EUDP ⟲

Final report

1. Project details

Project title	Efficient Power2Gas combining SOEC and biomass gasification (EP2Gas)
File no.	64017-0011
Name of the funding scheme	EUDP
Project managing company / institution	Technical University of Denmark, Department of Energy Conversion and Storage (DTU Energy)
CVR number (central business register)	30060946
Project partners	Haldor Topsøe A/S (HTAS) Department of Chemical Engineering, DTU (DTU KT) Department of Mechanical Engineering, DTU (DTU MEK) Aalborg University (AAU)
Submission date	28 February 2022

2. Summary

English version:

The overall objective of this project was to develop a reliable, highly efficient, and cost effective Power2Gas (methane) solution based on an intimate integration of the SOEC, biomass gasification, and methanation technologies, and to further promote its commercialization by focusing two of the most critical issues, namely maturing the least developed of the technologies (the SOEC) with regard to life-time, scale and cost reduction and exploring synergies and technical challenges in integrating the three technologies. The five project partners (DTU Energy, HTAS, DTU KT, DTU MEK, AAU) have been working closely on solving these critical issues. By the end of the project, we have pushed stable operating point for SOEC cells from -1 to -1.25 A/cm^2 and have demonstrated years of stable electrolysis operation, showing a low degradation rate of 20 mV/kh at -1.25 A/cm^2. Via a 3000h stack test, we have proved that the SoA HTAS stacks (TSP-1) operate quite fine with no sweep gas to the oxygen electrode. This potentially opens the possibility for co-production of pure oxygen and could facilitate the integration of SOEC with the gasification system. We proved the reliability of the multi-stack SOEC-CORE via a >13000h test, demonstrating a degradation rate of only 0.5%/kh at the CORE level. We designed, built and extensively tested a new pyrolysis reactor for handling different biomass feedstocks. The brand new pyrolysis technology has awaken a significant commercial interest and is currently being up-scaled and commercialized. We further demonstrated integration of pyrolysis, SOEC and gas cleaning, ensuring high quality of syngas for further methane synthesis. All these results have contributed significantly to the commercialization of the Danish SOEC, gasification, and Power2X technologies and are in line with the Danish national strategies on Green Transition.

Danish version:

Det overordnede mål med dette projekt var at udvikle en pålidelig, højeffektiv og omkostningseffektiv Power2Gas (methan)-løsning baseret på en intim integration af SOEC, biomasseforgasnings- og metaneringsteknologier, og at fremme dens kommercialisering yderligere ved at fokusere to af de mest kritiske spørgsmål, nemlig modning af de mindst udviklede af teknologierne (SOEC) med hensyn til levetid, skala og omkostningsreduktion og udforskning af synergier og tekniske udfordringer ved at integrere de tre teknologier. De fem projektpartnere (DTU Energi, HTAS, DTU KT, DTU MEK, AAU) har arbejdet tæt sammen om at løse disse kritiske problemstillinger. Ved afslutningen af projektet har vi skubbet stabilt driftspunkt for SOEC-celler fra -1 til $-1,25$ A/cm^2 og har demonstreret mange års stabil elektrolysedrift, der viser en lav nedbrydningshastighed på 20 mV/kh ved $-1,25$ A/cm^2. Via en 3000 timers staktest har vi bevist, at SoA HTAS-stakkene (TSP-1) fungerer ganske fint uden sweep-gas til iltelektroden. Dette åbner potentielt for muligheden af co-produktion af ren oxygen og kan dermed bidrage til at lette integrationen af SOEC med forgasningssystemet. Vi beviste pålideligheden af multi-stack SOEC-CORE via en >13000h-test, hvilket viste en nedbrydningshastighed på kun 0,5%/kh på CORE-niveau. Vi har designet, bygget og i vid udstrækning testet en ny pyrolysereaktor til håndtering af forskellige biomasseråvarer. Den helt nye pyrolyseteknologi har vakt en betydelig kommerciel interesse og er i øjeblikket ved at blive skaleret op og kommercialiseret. Vi har yderligere demonstreret integration af pyrolyse, SOEC og gasrensning, hvilket sikrer høj kvalitet af syngas til videre metan syntese. Alle disse resultater har bidraget væsentligt til kommercialiseringen af de danske SOEC-, forgasnings- og Power2X-teknologier og er i tråd med de danske nationale strategier for grøn omstilling.

3. Project objectives

The overall objective of this project was to develop a reliable, highly efficient, and cost effective P2G (methane) solution based on an intimate integration of the SOEC, biomass gasification, and methanation technologies, and to further promote its commercialization by focusing two of the most critical issues, namely maturing the least developed of the technologies (the SOEC) with regard to life-time, scale and cost reduction and exploring synergies and technical challenges in integrating the three technologies. To facilitate monitoring progress to-wards the overall project targets, 16 milestones were formulated in the original project plan, specifying explicitly the project targets. A list of these milestones and their status at the completion of the project can be found in Section 5 of this report. At the end of this project, we have fulfilled or partially fulfilled all the 16 milestones. Overall we have achieved the project targets to a great extent.

Specifically, the project has accomplished the following technological or scientific achievements:

- By introducing electro-catalysts into the Ni/YSZ electrode, we have pushed stable operating point for SOEC cells from -1 to -1.25 A/cm^2 and have demonstrated years of stable electrolysis operation, showing a low degradation rate of 20 mV/kh at -1.25 A/cm^2.
- We have developed a phase field model, capable of modelling the 3D microstructure evolution of the Ni/YSZ electrode in a quantitative manner. This will serve as a good modelling tool for optimizing the Ni/YSZ electrode microstructure, in order to bring down the long-term degradation due to Ni coarsening and Ni migration.
- Via a 3000h stack test, we have proved that the SoA HTAS stacks (TSP-1) operate quite fine with no sweep gas to the oxygen electrode side. This reduces the safety hazard in SOEC systems due to production of pure oxygen and facilitate to a great extent the integration of SOEC with the gasification system.
- We proved the reliability of the multi-stack SOEC-CORE via a >13000h test, demonstrating a degradation rate of only 0.5%/kh at the CORE level.
- We designed, built and extensively tested a new pyrolysis reactor for handling different biomass feedstocks. The brand new pyrolysis technology has awaken a significant commercial interest and is currently being upscaled and commercialized.
- We further demonstrated integration of pyrolysis, SOEC and gas cleaning, ensuring high quality of syngas for further methane synthesis.
- A TwoStage Electro-Gasifier system to generate syngas from biomass for methanol synthesis has been analyzed with regard to system efficiency and fuel production cost. An input to output efficiency between 91.5 and 94.3% for the Electro-Gasifier was predicted from thermodynamic modelling. Compared with the competing technologies, the flexible system (i.e. TwoStage Electro-Gasifier) has higher methanol production cost, but also doubles the methanol production capacity due to integration of SOC. From a societal or TSO perspective, the flexible system is generally more competitive.
- We conducted energy system modelling on the role of the biomass gasification routes in the Danish (DK) and European (EU) 100% renewable energy system in Year 2050. Our analysis highlighted that bio-electrofuels or PtX fuels produced via biomass gasification route enhance the utilization of renewable electricity and reduce the overall energy system cost in comparison to CCU route fuels. An SWOT analysis of Power2X in Denmark points to Denmark being a P2X knowledge hub and highlights the need for improving the current regulatory framework to enable the faster deployment of the technology.

