activation process of the catalyst material.

Second test run was performed after 24 hours of continuous operation. This was to determine if the activation of the catalyst was an BOL issue. Following test-ID was performed again: 1,2,3 and 4. The test results are shown below:

Suggested compound	Concentration / ppb						
	Unknown	H ₂ S	Unknown	Thiophene	3-methyl-2-butanethiol	Unknown	THT
Retention time	1,4433	1,6300	2,1133	4,3100	5,2400	5,35	5,8533
Test 1-2A		1.280,0	18,5			20,9	3.150,5
Test 1-2B		917,0	12,3			16,7	2.471,1
Test 1-4A		1,8		13,5			
Test 1-4B		1,3		12,3			
Test 1-6A				13,4			
Test 1-6B	0,8			13,5		0,6	
Test 2-2A	2,7	973,2	8,6			14,9	2.227,0
Test 2-2B	4,0	923,8	8,4			13,8	2.152,3
Test 2-4A	5,0	2,6		5,3			
Test 2-4B	1,8	2,0		3,7			
Test 2-6A	1,0			3,1			
Test 2-6B	1,2			2,6			
Test 3-2A		778,5				45,2	1.686,5
Test 3-2B		740,0				40,9	1.595,5
Test 3-4A	4,5	2,2		1,9			
Test 3-4B	0,8	1,6		2,6			
Test 3-6A	1,0			1,4			
Test 3-6B	1,0			1,8			
Test 4-1A		684,4	16,4			6,8	1.440,0
Test 4-1B		685,5	15,7			7,0	1.446,7
Test 4-2A		512,1				8,1	1.046,5
Test 4-2B		479,6				7,9	967,5
Test 4-4A	2,9						
Test 4-4B	1,3	1,2		0,8			0
Test 4-6A	0,6						
Test 4-6B	0,9						

Again, the results show that the sulphur uptake happens between sample point 2 and 4. This shows that the activation is not a BOL issue but shows that a priming procedure should be performed before taking additional samples.

Third test run was performed after activation of catalyst bed using H₂S and after the system was flushed with inert gas, N₂. Test ID 1-4 was performed once again, to determine an initial proof of concept. Test results are shown in the figure below:

Suggested compound	Concentration [ppm]									
	Unknown	H ₂ S	Unknown	Unknown	DMS	Unknown	Unknown	Unknown	Unknown	THT
Retention time	1,481	1,7380	1,839	2,596	3,821	4,1570	5,9960	7,2030		7,762
Test 1-2A		1,205			0					3,868
Test 1-2B		0,009			0					0,011
Test 1-4A		2,349			0					0
Test 1-4B		2,647			0					0
Test 1-6A		0			0					0
Test 1-6B		0			0					0
Test 2-2A		1,312			0					3,408
Test 2-2B		1,302			0					3,533
Test 2-4A		3,152			0					0
Test 2-4B		5,715			0					0
Test 2-6A		0			0					0
Test 2-6B		0			0					0
Test 3-2A		0,121			0,007					0,262
Test 3-2B		0			0					0
Test 3-4A		7,448			0					0
Test 3-4B		0			0					0,006
Test 3-6A		0,625			0,010					0,477
Test 3-6B		0			0					0
Test 4-1A		0,264			0,260					0,260
Test 4-1B		0,237			0,194					0,294
Test 4-2A		0,313			0,130					0,324
Test 4-2B		0,037			0,020					0,026
Test 4-4A		2,478			0					0
Test 4-4B		2,856			0					0
Test 4-6A		0,055			0					0,023
Test 4-6B		0			0					0

The test results show hydrogenolysis of the sulphur compounds to H₂S, which is a result of the catalyst reaching its active state. The optimal hydrogenolysis using Catalyst A shows to be with a H₂ content of 5-10%. The test also shows that the H₂S is being adsorbed in the subsequent adsorption bed.

These test state an initial proof of concept using μ HDS method in the range of the system requirements.

Conclusion

The conclusion of the project is that an initial proof of concept has been achieved. The Hydrogenolysis is occurring in the catalyst bed and the H₂S compounds is being adsorbed in the subsequent adsorption bed. Tests show the output from the adsorption bed to be below the specified system requirements for the FCgen-HC2-mCHP system. Best performance of the Catalyst material A (CoMo) shows to be with a H₂ content of 5-10%, which corresponds with the specified 8-12%. With the use of μ HDS, a possible operation cost savings can amount to 14923,8 DKK/system. In a final product, the μ HDS method would be integrated in the reformer to achieve thermal benefits. The actual cost of the μ HDS system would therefore be a negotiation with the reformer supplier.

1.5.3 WP2 Polymeric tubing

For the development of the research regarding tubing optimisation, the Danish project "Demonstrating micro cogeneration based on Danish Fuel Cells" has been used, where polymeric tubing, seals and fittings have been adopted for conveying gases in the micro CHP fuel cell system. WP 2 is only related to the non-metallic tubing in the micro CHP fuel cell system from the gas connection to the flue outlet. The CHP fuel cell system is a type C appliance according to DS/CEN/TR 1749, and according to the Danish gas Regulation the fuel is a part of the appliance if it is a type C-appliance.

The general requirements for the conveyed media/gas have been used, due to the information they provide regarding the internal operating conditions that the material is exposed to and the minimum requirements that the material must withstand. The tubing must also be able to withstand the conditions of the surrounding environment. Therefore, the expected operation conditions are also considered.

To be able to perform an assessment on the tubing, to see if it can withstand the operation condition, several physical parameters have been used to describe the material, such as colour, material, flammability, permeability, chemical resistance, moisture absorption, hardness, electrical resistance and effect of weathering and UV exposure. The expected system lifetime and lifetime properties are also taken into consideration, since this is the time that the system is expected to operate and therefore the components must be able to last as long as the lifetime. A list of expected additional properties has been provided by Ballard, containing the following:

- Material Compatibility is of utmost importance;
- Must sustain 1.5 time maximum pressure;
- Zone 2 as pr. 60079-10 must have a maximum resistance of 1 megaohm (tests according to UL 1067 section 12 or must pass UL 1067, section 15) SEP: Sound engineering principal is most important. Justification for use of non-metal lines must be proven in the risk assessment.

Further to the operation conditions, expected system lifetime and other relevant aspects considered, the materials must comply with requirements given in relevant European standards. A review of existing standards, studies and manufacturers' material data sheets was conducted to establish the big picture of suitable materials and tests conducted. The terms and conditions applied for the purpose of this report are specified in DS/EN 50465:2012. To market the CHP fuel cell system in Europe it must comply with the Gas Appliance Directive (GAD). As a fuel cell appliance consists of several components, it might be necessary to comply with other directives such as:

- Machinery directive; 98/37/EC;
- Low voltage directive; 73/23/EEC;
- Electromagnetic compatibility directive; 89/336/EEC;
- Simple pressure vessels directives; 87/404/EEC, 90/448/EC;
- Equipment for explosive atmospheres (ATEX), 94/9/EC.

Since this Work Package is only related to the gas carrying parts in the mCHP fuel cell from the gas connection to the fuel outlet, only the tubing related conditions from the literature (such as tests and standards) are investigated. The study of plastic tubing is necessary to be able to prove that plastic tubing can fulfil the needed safety requirements since plastic tubing for fuel cell fuel BOP application is not a standardized area.

The tubing related conditions in the standard are:

- 5.4 Soundness – 5.4.1 Soundness of the gas carrying circuit;
 - 5.13 Materials – 5.13.1 General (Part of);
 - 5.19 Gas carrying circuit – 5.19.1 General (Part of);
 - 5.21 Requirements for adjusting, control and safety devices – 5.21.1 General (Part of);
- Operational requirements:
- 6.2.1 Soundness of the gas carrying circuit;

- 6.5.5.3 Gas / air controls – 6.5.5.3.1 Leakage of non-metallic control tubes;
- 6.9 Resistance of materials to pressure – 6.9.1 General; 6.9.2 mCHP appliances of pressure class 1; 6.9.3 mCHP appliances of pressure class 2; 6.9.4 mCHP appliances of pressure class 3; 6.9.4.1 mCHP appliance of sheet steel or non-ferrous metals; 6.9.4.2.2 Resistance to bursting; 6.9.4.2.3 Tie bars (if applicable);
- 6.10 Hydraulic resistance;
- 6.14 Requirements for plastic in the combustion product evacuation ducts, terminals and fitting pieces for mCHP appliances;
- 6.15 Requirements for elastomeric seals and elastomeric sealants in the combustion product evacuation ducts, terminals and fitting pieces;
Test methods:
- 7.2 Soundness – 7.2.1 Soundness of the gas carrying circuit
- 7.9 Resistance of the materials to pressure;
- 7.15 Tie bars;

Annex CC (normative)

A series of test methods to determine the effects of long-term thermal load, long-term condensate exposure, condensing/ non-condensing cycling and resistance to UV radiation are noted below.

Methods to determine the change in properties before and after exposure:

- Impact strength in accordance with EN ISO 179-1 (un-notched test bars, Charpy impact strength);
- If execution meets with problems, the impact strength may be determined in accordance with EN ISO 8256 (un-notched test bars, tensile-impact strength);
- Tensile modulus in accordance with EN ISO 527-1 and EN ISO 527-2;
- Yield stress in accordance with EN ISO 527-1 and EN ISO 527-2;
- Density in accordance with EN ISO 1183 (all parts);
- In the case of thermosetting plastic:
 - Flexural modulus and flexural strength in accordance with EN ISO 178;
- In the case of flexible pipes:
 - Impact strength, tensile modulus and yield stress shall be carried out on rigid test pieces, manufactured as close possible to the original manufacturing process;
 - Ring stiffness in accordance with EN ISO 9969.

Regarding the material of the pipes – plastics and fibres – the following Standards have been detected for test for flammability properties:

- UL 94 - Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances;
- UL 1694 - Standard for Tests for Flammability of Small Polymeric Component Materials - UL 1694 Test procedures specified have been determined to be applicable to small components with an overall volume of less than 2500 mm³ (0.15 in³).