4. Project implementation

Along with the project course most of the tasks were carried out according to the project plan, though a number of technical and non-technical challenges and deviations from the original plan were encountered still. The biggest challenge was due to relocation of DTU Energy from Risø to Lyngby in 2019 and the outbreak of COVID-19 in early 2020, where the experimental facilities at DTU Energy and DTU KT were offline for certain periods. This affected the other project partners, though to different degrees. To cope with the challenge, the project period was extended from the original 36 months to 52 months. The COVID-19 induced (international) travel restrictions have impacted the activity in WT5.2 as well. Originally it was planned to conduct an SWOT analysis with a Power-to-X workshop with Danish actors, scheduled for 24th of March 2020, with 35 participants that have signed up for the event. Due to the COVID-19, the workshop had to be cancelled, therefore the data gathering was adapted to the situation and the SWOT analysis was redesigned to a two-stage empirical study where four main expert groups were interviewed online. The project dissemination activities were also impacted by the COVID-19 pandemic, where the number of conference participations by the project members were reduced. But the project still resulted in a high number of scientific publications.

Several scientific or technological changes to the project tasks were also implemented, to reflect the actual development need of the SOEC and gasification technologies at the time when the project was running.

WT1.2 was originally devoted to exploring lifetime limiting factors for SoA coated ICs. The corrosion of ICs was deemed as one of the technical challenges at the time when preparing this proposal, but has become less critical due to successful coating development at HTAS. Both DTU Energy and HTAS agreed that it is more relevant to devote the effort to model the microstructure evolution in the active Ni/YSZ electrode during long-term electrolysis operation. This has been identified as the dominant degradation phenomenon in long-term tested SOEC cells. WT1.2 was thus modified to model microstructure evolution in the Ni/YSZ electrode using phase field modelling.

The milestone M3.2 (*M3.2 Steam drier and heat exchanger coupled to the pyrolysis reactor and successful system operation demonstrated.*) includes the coupling of a steam dryer to the pyrolysis unit. While the pyrolysis unit is central, the steam drying unit is not, and it was originally only thought of as a link in demonstrating the concept as a whole. The steam drying technology is proven and commercialized and not much research value remains in this framework. As the project has progressed, DTU KT has evaluated the plan and found that there could be extracted much more value of the funding by revising M3.2 to prove successful operation with alternative fuels – straw, biogas fibres and/or sewage sludge instead. The outcome of the new task would be substantial, as fuel flexibility is at the core of the process economics and sustainability of energy plants. M3.2 was thus modified to "*Successful pyrolysis operation with alternative fuels – straw, biogas fibres and/or sewage sludge*".

The original plan for WP4 put a lot of focus on coupling biomass pyrolysis with an SOC (SOEC/SOFC) stack setup, where the two systems are coupled and work in continuous operation. However, recent developments in biomass pyrolysis and following processes using the products of pyrolysis suggested that the focus should be slightly changed. Commercial interest is focusing on pyrolysis oils or bio-oils and biochar, which can be used as a carbon capturing agent and used in soil applications. WP4 was thus modified to put more emphasis on pyrolysis oils (bio-oils) and biochar. In the suggested new setup, during the pyrolysis process volatiles in the produced pyrolysis gas would be condensed into a bio-oil that would be upgraded to a green fuel oil, whereas the residual gas after bio-oil separation, would still be utilized. The gas quality will be suitable for further upgrading to a green gas and produce methane. The needs for hydrogen addition should be defined for the methane production. Besides bio-oil and green gas production, biochar for carbon sequestration, carbon storage would be separated and applied by Danish farmers on their fields.

5. Project results

Overview and milestones

The project was structured into five technical work packages (WPs), which were further divided into a number of work tasks (WTs) as listed below:

WP1 – SOEC cells and stack components
       WT1.1 – Durable Ni/YSZ based SOEC cells
       WT1.2 – Modelling microstructure evolution in the Ni/YSZ electrode
WP2 – SOEC stacks and multi-stack cores
       WT2.1 – SOEC stacks for integration with gasification
       WT2.2 – Multi-stack SOEC core
WP3 – Pyrolysis reactor and gas cleaning
       WT3.1 – Design, construction and testing of the updraft pyrolysis reactor
       WT3.2 – Pyrolysis gas cleaning
WP4 – Integration of SOEC and gasification
WP5 – BOP and energy system modelling
       WT5.1 – BOP modelling
       WT5.2 – Energy system modelling

Further listed below are the milestones that were set up in the project plan and their status at the completion of the project:

M1.1: Optimized SOEC cells with a 50% decrease in the fuel electrode resistance as compared to that of the standard Ni/YSZ electrode demonstrated.
[Milestone fulfilled. By introducing CGO as electrocatalyst into the Ni/YSZ electrode, we reduced the fuel electrode resistance by a factor of five. See Table 1.]

M1.2: A long-term single cell test carried out on improved SOEC cells developed in this project, operated at 1.25 A/cm^2 for a period exceeding one year, with a lifetime expectance of >5 years demonstrated.
[Milestone partially fulfilled. Three single cell tests (each running for one year) were carried out on improved SOEC cells, showing a low degradation rate of 20 mV/kh at -1.25 A/cm^2. Further efforts are needed to bring down the degradation to <5 mV (0.5%)/kh (corresponding to a cell lifetime of >5 years).]

M1.3 ~~Oxidation model for coated Crofer22APU established and lifetime of coated Crofer22APU at representative SOEC operation conditions predicted~~. Changed to *A phase field model for simulating evolution of the Ni/YSZ electrode 3D microstructure when tested in electrolysis mode established*.
[Milestone fulfilled. We developed a phase field model, capable of modelling the 3D microstructure evolution of the Ni/YSZ electrode in a quantitative manner. The phase field modelling simulations reproduced the experimentally observed Ni coarsening and Ni migration reasonably well.]

M2.1 Two stack tests to investigate stack degradation with different sweep gasses for the oxygen electrode side (pure oxygen, vacuum, O_2/H_2O or O_2/CO_2) for a period exceeding 1000 h completed.
[Milestone fulfilled. A 3000h stack test was conducted on a HTAS TSP-1 stack. The test results confirm that TSP-1stacks operate quite fine with no sweep gas to the oxygen electrode side.]

M2.2 Long-term testing of an SOEC Core for a period exceeding one year completed.
[Milestone fulfilled. A two-stack SOEC-CORE was tested for >13000h, demonstrating a degradation rate of only 0.5%/kh at the CORE level.]

M3.1 Updraft pyrolysis reactor built and successfully operated.

[Milestone fulfilled. We designed, built and extensively tested a new 100 kW pilot-scale pyrolysis reactor for handling different biomass feedstocks.]

M3.2 ~~Steam drier and heat exchanger coupled to the pyrolysis reactor and successful system operation demonstrated~~. Changed to *Successful pyrolysis operation with alternative fuels – straw, biogas fibres and/or sewage sludge*.
[Milestone fulfilled. The pyrolysis setup was tested with multiple biomass feedstocks, including wood chips, straw pellets and biogas fiber pellets.]

M3.3. Pyrolysis gas characterized.
[Milestone fulfilled. We characterized the main gas components in the produced gas from the updraft pyrolysis unit. See Table 2.]

M3.4. Gas cleaning systems operated and tested.
[Milestone fulfilled. A gas cleaning system (partial oxidation reactor – POX) has been installed and tested with the produced producer gas.]

M3.5. ~~Clean pyrolysis gas meeting the requirements of SOC cells~~. Changed to *Pyrolysis system optimized for collection of bio-oil in multiple stages and biochar production*.
[Milestone fulfilled. DTU KT has implemented a number of improvements in the system, including automized char removal, electric tracing of the removal system and piping to avoid condensation, temperature profile measurement and measuring the influence of temperature on system performance.]

M4.1. A combined POX and char gasification reactor built and connected with the updraft pyrolysis unit.
[Milestone fulfilled. The integration of the pyrolysis unit and the gas cleaning system was finalized in the fall of 2019.]

M4.2. ~~Continuous operation of the TwoStage gasifier system in multiple campaigns completed and stability of the components assessed~~. Changed to *Continuous operation of the pyrolysis unit with bio-oil and biochar production and investigation on methane synthesis from the clean residual gas after oil condensation*.
[Milestone partially fulfilled. The bio-oil condensation unit and biochar separation have been heavily tested, especially with wheat straw as fuel. The investigation on methane synthesis has been performed by a modelling study, and was not verified by experimental results.]

M4.3. ~~Long-term operation of a SOC stack with cleaned pyrolysis gas~~. Changed to *Long-term test of the newly developed pyrolysis system and char removal*.
[Milestone fulfilled. In October 2019, test of gas cleaning with the POX reactor and oxygen from the SOEC was performed using hot pyrolysis gas from the updraft pyrolyzer.]

M5.1 Analysis on the expected operation of the integrated gasification and SOC system based on prices of biomass, electricity and fuel completed.
[Milestone fulfilled. A flexible TwoStage Electro-Gasifier system, integrating gasification and SOC to generate syngas from biomass for methanol synthesis, was analyzed with regard to system efficiency and fuel production cost. An input to output efficiency between 91.5 and 94.3% for the Electro-Gasifier was predicted from thermodynamic modelling.]

M5.2 Economic performance of the system calculated and compared with competing technologies.
[Milestone fulfilled. Compared with the competing technologies (electricity storage single-mode and conventional single-mode production), the flexible system (i.e. TwoStage Electro-Gasifier) has higher methanol production cost, but also doubles the methanol production capacity due to integration of SOC. From a societal or TSO perspective, the flexible system is generally more competitive.]

M5.3 Incentive structures and niche markets for P2G in the Danish energy system defined.

[Milestone fulfilled. Energy system modelling was conducted on the role of the biomass gasification routes in the Danish (DK) and European (EU) 100% renewable energy system in Year 2050. In addition, an SWOT analysis of Power2X in Denmark was conducted and the results point to Denmark being a P2X knowledge hub and highlight the need for improving the current regulatory framework to enable the faster deployment of the technology.]

WP1 – SOEC cells and stack components

This work package focused on the SOEC cells and stack components. The activities were grouped into two WTs: WT1.1 Durable Ni/YSZ based SOEC cells and WT1.2 Modelling microstructure evolution in the Ni/YSZ electrode. The tasks were carried out mainly by DTU Energy, with additional support from HTAS.

WT1.1 Durable Ni/YSZ based SOEC cells

In WT1.1, DTU Energy focused on introducing electro-catalysts into the Ni/YSZ electrode to accelerate the steam splitting reaction and to reduce cell degradation. This work was initiated in the previous project (ForskEL 12276 Towards Solid Oxide Electrolysis Plants in 2020) and was continued in the current project (EP2Gas). Different electro-catalysts and their effects on reducing Ni/YSZ electrode degradation were evaluated at the single cell level. The results pointed to gadolinia doped ceria (CGO) as the best electro-catalyst. As listed in Table 1 below, a large part of the cell resistance originates from the Ni/YSZ electrode ($R_{\text{Ni-TPB}}$, accounting for approximately 40% of the cell resistance). By introducing CGO, $R_{\text{Ni-TPB}}$ is reduced by a factor of five. The milestone M1.1 (*Optimized SOEC cells with a 50 % decrease in the fuel electrode resistance as compared to that of the standard Ni/YSZ electrode demonstrated*) was considered fulfilled.

Table 1. Results of fitting equivalent circuit models to the impedance spectra for cells without and with CGO electro-catalysts during long-term steam electrolysis at 800 °C and -1.25 A/cm².

Cell	Time (h)	R_s (mΩ cm²)	R_{ion} (mΩ cm²)	$R_{\text{Ni-TPB}}$ (mΩ cm²)	R_{ox} (mΩ cm²)	R_{Diff} (mΩ cm²)	R_{Conv} (mΩ cm²)
Without	0	66.7	15.9	**165.7**	42.1	**2.1**	166.4
CGO - 70%	0	116.6	8.7	**38.1**	26.6	**6.1**	145.3
	1000	113.4	31.2	128.3	38.1	27.4	218.8
CGO - 42%	0	92.8	3.9	**31.6**	11.4	**8.5**	52.6
	1000	93.4	18.1	76.2	12.9	14.9	62.2