When considering the permeability of plastics and fibres, it must be noted that it decreases with increasing crystallinity. In general additives like fillers, pigments and plasticizers influence the permeability. For natural gas pipelines a special quality "PE-MD" is used.

The following UL Standards have been found relevant for the focus of the Work Package:

- 746A - Standard for Polymeric Materials - Short Term Property Evaluations;
- 746B - Standard for Polymeric Materials - Long Term Property Evaluations 746C - Standard for Polymeric Materials - Use in Electrical Equipment Evaluations;
- 746D - Standard for Polymeric Materials - Fabricated Parts;
- 746E - Standard for Polymeric Materials - Industrial Laminates, Filament Wound Tubing, Vulcanized Fibre, and Materials Used in Printed-Wiring Boards.

In the IEC 62282-6-100 relevant information regarding elastomeric materials such as gaskets and tubing in contact with fuels is stated.

IEC 62282-2 contains specifications regarding plastic or elastomeric materials used in a hazardous location. In the Second edition of the Standard, it is specified that flexible piping and associated fittings, when used for conveying gas shall comply with the following standards: ISO 1307, ISO 37, ISO 188, ISO 4672, ISO 1402, ISO 1436-1. Special consideration shall be applied for hydrogen pipes.

IEC 62282-3-1 – Second edition 2nd Committee Draft contains information regarding Guidance to account for the degradation effects of hydrogen on the mechanical performance of a material can be found in.

In the IEC 62282-5-1/Ed. 2 Fuel cell technologies – Part 5-1: Portable fuel cell power systems - Safety, Chapter 4.2.2, points 1) and 4), together with Chapter 7.29 Non-metallic tubing conductivity test, 7.30 Non-metallic tubing test for accumulation of static electricity have been found of relevance for the WP in cause.

In DS/ISO 16110-1 Brintgeneratorer der anvender brændstof-procesteknologi – Del 1: Sikkerhed, points 4.5.5.4, 4.5.6 and 4.6.2.1 contain specifications regarding plastic and elastomeric materials.

ISO/DIS 22734-2 Hydrogen generators using water electrolysis process – Part 2: Residential applications contains the following to be considered: point 5.2 and Chapters 10.1.5.2 Pressure test – Gas containing parts and 10.1.6.3 Additional Leakage Testing of hydrogen gas component connections and piping joints.

Regarding the aging and lifespan determination of plastics, there are several aspects that must be considered.

The parameters that have influence on the aging of plastic can be divided in three categories: parameters related to the material; parameters related to the subject / item; parameters related to the surrounding environment. Time and thermal pre-history of the item have also an influence on the aging of the plastic.

The following standards have been found useful for determining the influence of chemical on plastic:

- ISO 175 - Plastics -- Methods of test for the determination of the effects of immersion in liquid chemicals;
- ASTM C581 - 03(2008) e1 - Standard Practice for Determining Chemical Resistance of Thermosetting Resins Used in Glass-Fibre-Reinforced Structures Intended for Liquid Service.

The number of standards that contain relevant information regarding natural and artificial, climatic aging and testing of plastics, together with standards for investigation of biological attacks on plastic is quite substantial. Refer to the report of WP2 for more details. Standard ISO 16871 - Plastics piping and ducting systems -- Plastics pipes and fittings -- Method for exposure to direct (natural) weathering can be also of good use for the application in cause.

A Drop Weight Impact Tester for Plastic Pipes, depicted to the right, has been found as a tool for performing tests on plastic pipes, conforming to ISO 3127, EN744 and EN14111.



For testing the PE piping system for gaseous fuels, Standard EN 1555 Plastic piping systems for the supply of gaseous fuels – polyethylene (PE) is one of the standards that can be used. With the projects focus on plastic piping the parts of the 1555 standards that are most relevant must be Part 1. General; 2. Pipes and 5. Fitness for purpose of the system.

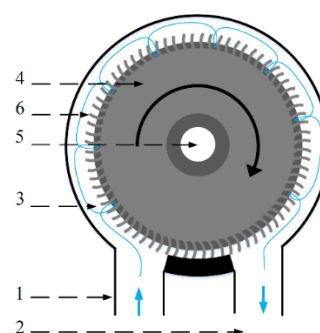
The work of this project also resulted in knowledge of companies who work in the area of plastics, such as testing of plastic and pipes, producers and vendors of testing equipment and producers of plastic material and tubes.

Conclusion

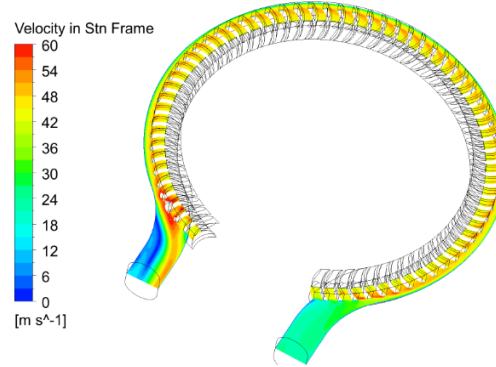
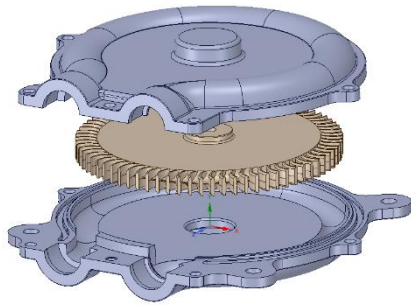
The study shows that existing standards to be used for fuel cell BOP constructions are less than ideal for that purpose, and many of the standards have very high – if not too high – requirements. The standards do not fit the manufacturers' purpose of constructing a balance of plant (BOP) for use in fuel cell systems: Requirements are simply too complex for that purpose, which also means that the costs of complying with these standards would be very high, thus making fuel cell systems not only more complex, but also more expensive than necessary. Furthermore, these standards do not consider new materials that can be used to make the BOP system less complex and to lower the costs. Lower costs are essential for fuel cell systems for them to gain a higher market penetration.

1.5.4 WP3 Air supply

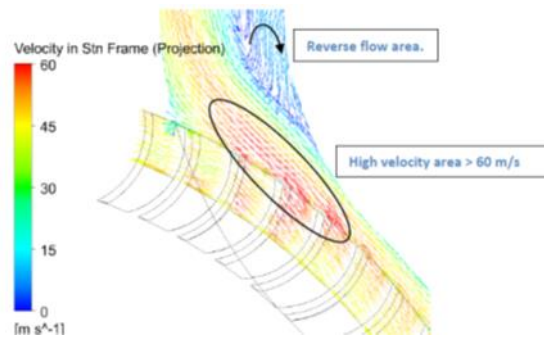
The first main activity in the project was to examine the fluid dynamics of a regenerative blower to get an understanding of the fluid's motion through the blower and to form a basis for a mathematical model describing this flow.



An investigation of the flow in the VRB2-18 air blower was performed at Aalborg University, with the help of the multiple reference frame (MRF) capability in ANSYS FLUENT.



The areas of high velocity (red) and reverse flow (blue) are affecting the performance of the pump. Improvements in the geometry of the pump and the results given by the ANSYS analysis were discussed with Vairex.

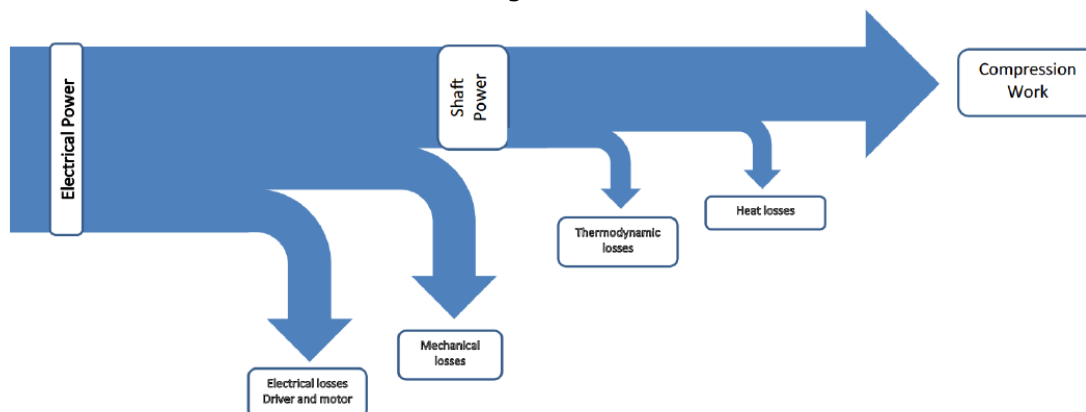


The performance of the compressor can be represented in a compressor map, which shows the relation between the mass flow and pressure ratio for different rotational speed values. The map can additionally include the efficiency and power curves of the compressor. The procedure to generate a compressor map can be split in three well distinguished tasks:

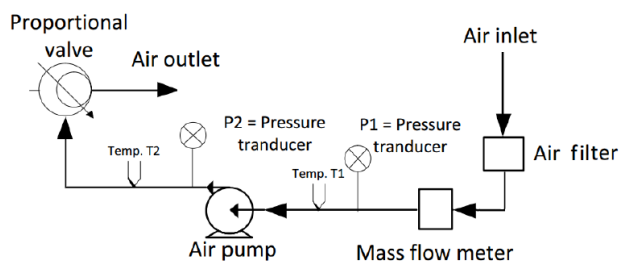
- Test performance and data acquisition
- Efficiency calculation
- XYZ data set plotting

Previously obtained compressor maps show differences compared to the manufacturer data. In addition, sets of data obtained from different tests lead to different maps.