Furthermore, three one-year single cell tests were completed within the EP2Gas project period. In these cells, the Ni/YSZ electrode was infiltrated with either CGO or both CGO and Ni. The cells were tested at -1.25 A/cm² and 750 or 800 °C. The cell voltage curves are shown in Figure 1. Though operated at different temperatures (750 or 800 °C), both cells (11test108 and 3test141) showed a degradation rate of ~20 mV (1.7%)/1000 h. Generally speaking, the SOC cells degrade more when reducing temperature but keeping the other operating conditions unchanged. On the other hand, reducing temperature is beneficial in terms of extending interconnect and hence stack lifetime. In EP2Gas, DTU Energy was able to reduce the cell operating temperature by 50 °C with the same low degradation rate at such high current density, hence extending the cell/stack lifetime. This is a good achievement with regard to the SOEC technology development. The milestone M1.2 *(A long-term single cell test carried out on improved SOEC cells developed in this project, operated at 1.25 A/cm² for a period exceeding one year, with a lifetime expectance of >5 years demonstrated.)* is considered partially fulfilled. Further 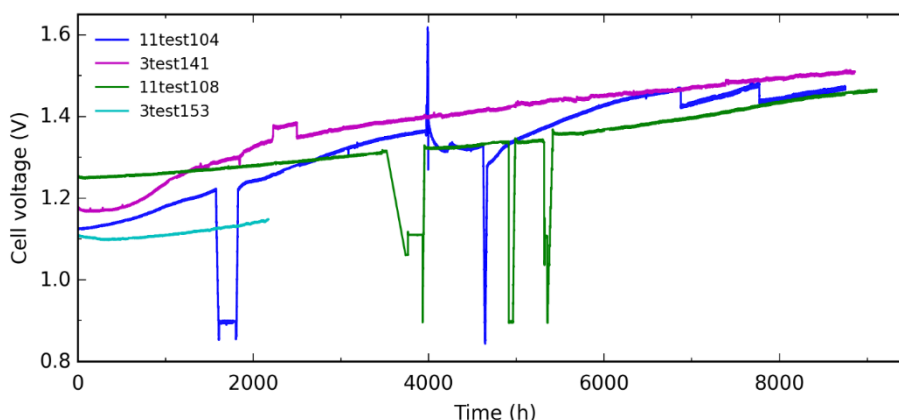efforts will be needed to bring down the degradation to <5 mV (0.5%)/1000h (corresponding to a cell lifetime of >5 years).

Figure 1. Galvanostatic long-term steam electrolysis durability tests under -1.25 A/cm^2. 11test104: infiltration of CGO into Ni/YSZ, tested at 800 °C; 3test141: infiltration of both Ni and CGO into Ni/YSZ, tested at 800 °C; 11test108, infiltration of CGO into Ni/YSZ, tested at 750 °C; 3test153: infiltration of CGO into modified Ni/YSZ, tested at 800 °C.

Developments were also devoted to the oxygen electrode side, where SOEC cells with two nano-engineered electrodes were successfully developed and tested. The O$_2$-electrode consists of a La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ (LSC) and Gd,Pr-co-doped CeO$_2$ (CGPO) nanocomposite coating deposited on a Gd-doped CeO$_2$ (CGO) scaffold, and the H$_2$-electrode comprises a Ni/yttria stabilized zirconia (YSZ) electrode modified with a nano-granular CGO coating. As shown in Figure 2, the resulting cell with an active area of 4×4 cm^2 exhibits a current density exceeding 1.2 A/cm^2 at 1.3 V and 750 °C for steam electrolysis, while also offering excellent long-term durability at 1 A/cm^2 with a high steam-to-hydrogen conversion of ~56%. The low R_{OER} resistance of 0.012 Ω cm^2 after 900 h operation and no obvious change in the microstructure suggest that the nanostructured LSC-CGPO-CGO is highly active and durable for the oxygen evolution reaction (OER), which demonstrates the potential of designing robust O$_2$-electrode via infiltration for large-scale manufacture of SOECs. The introduced CGO coating effectively mitigates the microstructural deterioration (typically disconnection between Ni and YSZ at the TPBs) seen on non-modified Ni/YSZ electrodes under these conditions, thus significantly enhancing cell durability. These findings represent an important advance towards development of long-term stable SOECs, and improve the commercial feasibility of integrating SOEC technology into sustainable energy future. This work has been published as a full journal paper on ACS Applied Materials & Interfaces (Paper 5).
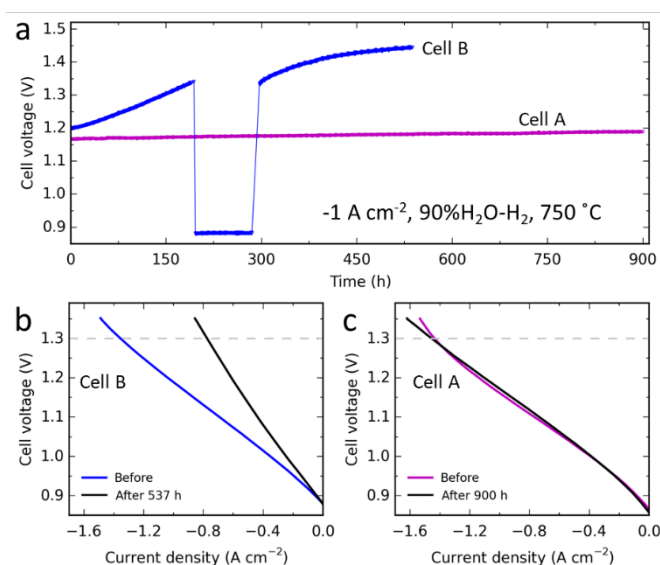

Figure 2. Comparison of the cell durability during steam electrolysis. (a) Evolution of cell voltage during long-term test under a constant current density of 1.00 A/cm^2 at 750 °C. (b, c) *I-V* curves collected before and after the durability tests. A 90%H$_2$O-10%H$_2$ gas mixture was fed to the H$_2$-electrode and pure O$_2$ was supplied to the O$_2$-electrode.

To enable a sufficient porosity in the Ni/YSZ H_2-electrode structure for infiltration and to avoid the chemical expansion of the CGO barrier layer and the decomposition of LSCF during reduction, the full cell was pre-reduced with a "two-atmosphere-reduction", i.e., the NiO/YSZ H_2-electrode was exposed to reducing atmosphere while the LSCF/CGO O_2-electrode was exposed to air by using an in-house built test rig. However, the upscaling of this infiltration method is indeed impeded by the need of "two-atmosphere-reduction". In the latter part of the project, DTU Energy conducted work on simplifying the aforementioned infiltration method to fit the upscaling requirement by replacing the complicated "two-atmosphere-reduction" procedure with a facile one-atmosphere-reduction, which can be carried out during the cell sintering process. The performance and durability of the infiltrated cell and a non-infiltrated sister-cell (as reference) were evaluated. As shown in Figure 3, the infiltrated cell shows more than one order of magnitude lower degradation rates than the non-infiltrated cell when tested at −1.25 A/cm^2 and −1.00 A/cm^2, 750 ˚C. The results of this work was published as a conference proceeding paper at the SOFC XVI conference in Japan in September, 2019 (Paper 2).
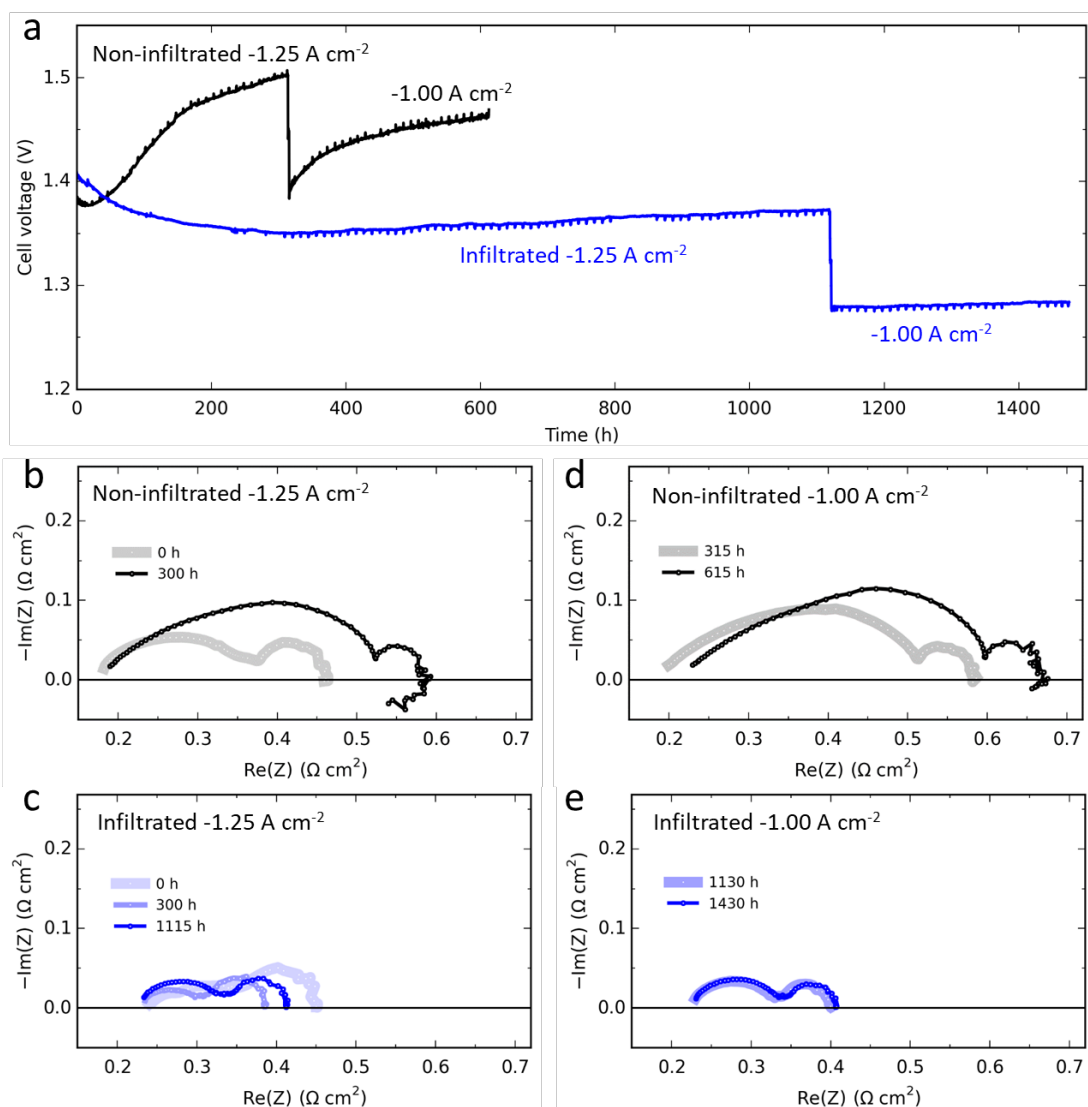
Figure 3. Comparison of the cell durability during continuous steam electrolysis at 750 °C with 90%H_2O-10%H_2 to the H_2-electrode and pure O_2 to the O_2-electrode. (a) Evolution of cell voltage as a function of time. Nyquist plots of EIS data recorded under current during the durability test period. (b) -1.25 A/cm^2 on non-infiltrated cell, (c) -1.25 A/cm^2 on infiltrated cell, (d) -1.00 A/cm^2 on non-infiltrated cell, and (e) -1.00 A/cm^2 on infiltrated cell.

The state-of-the-art SOEC cells use strontium and cobalt co-doped lanthanum ferrite (LSCF) as the oxygen electrode material. Its chemical stability is limited, which together with the volatilization and diffusion of cobalt