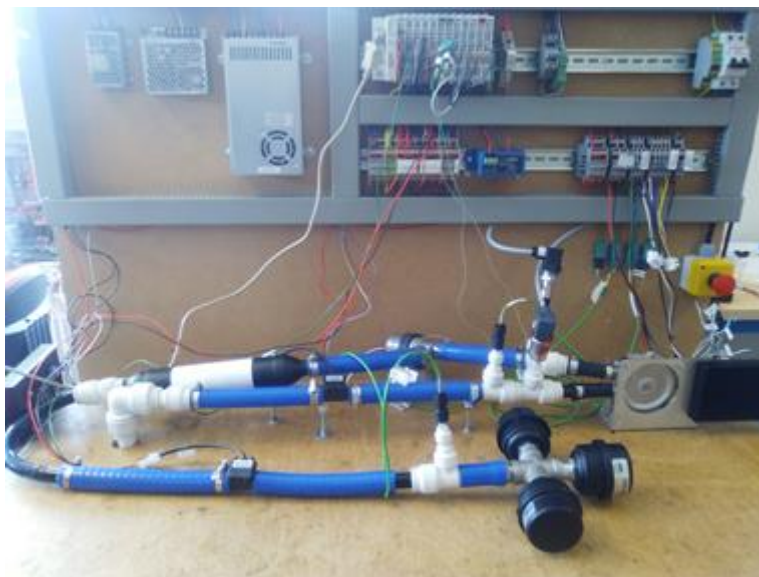
When calculating the compressor's efficiency, the different energy losses on its performance must be considered. First, the electrical energy provided to the blower DC motor is converted into mechanical power, however losses are found in the driver and motor windings as Joule losses. On the other hand, part of the mechanical power is lost due to friction in the mechanical components. The net power provided to the shaft moves a propeller that sets the mass of air in motion, increasing its temperature and pressure. However, not all the mechanical work provided to the fluid implies a pressure rise. Finally, some heat losses are transferred from the blower housing to the environment.



From the formula that accounts all the losses described above, it is clear that the efficiency of the blower is computed as a function of the mass flow circulating through the compressor, the inlet temperature and pressure, the outlet pressure and the motor power consumption. Therefore, a test bench was built to acquire this data. The starting point for the test bench design is illustrated to the right.



The test bench contained the following hardware components: three power supplies with voltages of 24, 12 and 5V; Posifa mass flow meter, PMF4103; LEM current transducer, DK 20 C10 U; Danfoss pressure transducer P1, MBS 3000; Prignitz pressure transducer P2; thermocouples Type K, Beckhoff PLC unit, Bürkert 6024 proportional valve and a Vairex VRB2 pump which was supplied with 24V and controller by a Moog BDP-Q2-50-10 driver. The software to control the test bench was implemented in LabView. Its specifications were determined based on the experience acquired by testing the motor. Picture of the test bench:



A set of functions to post-process the test data was developed in MATLAB. These functions can generate a compressor map that includes the ISO speed, ISO efficiency and ISO power curves. The Matlab scripts provided by Vairex (Vairex, 2013) and Mads Pagh Nielsen (Freeman, 2011) from Aalborg University were used as a reference and similarities in the post-processing are found.

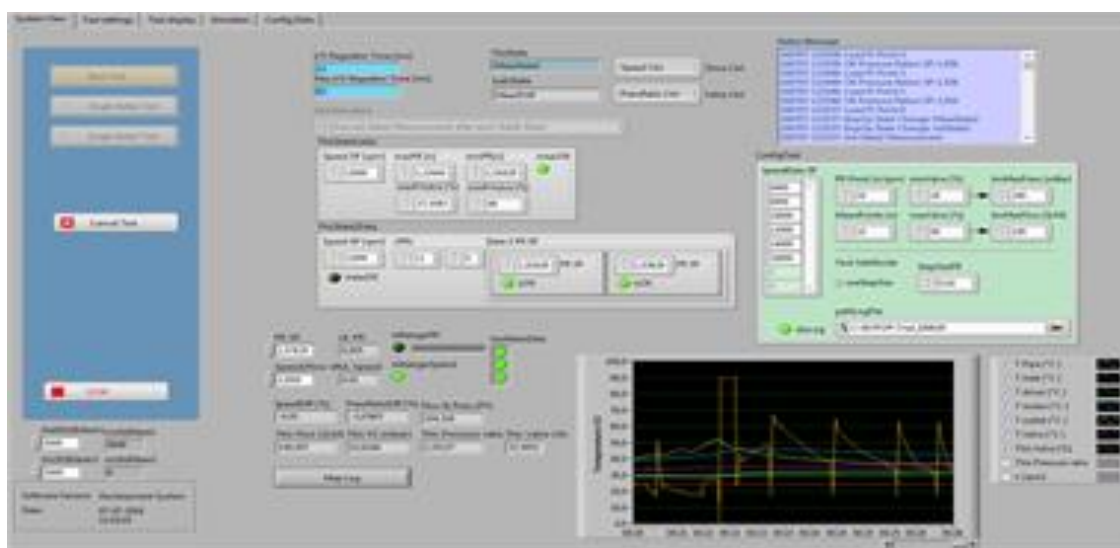
The built-in function "Contour" was used for the generation of either ISO efficiency or ISO power curves, since it can plot a variable z as a function of two independent variables x and y . The functions arrange and Gridfit are used for the two different codes, since they have different methods of converting the vectors into the matrices requested by Contour.

In addition, new functions were developed to validate the mapping work and calculate the efficiency uncertainty, such as the uncertainty calculation tool, the validation tool and the efficiency graph tool.

The above-mentioned functions were applied to three different test set-ups.

1. Fixed speed and pressure ratio: The test consisted on obtaining different measuring points by setting the motor speed and the pressure ratio. The speed was varied from 6000 to 14000 rpm with steps of 2000 rpm, while the pressure ratio was varied from 1 to 1.25 with steps of 0.2;
2. Fixed speed and mass flow: The test consisted on obtaining different measuring points by setting the motor speed and the mass flow. The same speed step size, initial and final value than in Test 1 were used. The mass flow was varied from 0.5 to 4 g/s with steps of 0.25 g/s;
3. Fixed mass flow and pressure ratio: The test consisted on obtaining different measuring points by setting the mass flow and the pressure ratio. The pressure ratio was varied from 1 to 1.25 with steps of 0.05, while the mass flow was varied from 0.5 to 4 g/s with steps of 0.5.

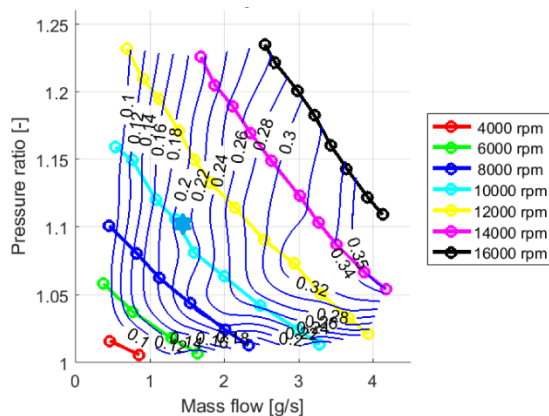
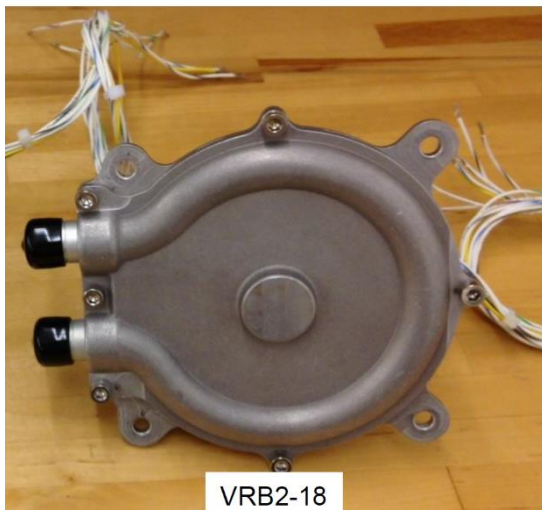
The results from the plotting of the functions to the three test set-ups indicate that the test bench is able to automatically obtain the data required to generate a map, with suggestions for improvement: The valve, the mass flow meter and the pressure transmitter should be replaced with other models, as to improve the performance and measurement capabilities. There should still be kept into consideration that an increase in the measurement devices range usually implies a decrease on their resolution, which can lead to an increase in the measurements uncertainty. The measurements variance obtained in Lab-View (type A evaluation) should be observed to determine the impact of increasing the measuring range in the uncertainty. Screenshot of the GUI graphic user interface:



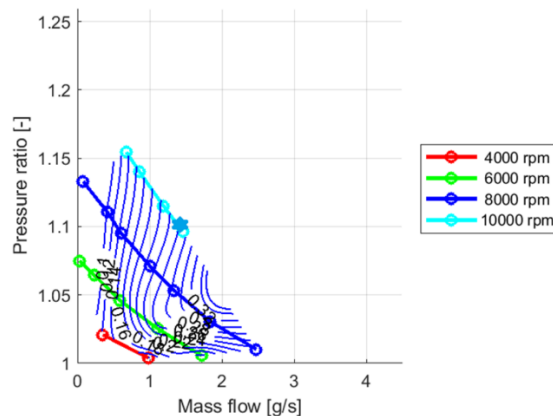
Different versions of the Vairex VRB-2 centrifugal cathode blower were tested in order to display their performance under various conditions. Five samples have been tested on the automated test stand under various setups such as blocking the leakage to ambient through the motor casing which is suspected to lower performance and cause premature failure of the ball bearing positioned at the pump head. Previous study shows that Version 4 referred to as V4 has been an increased by passage from pump head to motor casing which supposedly eases the air passage through the ball bearing. This has shown some critical performance losses when applied to our fuel cell system not being able to run system at full performance. A second version of V4 was returned to Vairex under suspicion of a rubbing impeller. V4 was re-machined by Vairex Corporation. The newly designed EUDP

V3 was received and included in the testing. The performance variations between two versions of the Vairex VRB-2 centrifugal cathode blower and the EUDP V3 version. Different motor types are used and the blowers were tested on the automated test stand:

- EUDP V3 series – serial number #1 referred to as "EUDP V3" - uses the originally supplied Moog brushless motor (Graph X).
- EUDP V3 series with a Maxon motor, referred to as "Maxon".