during high-temperature sintering cause various cell fabrication issues. Furthermore, cobalt is price volatile and it may become resource-limited due to the rocketing demand of cobalt oxide for lithium-ion batteries. Finally, it is considered carcinogenic. All these factors push the development of cobalt-free electrodes for SOCs. In EP2Gas, DTU Energy looked into cobalt free oxygen electrode material. A remarkable enhancement of electro-catalytic activity of cobalt-free $(La_{0.6}Sr_{0.4})_{0.98}FeO_{3-\delta}$ (LSF) electrodes was achieved by applying a nanoengineered hybrid catalyst coating composed of nanoparticles of $Ce_{0.85}Gd_{0.15}O_{2-\delta}$ (CGO) and Pr_6O_{11} via co-infiltration. Different from the conventional infiltration with a precursor of metal nitrate, here a mixture solution of colloidal CGO nanocrystals and $Pr(NO_3)_3$ was used for infiltration to enable the desired nanoengineered architecture. The resulting hybrid-catalyst-coated LSF electrode exhibits a very low polarization resistance of 0.017 Ω cm^2 at 750 °C, about one order of magnitude lower than that of bare LSF (0.197 Ω cm^2). The unique catalytic activity of the hybrid-catalyst-coated LSF electrode is attributed to the combined effects of accelerating oxygen surface exchange kinetics by Pr_6O_{11} and enhancing the available surface area by the nanoporous architecture of the catalyst coating. Furthermore, the Ni/yttria-stabilized zirconia (YSZ) fuel-electrode-supported cell with this hybrid-catalyst-coated LSF electrode displays excellent performance in both fuel-cell and electrolysis operations. Moreover, combining with the modification of the Ni/YSZ electrode, stable electrolysis operation at 650 °C under -0.5 A/cm^2 with a voltage close to 1.3 V is achieved on a cell prepared without cobalt. This work not only opens the opportunity for applying cobalt-free oxygen electrodes in SOCs but also proposes a co-infiltration strategy to develop highly active and robust catalyst coating by combined tuning of composition and morphology. In addition, the operation window of SOEC cells has been extended down to 650 °C. This work has been published as a full journal paper on Journal of Materials Chemistry A (Paper 9).
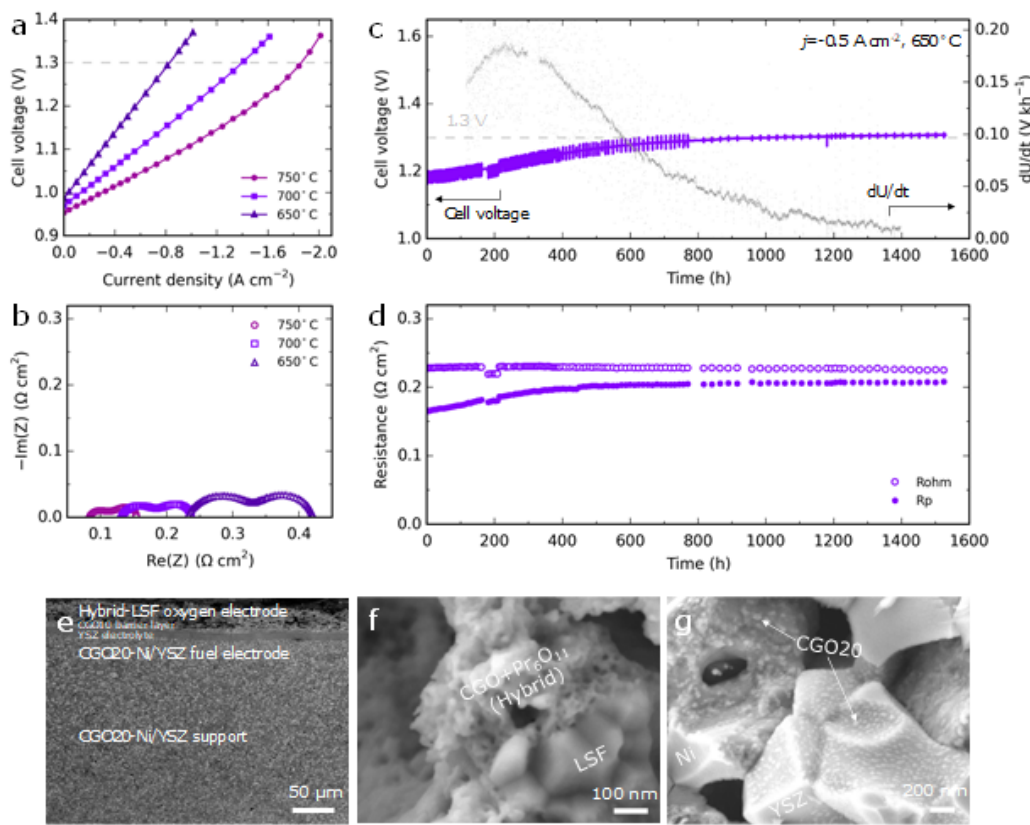

Figure 4. Electrochemical performance and durability for electrolysis operation on the double-side modified cell measured with 50%H_2O-50%H_2 fed to the fuel electrode and dry air to the oxygen electrode. (a) I-V curves and (b) Nyquist plots of EIS data measured at 650–750 °C. Evolution of (c) cell voltage and (d) R_{ohm} and R_p during the durability test. Note that the EIS data in (b) was recorded under OCV condition, while the data in (d) was recorded under a current density of -0.5 A/cm^2. SEM characterization of the double-side modified cell after the durability test. (e) Full cell. (f) Hybrid-catalyst-coated LSF oxygen electrode. (g) CGO20-coated Ni/YSZ fuel electrode.

Potentiostatic operation of solid oxide electrolysis cells (SOECs) at the thermoneutral voltage enables the advantages of close to 100% electrical efficiency and simplifies the heat management of stacks and systems. The operating current of an SOEC system in potentiostatic mode determines the hydrogen production rate and thereby also the economic payback period of the SOEC system investment. Therefore it is crucial to investigate the long-term durability of SOEC operated potentiostatic at the thermoneutral voltage at various temperatures. In EP2Gas, DTU Energy analyzed in detail previously conducted electrolysis single cell tests operated at the thermoneutral voltage of 1290 mV at three different temperatures (800, 750, and 700 °C). The cells are state-of-the-art planar Ni/YSZ fuel electrode supported SOECs from the same production batch. Severe degradation occurs in the first 300 h for all three cells, with the current densities decreasing from 1.55, 1.28, and 0.93 A/cm^2 to 0.711, 0.700, and 0.398 A/cm^2, and the degradation rates are 1.80, 1.51, and 1.90%/kh during the first 300 h of tests at 800, 750, and 700 °C, respectively. The increases in ohmic and Ni/YSZ electrode polarization resistance cause the majority of the degradation for the cell tested at 800 °C, while the degradation of the cell tested at 700 °C is ascribed to the polarization resistance increase for both the Ni/YSZ fuel electrode and oxygen electrode. Interestingly, the least degradation was observed for the cell tested at 750 °C. It is found that 750 °C is the optimum operating temperature for the Ni/YSZ fuel electrode supported SOECs operated at 1290 mV for steam electrolysis.
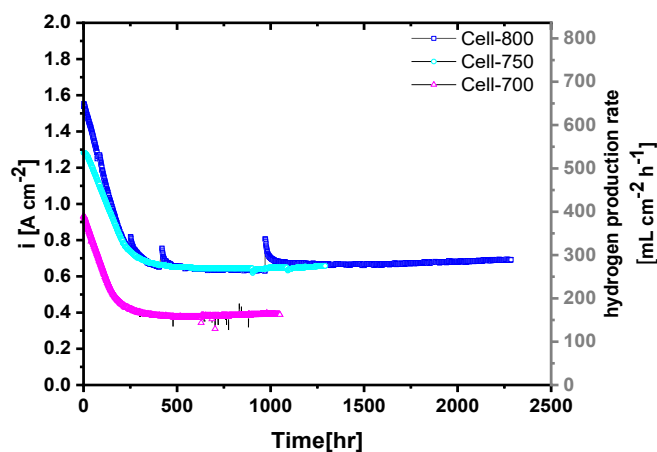