EUDP V3 series with Maxon motor: Efficiency curves – with Gridfit
 The Maxon blower has an efficiency of approx. 26% at the same measured point.



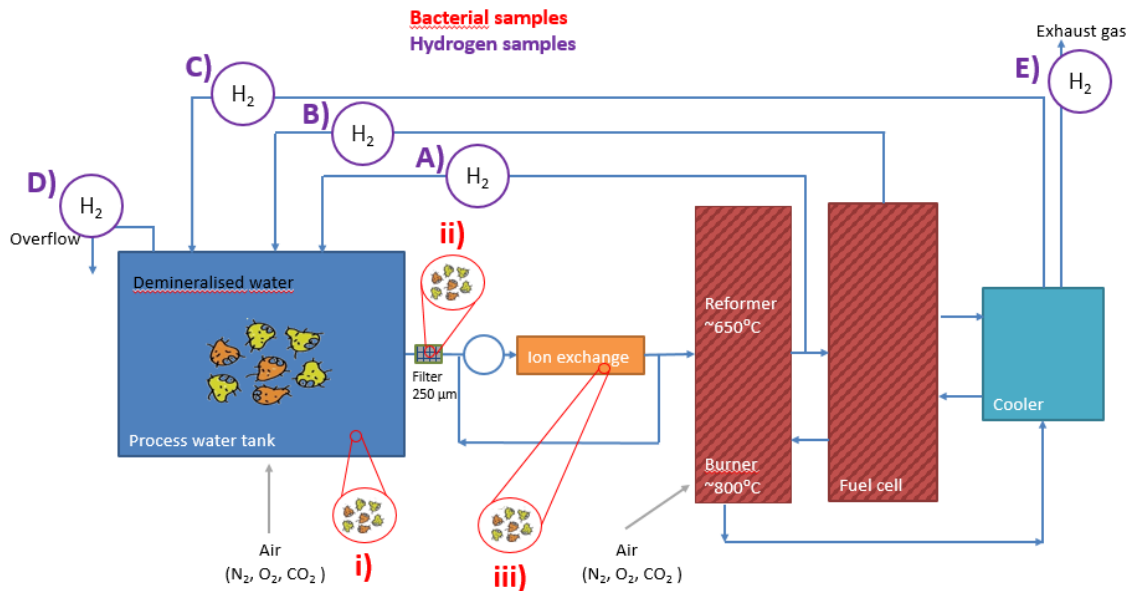
EUDP V3 #1: Efficiency curves – with Gridfit
 At the highest measured point the EUDP V3 blower has an efficiency of approx. 21%.

Conclusion

The developed blower offers a net gain efficiency of 2% under EOL condition (33.5% to 35.5%). A modified version of the new blower was equipped with a Maxon electrical motors and driver. An additional 4-5% of efficiency was achieved but we were not able to fully benchmark the second iteration due to speed limitations of the hardware (11.000 RPM instead of 16 000 RPM). The increased in adiabatic efficiency reduced the amount of parasitic power, therefore the amount of rejected heat which could lead to further system simplification.

1.5.5 WP4 Cost reduction and optimisation of the water treatment module

Biofilm is produced in the process water of the system. The schematics of the process water circuitry represented below shows the possible sources of nutrition for bio-growth support.



The hypothesis built on basis of the diagram relies on an abundance of hydrogen as a source for energy for the bacterial growth. On basis of the P-diagram, an abundance of samples was taken for DNA sequencing. The found bacteria species confirm the Hydrogen as energy hypothesis. The tables below present the percentage distribution of bacteria species in sampling spots. It reveals a low-complexity composition, with a few species dominating.

f_Bradyrhizobiaceae_OTU_39	11.8	31.8	70.6	35.2	3.7
Ralstonia	17.6	42.6	4	1.9	71.1
Hydrothalea	11.8	6.2	0	0	9.7
Acidovorax	23.5	0	0	0	0
Sphingobium	0	1.6	6	9.3	0.3
c_Gammaproteobacteria_OTU_620	0	0.8	4.8	7.4	0
Chitinophaga	5.9	1.6	0.2	1.9	3.4
Paucibacter	11.8	0	0	0	0
Pelomonas	0	0	5.1	3.7	1.4
f_Phyllobacteriaceae	5.9	0	0	0	3.9
Alicyclobacillus	0	0	1.9	7.4	0.1
Sediminibacterium	0	1.6	3.6	3.7	0
f_Comamonadaceae_OTU_837	0	3.9	0	0	4.1
Rhodococcus	5.9	0	0	0	0
f_Comamonadaceae_OTU_2601	5.9	0	0	0	0
	Tube outer side	Filter outer side	Tube sonicated	Filter sonicated	Water from ion exchanger

Alicyclobacillus	2.7	0.3	84	96.3	1.1	2.6
Bradyrhizobium	24.7	12.7	2.5	0	24.4	29.4
f__Obscuribacteraceae_OTU_8	18.3	0.3	3.1	0.1	21.1	14.8
Ralstonia	9.9	2.3	1.2	0.3	10.7	13.3
Aquabacterium	8.8	0.5	1.2	0	10.4	10
c__TM6_OTU_6	0.1	31.3	0	0	0.1	0.4
Legionella	10.1	0	0.5	0	4.1	2.6
Acidibacter	0.4	25.1	0	0	0.1	0.7
Pelomonas	0.7	19.4	0.3	0.1	2.1	1.2
Candidatus Obscuribacter	1.8	0.1	0.3	0	5.9	3.8
	Biofilm - Process tank	Biofilm - Front side of filter in loop	Water- Cathode	Water- Fuel cell	Biofilm - First pre-filter	Biofilm - Second pre-filter

The analysis also showed that the biofilm from the water tank was the cause of the biofilm problem in the ion exchanger, because many of the bacteria in the water tank are similar to the bacteria in the water/biofilm at different locations in the loop and the ion exchanger. Most likely, some bacteria released from the biofilm in the water tank is caught in the filter and either growing here or degraded and thus providing substrate to other bacteria. When the filters grow full of biofilm, the biofilm is dragged through the loop and then to the ion exchanger with performance decrease to follow. Furthermore, bacteria of types that can survive at high temperatures was found in the return cooling water from anode, cathode and reformer. Therefore, it was decided to limit the growth in the water tank by cleaning it in 3% hydrogen peroxide and remove the pre-filter acting as a hatching ground for bio growth.

CONCLUSIONS AND RECOMMENDATIONS

After analysing the systems, it can be concluded that biofilm is only a problem in the 1 kW system. Therefore, testing of the optimization methods was only conducted here. The testing was performed on a 1 kW test system in field trial. It was concluded after the first extensive analysis including microscopy, gas chromatography, and DNA-analysis that the biofilm was caused by bacteria utilizing leftover hydrogen, produced by the system, as a substrate for growth. It was not feasible to limit these nutrients:

- H₂, CO, CO₂ found in return water.
- Atmospheric air is pumped into process tank.

Biofilm was observed on many different components in the system, however the bacterial community had a low complexity so only a few very specialized species might be able grow there. Some of the observed bacteria belong to genera that are known to use hydrogen as a substrate for growth. In general, it was the same few bacterial genera that were found on all the components. The DNA-analysis also showed that recirculated bacteria from the process tank might be the source of growth of bacteria on downstream filters. Bacteria then survive in the system by consuming recirculated nutrients and bacterial compounds.

To reduce the amount of biofilm and thereby enhance the durability of the different components in the water cleaning system, it was decided to implement a pre-filtration setup. Thereby, change the setup in the water treatment loop as bacterial compounds are recirculated here. The system was analysed 4 times over a year and after each sampling, it was seen that less biofilm was formed on the different components. It seems to improve the system performance to insert filters and clean the process (water) tank. Therefore, the recommendations are to keep these changes in the system and loop setup and continue to clean the water tank and treat with 3% hydrogen peroxide at service. With a clean water tank, it is possible to minimize and hold back the bacteria in the prefiltration setup.

Recommendations:

- Reduce the amount of biofilm circulated in system;
- Keep the process water tank clean;
- Loop optimization – Keep new loop setup;
- Flush hoses with 3% hydrogen peroxide.
- Continue to limit the amount of biofilm in process tank:
 - Active: Treating process tank at service with 3% hydrogen peroxide;
 - Passive: Future reduction of growth by UV-light treatment if needed.

1.5.6 WP5 Aluminium heat exchanger

Reformate Cooler HEX:

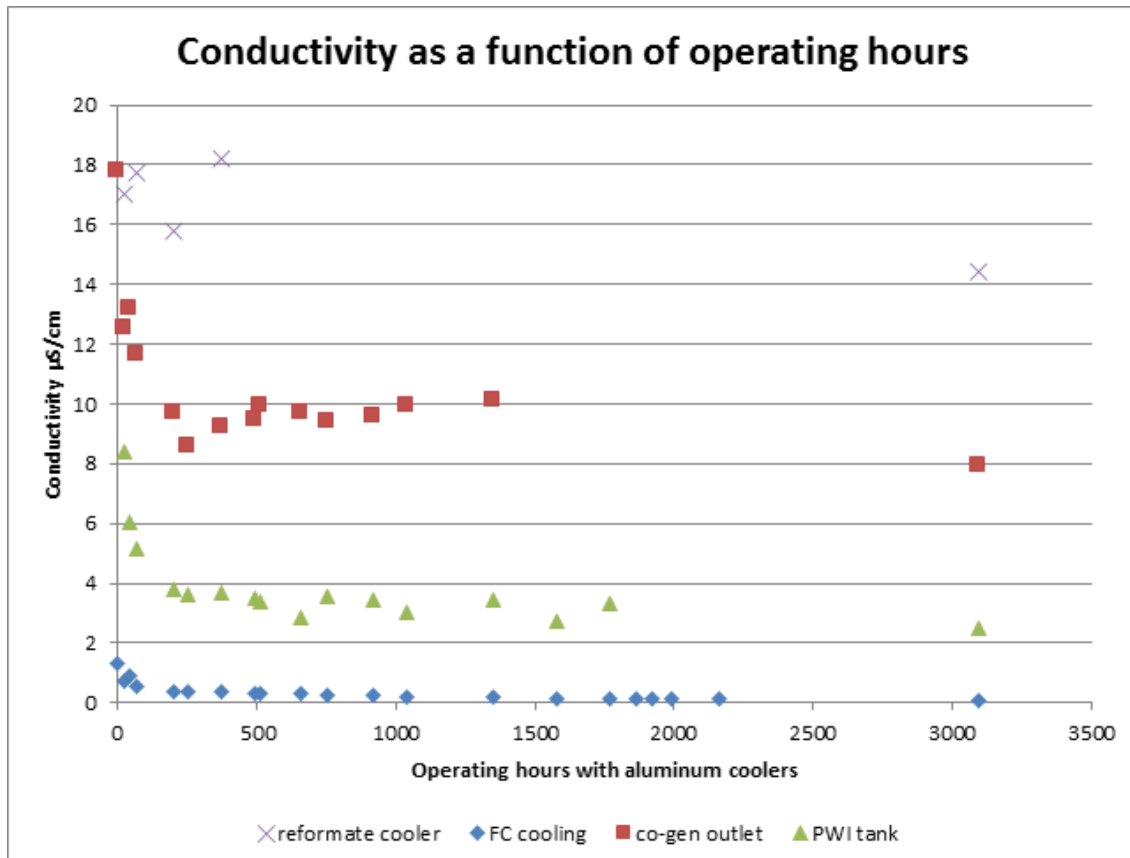
During the project start up aluminium cooler components were tested in a 1 kW set up, over a duration of 3000 operating hours, and compared to the experience gained during operation with conventional stainless-steel heat exchangers.

	pH
pH cogen condensate	5,3
FC cooling	6,81
Reformate condensate	5,16

Ph measurement of the FC system relate condensate streams. All measurements are with safe operating values for an aluminium solution.

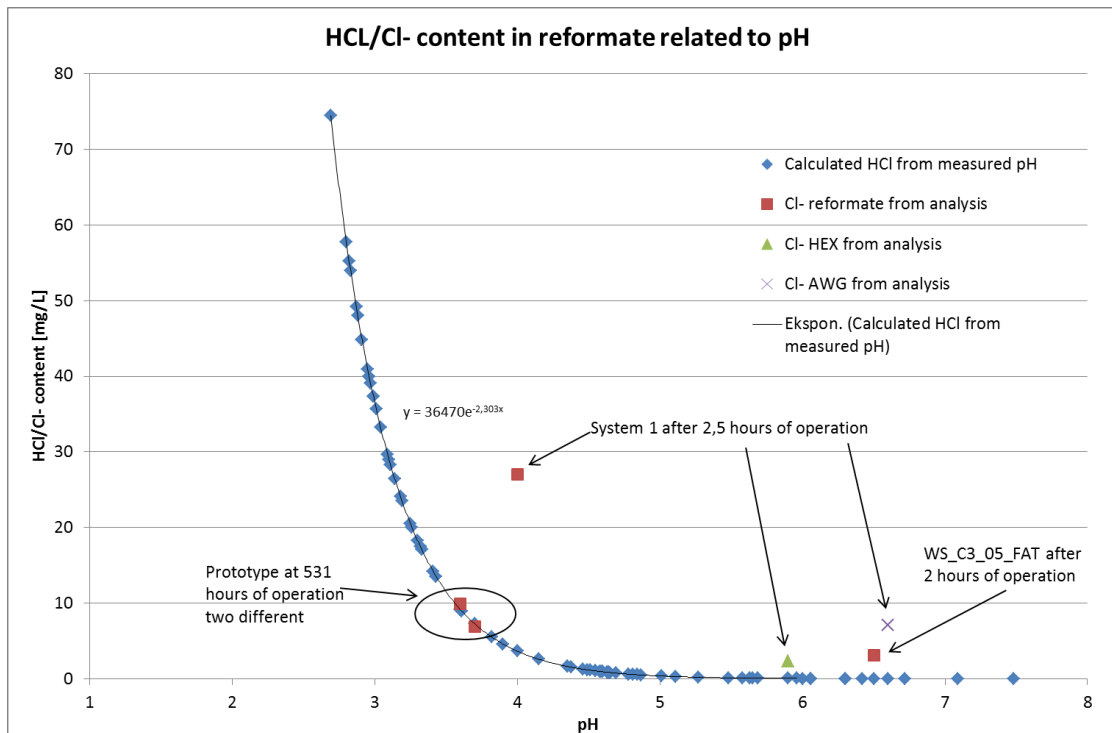
µS/cm	PWI tank	co-gen outlet	reformate cooler	FC cooling
Condensate conductivity	2,76	10,0	15,7	0,07

Average conductivity measurements of condensate lines with stainless steel heat exchangers in 1 kW system.



Conductivity measurements in the 1 kW test system, indicating satisfactory performance of the aluminium coolers with regards to ion leaching and stream contamination. The measurements are equal or lower than the corresponding measurements in the stainless system. The initial higher values were traced to the brazing flux, and an important learning is to specify a through flux wash out from the manufacturer, to ensure trouble free system commissioning.

As the test environment evolved into the next generation 2,5-kW platform, it very quickly became evident that the test conditions were different, and especially the conditions for the reformate cooler did not sustain continued operation with the aluminium solution. A post mortem analysis of the reformate cooler revealed heavy corrosion. Out 6 measurements of the reformate condensates, the HCL concentration correlates very well with PH /HCl curve.



The picture shows the corroded fins of the novel type fin-core of the reformate cooler. The reason for the severe corrosion was traced to hydrochloric acid from the reforming process.



It is obvious that continued operation with chloride acid containing reformate prevents the use of aluminium in the reformate stream. If the chloride diffuses to other streams, the use of aluminium could potentially jeopardise the integrity of adjacent streams. With a reformate condensate PH comprised between 2.5 and 4, we are in the region where aluminium material corrodes. The Pourbaix diagram indicates high corrosion for fluid with PH comprised between 5 and 8.5. While the reduction of chloride is the long term solution, some attempt were made to passivate the Aluminum heat exchanger.

The aluminium cooler had to be abandoned in the reformat cooling circuit, and a SS316L fusion welded, micro channel heat exchanger was used instead. This secured the continuation of the project, and a successful field trial. Picture of the replacement stainless steel cooler for the reformat conditioning.



A parallel path was investigating regarding some passivation method of aluminium HEX: The literature search by AAU inspired to verify the effect of passivation by ChromitAL treatment, to increase corrosion resistance. The work resulted in the report "ChromitAL TCP treatment of Nissens brazed Heat Exchangers".

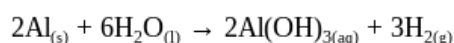
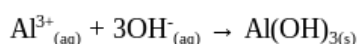
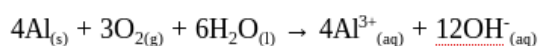
The turbulator plate (AMP 03932) acts as a sacrificial anode with respect to the other aluminium types used in the heat exchanger. The ChromitAL TCP treatment causes slower corrosion and does not change the sacrificial behaviour of the turbulator plate.

The 5% oxalic acid cleansing does not remove all the flux from AA300# and AMP 0336, but it seems it has been removed completely from the AMP 0393. The flux is considered to be insoluble in water and it is thus reasonable that it is not completely removed. The flux seems to hinder the ChromitAL TCP treatment; on the other hand the flux is also considered to form some protection against corrosion as it is insoluble in water. However, SurTec, who is the producer of ChromitAL TCP treatment solution, recommends alkaline degreaser followed with oxide removal in SurTec 495 L, which contains sulfuric acid, fluorides and nitrates.

This task was modified to concentrate on the suitability of the CAB brazed heat exchangers and the alloys used in their fabrication. The conclusion is that the Long-Life alloys do live up to their name, and have a good corrosion resistance, as long as the operation conditions stay within the conditions described above. On top of that the advanced cladding material, and turbulator incorporated within the heat exchangers act as sacrificial anodes, in case of undesired operating conditions, and protecting the integrity of the water fluid carrying circuitry. This means that the heat exchangers will maintain integrity

Reformat Cooler HEX:

We have observed some additional challenges related to the stack cooler and combined exhaust cooler. Some scaling was produced and almost closing some of the external circuitry. It appears that PH of external cooling circuit was around 9 which outside the corrosion boundary of aluminium. This leads to the production of Aluminum hydroxide.