Figure 5. Evolution of current density and hydrogen production rate with time for the three cells during the long-term stability tests at the thermoneutral voltage of 1290 mV, feeding 13.3 l/h H_2O+H_2 mixture (H_2O/H_2 = 90/10) to the Ni/YSZ electrode and 50 l/h O_2 to the oxygen electrode.
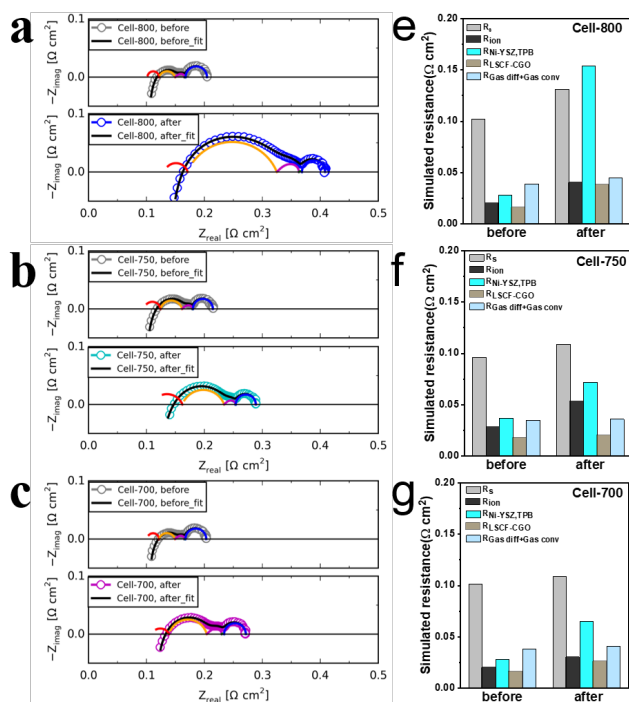
Figure 6. (a,b,c) Impedance spectra measured before and after the durability test. Impedance spectra measured at 750 °C and OCV, with 24 l/h 50%H_2O+50% H_2 supplied to the fuel electrode and 50 l/h O_2 to the oxygen electrode, (e,f,g) The summary of results from equivalent circuit modeling of EIS recorded for the three cells.

WT1.2 Modelling microstructure evolution in the Ni/YSZ electrode

WT1.2 was originally devoted to exploring lifetime limiting factors for SoA coated ICs. The corrosion of ICs was deemed as one of the technical challenges at the time when preparing this proposal, but has become less critical due to successful coating development at HTAS. Both DTU Energy and HTAS agreed that it is more relevant to devote the effort to model the microstructure evolution in the active Ni/YSZ electrode during long-term electrolysis operation. This has been identified as the dominant degradation phenomenon in long-term tested SOEC cells. WT1.2 was thus modified to reflect the actual need of the SOEC technology development at the time when the project was running.

During long-term electrolysis operation, the Ni/YSZ electrode is exposed to high temperature (700-850 °C) and high content of steam or CO_2, and in addition current. At such temperature Ni coarsening occurs, resulting in a decrease in the number of active electrochemical sites. When the cell is operated in electrolysis mode, a new phenomenon of Ni migration away from the electrode/electrolyte interface is observed. This results in a significant decrease in the number of active sites, much more than just due to simple Ni coarsening. The Ni migration phenomenon has been well observed by a number of SOEC research groups and has been regarded as the most dominant degradation mechanism in long-term tested SOEC cells. It was reported that the migration of Ni away from the electrode/electrolyte interface is affected by current density, electrode overpotential, humidity, and temperature. In the project Synfuel – Sustainable synthetic fuels from biomass gasification and electrolysis (funded by Innovationsfonden, project no. 4106-00006B), a phase field model was developed by DTU Energy which can simulate evolution of a real 3D microstructure of the Ni/YSZ electrode due to Ni coarsening, i.e. accounting for the effect of temperature only. In EP2Gas, this model was extended in order to account for both temperature and current, hence be able to simulate evolution of the 3D Ni/YSZ electrode microstructure when exposed to electrolysis current.

The Ni/YSZ electrode is a cermet composite consisting of the pore, Ni and YSZ three phases. In the model developed in Synfuel, an assumption has been made on the YSZ phase, where it was assumed to be immobilized. This is not 100% correct. As the first step in EP2Gas, a more precise model (multi-phase-field) was

adopted. The new model is capable of solving the three-phase problem, instead of assuming one phase not evolving. The new model was validated against microstructure data of real Ni/YSZ electrodes, where all the model parameters have been optimized (Figure 7). Also the model is capable of reproducing Ni migration in a model system, when a gradient in the Ni-YSZ contact angle is introduced (Figure 8). Ni migrates from the location with high contact angle towards the one with low contact angle, as expected.
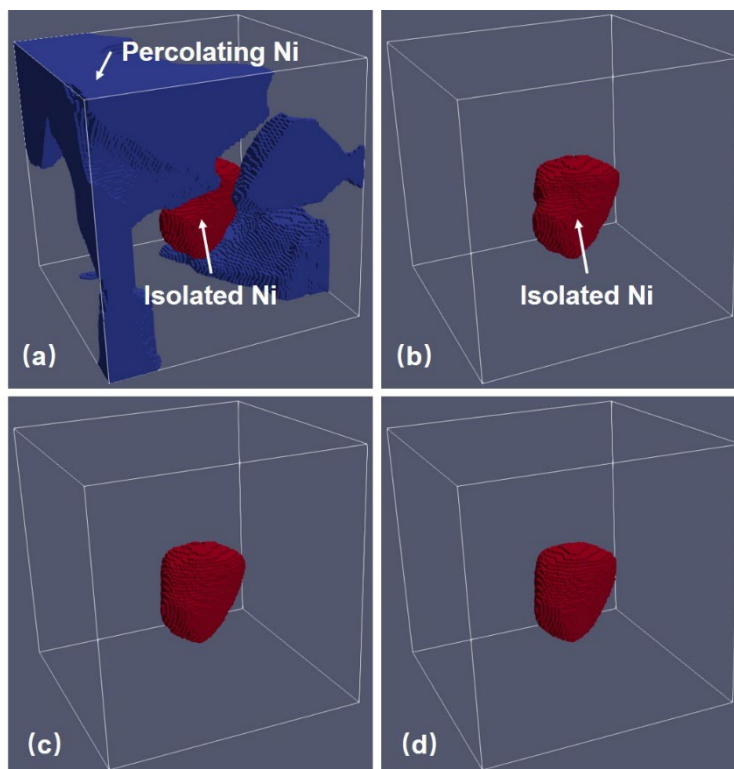

Figure 7. Morphology of the isolated Ni particle in a simulated microstructure performed in a domain of 1.8×1.8×1.8 µm^3 at different aging times: (a) and (b) 0h, (c) 3h, and (d) 8h.
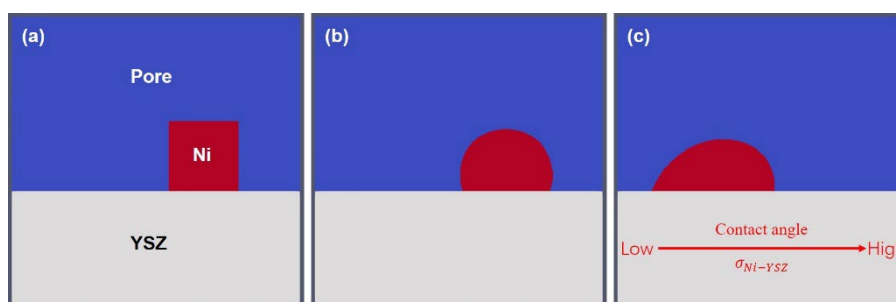
Figure 8. Simulation results of a model microstructure (a) containing pore, YSZ and Ni phases with a domain $5.49 \times 5.49 \times 5.49 \ \mu m^3$ using the constant (b) and gradient contact angle (c).