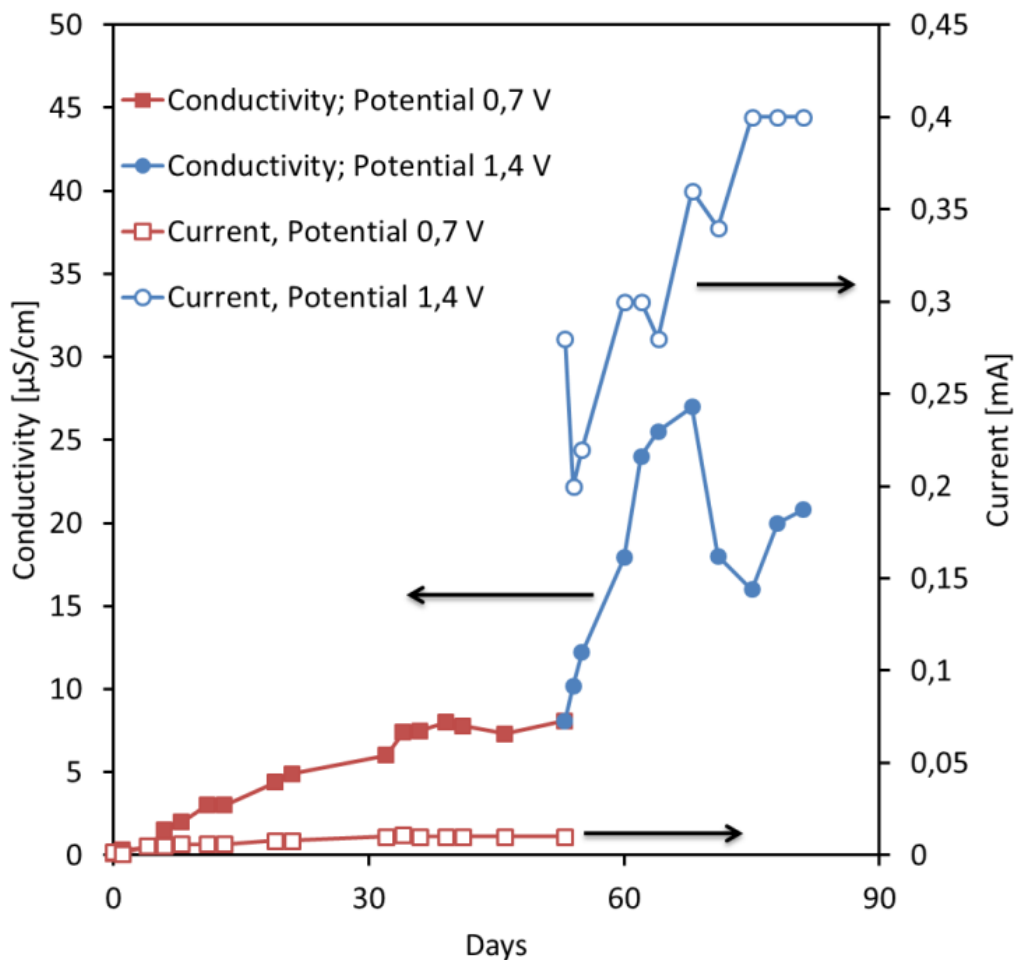
The main reason of the increase in alkalinity and pH of tap water is the presence of carbonates and bicarbonates. The accelerated corrosion of the Al heat exchanger in the domestic water heating system is also due to the combined effect of temperature, dissolved oxygen concentration, concentration of chloride, and sulphate ions etc. Therefore, it is strongly recommended that Al heat exchanger should not be used with untreated water as coolant. It is also highly recommended that in the current scenario inhibitors must be used as coolant in the external closed loop connected to domestic heating system. An appropriate inhibitor was found in the Long-Life inhibitor XLI, from L.C. Glad. With a usage dilution to 7,5 % it is a non-toxic organic based inhibitor. During the 1-year field trial there were no sign of corrosion or precipitation, in the closed system of the co-generation cooling loop.

FC cooling loop HEX:

During the project period, a situation of premature exhaustion of the Ion-exchange filter in the fuel cell cooling loop sparked an in-depth investigation on the cooling loop of the fuel cell, and the possible reactions in the graphite compounds within the fuel cell cooling media. The work highlights the essential need to control and maintain the proper cooling media conditions during operation. To examine the possibility of the effects discussed above, a test setup was established. An interesting result was the possibility that the release of graphite components, from the cooling water channels could lead to corrosion issues and ions exchange resin exhaustions.

A test stand for measuring the material characteristics in a saturated calomel electrode reference electrode bath using a Gamry 600 potentiostat. During the first 53 days a potential of 0.7 V was maintained between the bipolar plates. After 53 days the potential was raised from 0.7V to 1.4 V. The 0.7 V was chosen to duplicate the voltage between two adjacent bipolar plates. The temperature was kept constant at 60°C. The amount of water was 200 ml. The dimensions of bipolar plates were 10 x 40 mm and the distance between them were approximately 1 mm.





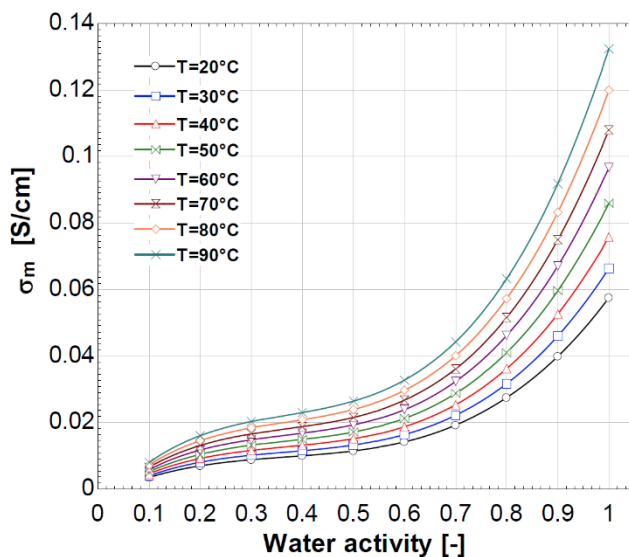
As can be seen the conductivity increased. In the same period the pH decreased from 5.9 to 4.5. The pH measurement (not shown on the graph) contains some uncertainty due to the difficulties of measuring the pH of low-conductivity water. The water was analysed by UV-Vis spectroscopy and GC-MS after up-concentrating using a vacuum-evaporator. The UV-Vis revealed that there were aromatic compounds present in the water. The GC-MS showed a lot of high molecular compounds, however it was impossible to detect exactly which compounds. A theoretical analysis showed that it is possible to oxidise graphite to CO₂ at the anode and reduce graphite to CH₄ at the cathode. See appendix C for details. If it is possible to oxidise graphite to CO₂, then thermodynamically it is also possible to oxidise graphite to various oxygen (+ hydrogen) containing organic compound, which includes acids. This has been confirmed by other research studies. The low degree of oxidation and low number of compounds in this experiment can be explained by the use of a low potential. Carbon dioxide alone dissolved in water also affects the pH of water as it dissociates. This correlates well with the PH measurement observations.

CONCLUSIONS AND RECOMMENDATIONS

Three failure modes have been identified which jeopardized the usage of Alumimun heat exchanger. The reformate cooler issue should be solved by changing the composition of the catalyst bed responsible for the generation of HCL (USDAN). The two others are inherent to the technology and extra attention should be paid to the bipolar plate compounds. Adding additive in the external cooling should solve issue with aluminum carbonate corrosion. Regardless the stream the PH of the conveyed fluid should be kept between 5 and 9 to limit corrosion process. Operation outside this boundary might possible with coating of the HEX in principle. Attempt performed on HEX has shown mitigated result and further work will be required to identify the correct post manufacturing treatment process.

1.5.7 WP6 Humidification

Humidifiers for PEM fuel cell stacks are essential components to reach acceptable performance and operational life. PEM fuel cells utilize Nafion membranes or polymers with similar properties. Nafion is a material which contains perfluorosulfonic acid and PTFE (Poly-Tetra-Fluoro- Ethylene) copolymer. This PTFE, also known commercially as Teflon, is highly resistant to chemical reactions, due to the presence of strong carbon fluorine bonds. Thus, rugged polymer membranes can be manufactured thinner than 50 μm . Hydrophilic sulfonic acid groups and their volume expanding nature absorbing water provides Nafion with the proton exchange properties. However, the Nafion electrolyte membranes in PEM fuel cells must be fully hydrated with water in order to act as an efficient proton conductor. The specific proton conductivity in S /cm as function of water activity fuel cell membrane is shown in the figure below:



Through the electrochemical conversion in a fuel cell, the reactants (hydrogen and oxygen) are converted to water. Membrane humidifiers offer the advantage of utilizing the product water in the depleted cathode exhaust air to humidify the dry inlet streams, simultaneously preheating the gasses to the operational temperature of the fuel cell stack. Typically, the outlet air from the cathode is saturated with water at the operational temperature of the fuel cell stack (typically $\sim 60\text{--}70^\circ\text{C}$). Either an air or a water cooling system makes sure that the stack temperature is maintained within a certain margin. The humidification is thus a balance of ensuring sufficient water to hydrate the electrolyte membrane, while simultaneously avoiding flooding of liquid water in the various parts of the fuel cell MEA.

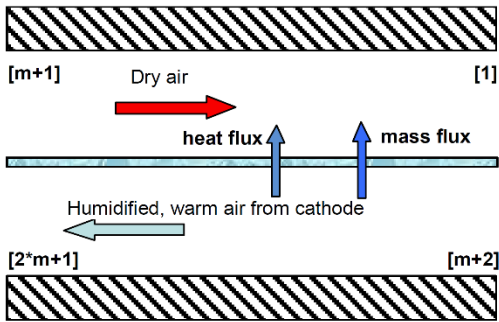
An air compressor supplies the air to the fuel cell stack cathode-side. Through the compression process, the temperature increases and thus the relative humidity and thus the water activity of the humid ambient air decrease significantly. At EOL-conditions (normally after 10-20,000 hours of operation, depending on the application), the compressor efficiency has typically decreased meaning that the incoming air is further heated. Simultaneously, the fuel cell stack has also degraded affecting the operational conditions of the humidifier. An increased flow of both reactant gasses (air & H₂) to the fuel cell stack is necessary to maintain the required stack power output. At very dry ambient conditions, the temperature of the dry air inlet to the humidifier can be as high as 80°C. A work-around to resolve this is to add an air-cooler after the air compression to cope with these EOL-extreme-conditions but this component adds to system cost and complexity.

This WP shows the behaviour of the humidifier at nominal BOL-case and EOL-case. A shell and tube membrane humidifier with Nafion tubes was used to present a 1D distributed parameter steady-state model. The water transport in Nafion has been extensively researched along the years, in which the water diffusion coefficients were determined by measuring the diffusion coefficient at very different conditions with varying methods. Several commercial Nafion-based membrane humidifiers were tested in fuel cell systems subject to real-life conditions by the Danish fuel cell system manufacturer BPSE (previously Dantherm Power A/S). Tests were conducted at different conditions on a commercial 3kW Ballard® PEM fuel cell stack system reflecting expected EOL stack conditions and extreme ambient conditions. The tests showed that the humidifiers would work at nominal conditions at BOL but would fail at high ambient temperatures at EOL due to limited water transport.

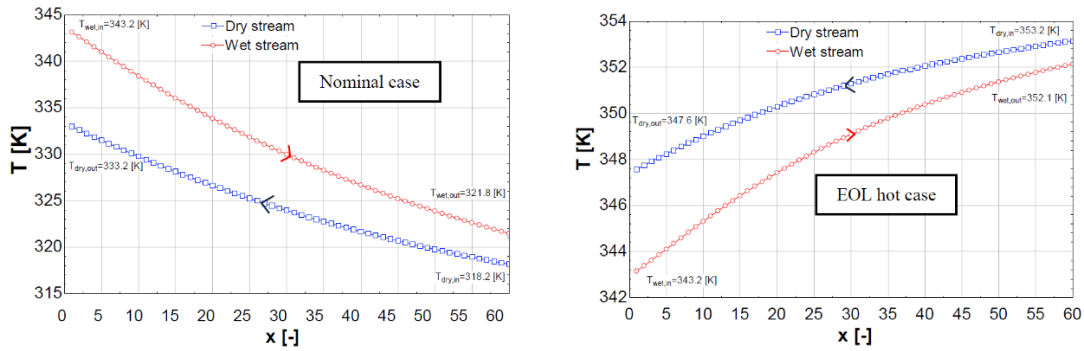
A numerical model was developed to understand this phenomenon and to investigate how to optimize the system to be able to handle these extreme conditions at the lowest possible cost. The model was based on the same conditions as used in the abovementioned tests. The following inlet and outlet conditions were studied for the 2 cases:

Nominal BOL Case:	Extreme EOL Case:
<ul style="list-style-type: none"> Humidifier Nafion tube total surface area: 0.5 m² Humidifier (dry side) inlet temperature: 45°C Humidifier (dry side) inlet pressure: 1.145 bar Humidifier (wet side) inlet temperature: 70°C Humidifier (wet side) inlet pressure: 1.1 bar Relative humidity at humidifier dry inlet: 14% Relative humidity at humidifier wet inlet: 100% Flow (on either side of humidifier) ~ 170 NLPM 	<ul style="list-style-type: none"> Humidifier Nafion tube total surface area: 0.5 m² Humidifier (dry side) inlet temperature: 80°C Humidifier (dry side) inlet pressure: 1.145 bar Humidifier (wet side) inlet temperature: 70°C Humidifier (wet side) inlet pressure: 1.1 bar Relative humidity at humidifier dry inlet: 0% Relative humidity at humidifier wet inlet: 100% Flow (on either side of humidifier) ~ 180 NLPM

The modelling was performed in the tool Engineering Equation Solver (EES). In the modelling, it is assumed that the humid air will properly reflect the actual conditions with oxygen-depleted air due to the similarities of oxygen and nitrogen.



Modeling results for the humidifier temperatures in counter-current mode are illustrated in the figures below.

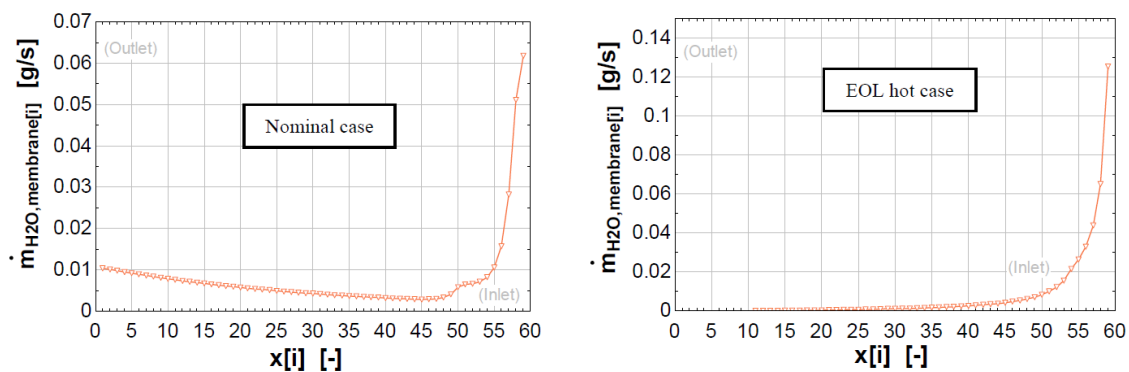


From the calculations made, it resulted that the membrane humidifier works properly at the nominal BOL-case where it saturates the cathode air with water ideally at a temperature close to the desired inlet temperature. At the extreme EOL conditions, the humidifier fails to reach the desired water transfer. This contradicts theoretical studies with other Dw-relations which indicate that the humidifier should work properly under such conditions. The present model agrees with the experiences from field tests.

In extreme EOL cases, where the operation takes place with worn system components and extremely dry and warm conditions, no equilibrium is reached, but the absolute humidity keeps increasing slightly, while the temperature decreases. A certain degree of cooling will be required. In this case, the critical issue is not the dry ambient air but rather the high temperature resulting in a very low water activity at the dry air inlet to the humidifier limiting the mass transfer of water.

The membrane water transport from the wet to the dry side of the humidifier shows that the area of the membrane in many cases is less important in terms of water transfer as the majority of the mass transport will take place over a very limited area of the Nafion-membrane-tubes in the humidifier. This leaves a potential for constructing part of the tubes with a cheaper material having acceptable heat transfer properties. Nafion is a quite expensive material, so this is a quite relevant issue.

The streams must also be heated to the stack temperature, so the heat transfer area is required. In some cases, when operating the system at warm EOL conditions, it might be beneficial to bypass part of the insulated membrane humidifier area, since this leads to a better water transfer in this particular case if the humid air could be cooled in an intelligent way not requiring additional components.

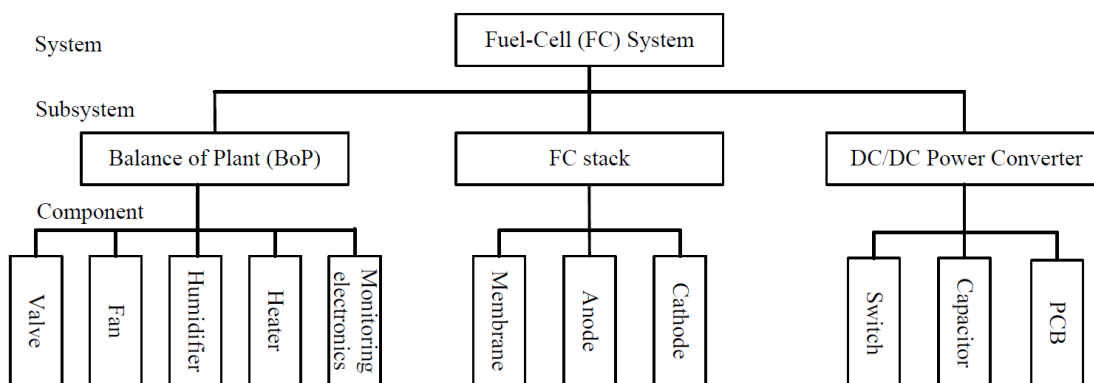


Conclusion

A steady-state distributed parameter model of a membrane humidifier has been developed. It has been found that the present simplified 1D modeling approach has been able to replicate the physical phenomena and trends occurring during real life conditions in membrane humidifiers quite well. It is believed that the model with further improvements and comparison with more detailed experiments can be a very useful tool when designing and optimizing membrane-based humidifiers for PEM fuel cell applications.

1.5.8 WP7 System reliability

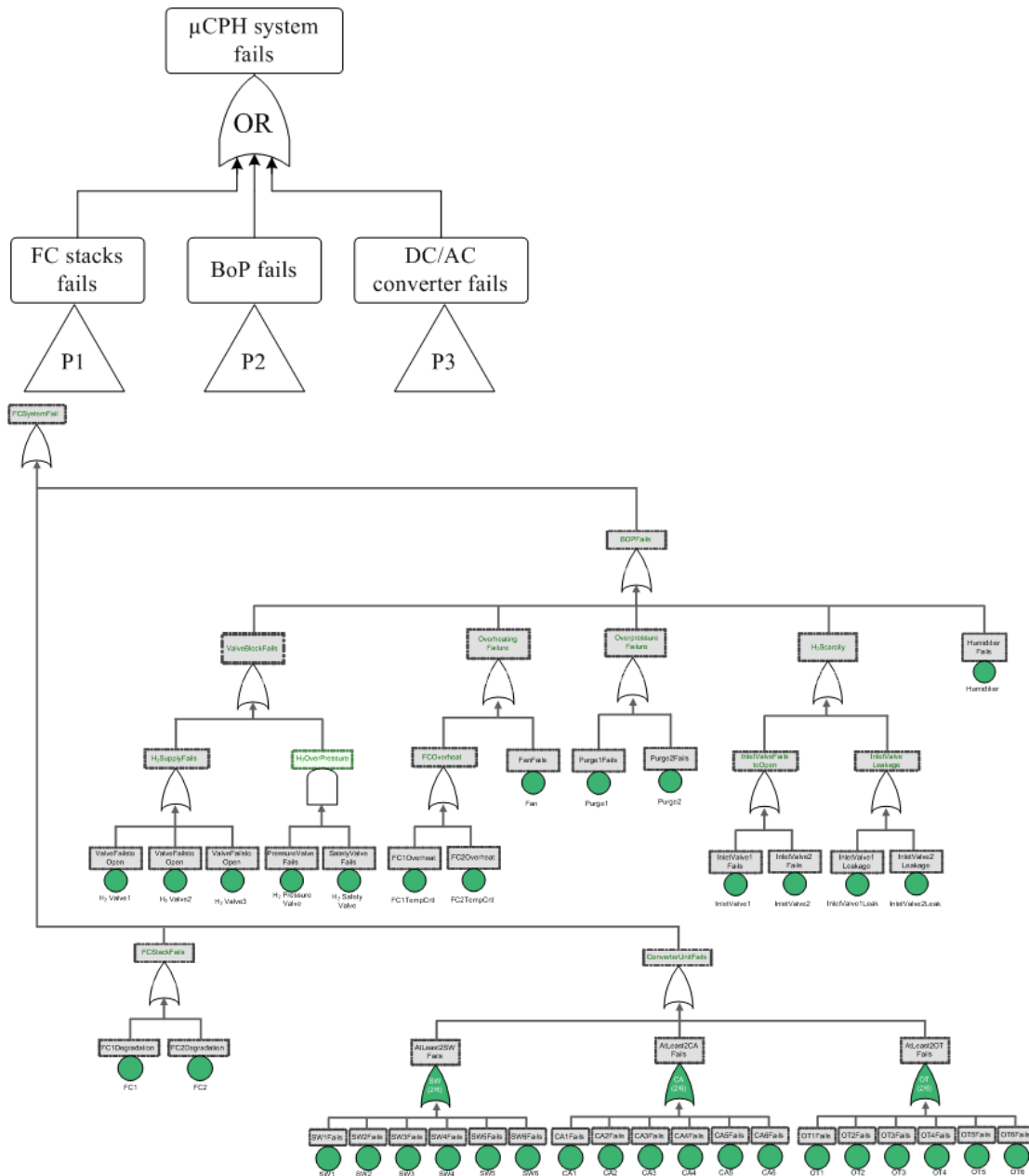
The system-level reliability of micro CHP system is started by defining the critical components required to perform a Failure Mode and Effect Analysis (FMEA). The Failure Modes and Effects Analysis (FMEA) is a structured methodology for identifying potential modes with objectives of the potential hazards identification, and remedial proposals [1]. The failure mode is a manner or mechanism, where the component fails to meet or deliver the intended function. The effect of the failure mode is determined by the system's response to the equipment failure. The FMEA is performed at the component level, where the likelihood of potential failure occurrence and potential severity of the impact are also concerned.



[1] US Department of Transportation Report, "Failure modes and effects analysis for hydrogen fuel cell vehicles – subtask 1", Feb. 2009

The FMEA shows that in the sub-system of the BoP, the purge valve, pressure sensor, humidifier and fan have the most frequent failure occurrence, and all of them have the severest failure consequence. For the fuel cell stack, it is evident that the membrane is the most fragile part due to its mechanical degradation, thermal degradation and chemical degradation. Meanwhile, the semiconductor, capacitor and PCB are the critical parts in the sub-system of dc/dc power converter.

A Fault Tree Analysis (FTA), created with the software ReliaSoft BlockSim[®] highlights the system reliability of the micro CHP. The top event of the fault tree is fuel cell system failure. According to the FMEA, selective accident scenarios of which the outcome is the top event were included in the Fault tree. The fuel cell system is assumed to be failed in case of the failure of its three sub-modules: Balance Of Plant, FC stack and Converter Unit.



The BOP is assumed to fail in case of failure of the Valve Block, if Overheating or Overpressure occurs, if there is H₂ shortage or if the Humidifier fails. The cases when the Valve Block can fail are when the H₂ supply fails, therefore if one of the three valves fail to open, or if there is over pressure of the H₂, which takes place when pressure valve or the safety valve fail. Overheating failure occurs when one of the two FC overheat, or when the Fan fails. Overpressure failure is the result of the failure of either of the two Purges. Scarcity of H₂ takes place when either of the two Inlet Valves are not opening, or when either of the two Inlet Valves are leaking.

The Converter Unit fails in cases when at least two switches (SW) fail, or at least two capacitors (CA), or at least two over temperatures (OT).

For determining the Reliability Function of the Fuel Cell system, the Weibull distribution was applied. A distribution is mathematically defined by its pdf equation, where the Weibull distribution is described by a three-parameter expression:

$$f(T) = \frac{\beta}{\eta} \left(\frac{T - \gamma}{\eta} \right)^{\beta - 1} e^{-\left(\frac{T - \gamma}{\eta} \right)^\beta}$$

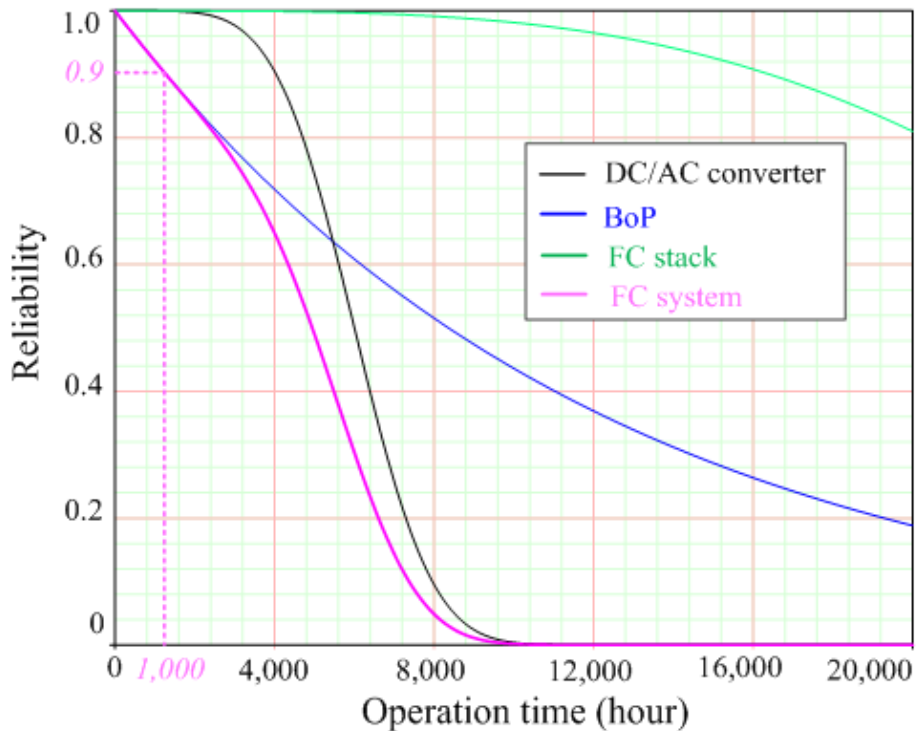
Where:

- β is the shape parameter, also known as the Weibull slope;
- η is the scale parameter;
- γ is the location parameter - it is not used; therefore, it is set to 0;
- T is time.

The specifications of the subsystem (Table X) were taken from the "OREDA - Offshore Reliability Data Handbook," Trondheim, Norway, 2002.

Subsystem	Critical component	Shape parameter β	Scaling parameter η
FC stack	Fuel cell stack	3.5	3.8E4
BoP	Humidifier	1.0	4.65E5
	Purge	1.0	1.40E5
	Fan	1.0	1.29E5
	Hydrogen inlet valve	1.0	1.37E5
	Hydrogen safety valve	1.0	1.27E5
	Hydrogen pressure valve	1.0	6.87E4
DC/AC converter	Power switch	2.5	1.20E5
	Capacitor	3.0	1.00E5

The reliability graph/pdf shows the evolution of the reliability at a component-level according to the operation time. It is understood that the FC stack is the most reliable, with a small decrease after 8.000 hours of operating time. BoP shows a more significant but steady decrease from the beginning of the system's performance. The DC/AC converter performs at full reliability until reaching approximately 2500 hours operating time, after which a drastic decrease follows. Overall, the FC system reaches quite fast from 100% reliability at starting point to 90% reliability at 1000 hours operating time, after which a more dramatic decrease of the reliability takes place, until it reaches zero reliability at approx. 9000 hours operating time.



Conclusion

The system reliability structure of the micro CHP was performed, from component-level, subsystem-level to system-level. An FMEA evaluation of the micro CHP system together with its fault tree analysis was conducted. Based on the Handbook of Reliability Data, an assessment of the components' reliability along the amount of 20000 hours operating time was illustrated.

1.6 Utilization of project results

1.6.1.1 WP 1.1 Fuel treatment – Sulphur and Analytical tools

1.6.1.2 WP 1.2 Hydrodesulphurisation

With the initial proof of concept achieved, a baseline has been made for further testing. Further testing is needed to document if the μ HDS method can be used in a μ CHP system. Further testing should document COS content when CO_2 being introduced in the reformat. Furthermore, accelerated capacity tests should be performed to establish lifetime of the catalyst and adsorbent material. Sulphur free tolerant Steam reforming catalyst might drastically change the reformer but it will imply to use a sacrificial Zinc oxide adsorbent bed.

1.6.2 Polymeric tubing

The European Committee for Standardization (CEN) should start to develop standards and test standards that would render the use of alternative cheaper material. The standards should ensure the safety aspects, while being easy to comply with and facilitating the development of more cost-effective BoP systems, which would also lead to cheaper fuel cell systems.

1.6.3 WP 3 Air supply

A future step could be to have Vairex constructing a blower with a 24V Maxon motor, solve the speed monitoring issue on test bench and test it at full performance range.

1.6.4 WP4 Water treatment

The results from the thorough analysis and the related field tests have resulted in new realisations and strengthened the knowledge base of the university. The recommendations are integrated in the revised service bulletins for the μ CHP systems, and will be utilized in future water management systems

1.6.5 WP5 Aluminium heat exchanger:

All identified failure mode and failure mode mitigation approach will be applied on all future design regardless of the final application.

1.6.6 Humidification

Future work will include the investigation of the influence of dynamic phenomena in the water transport process and a further study of the two-phase effects in membrane humidifiers.

1.6.7 WP7 Reliability

As a further step of the WP, an updated failure data by using the field experience instead of the Handbook is recommended.

1.7 Project conclusion and perspective

The future development is influenced by the project results on many aspects, with:

- Possibility to simplify reformer by adding Zinc Oxide absorbent into the reformer. The usage of Sulphur tolerant reforming catalyst is also considered;
- Further evaluation of passivation Heat Exchanger and application on the finding on all new fuel cell system design.
- Continuation of similar project but related to liquid cooled motive application;
- Utilization of testing tools (air compressor test bench), system simulations, components test data, data processing method for other markets such as back-up and automotive.
- Utilization of all learnings on BPSE's Back-up product platform;
- Integrate all acquired learning of liquid cooled stack into cross-over application such as automotive;