The model was then used to predict Ni migration in long-term tested SOEC cells. An experimental 3D structure of the Ni/YSZ electrode was used as the input to the phase field modelling. The 3D structure was generated from an SOEC cell reduced at 1000 °C (Figure 9a). When an SOEC cell is exposed to the current, an electro-chemical potential gradient is generated in the Ni/YSZ active electrode along the current direction. This further impacts the wetting of Ni on the YSZ surface, driving Ni moving from high Ni/YSZ contact angle to low contact angle. In the phase field model, a gradient in the Ni/YSZ contact angle (θ) was implemented with θ = 125° at the electrolyte – electrode interface and θ = 95° at the electrode – support layer interface. Figure 9b shows the Ni phase in the 3D structure from initial (experimental input) and after 3472 h testing (simulated). It clearly shows that both Ni coarsening and Ni migration towards the support layer happen in the Ni/YSZ electrode

exposed to a cathodic polarization (i.e. operated in SOEC mode). The first 1-2 μm from the electrolyte – electrode interface is more or less free of Ni. To quantify the extent of the Ni migration, we further calculated the locations for the center of mass for the Ni, YSZ, and Pore phases in the 3D structure. The location is given in term of the Z coordinate along the current direction (Figure 10). The results confirm that Ni moves towards the support layer and the pore phase moves in the opposite direction, whereas the YSZ phase remains static. After 3472h testing in SOEC mode, the center of mass for the Ni phase moves about 0.5 μm along the current direction towards the support layer. The phase field modelling simulations reproduce the experimental observations reasonably well.

a)

b)
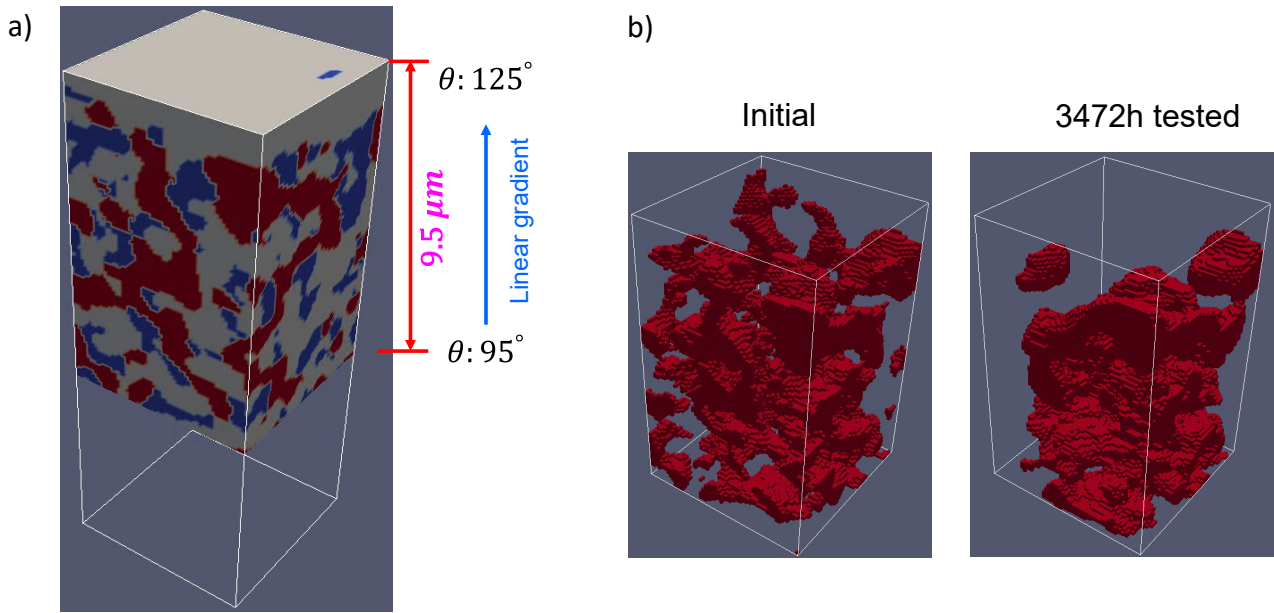
Simulation size:
$6 \times 6 \times 9.5 \ \mu m^3$

Figure 9. a) 3D structure of the Ni/YSZ electrode used as the input to phase field modeling. Gray: YSZ, Blue: pore, Red: Ni. As the driving force for Ni migration, a linear gradient in the Ni/YSZ contact angle (θ) from 125º at the electrolyte – electrode interface to 95º at the electrode – support interface was assumed. b) 3D structures showing the Ni phase only. The YSZ electrolyte layer (not shown) is on the top.
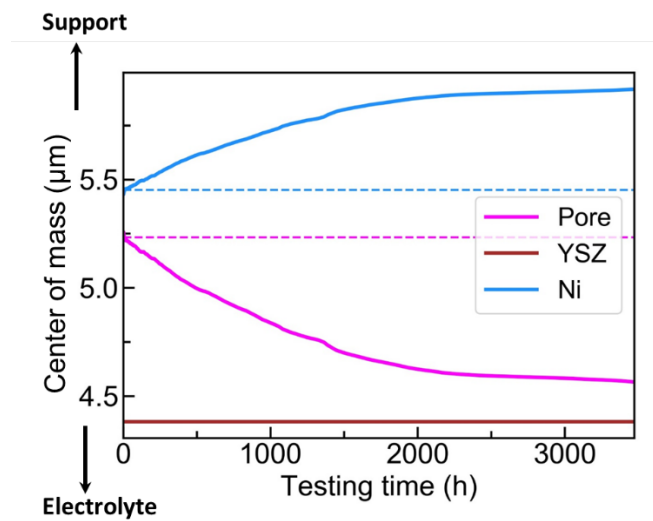
Figure 10. Center of mass for the Ni, YSZ, Pore phases predicted from phase field modelling simulations based on the initial structure of the Ni/YSZ electrode and the contact angle gradient presented in Figure 9.

WP2 – SOEC stacks and multi-stack cores

This work package involved two tasks, one focusing on SOEC stacks and the other on multi-stack cores.

WT2.1 – SOEC stacks for integration with gasification

This task was dedicated to evaluate SoA HTAS stacks (TSP-1) with regard to performance, durability, and robustness, under scenarios targeting intimate integration with biomass gasification. To achieve high efficiency and low system cost for the integrated SOEC + gasification system, oxygen produced by SOEC should be utilized in the gasification process (i.e. oxygen-blown gasification). This requires extraction of pure oxygen from the oxygen electrode side, which may pose a safety hazard and other problems (such as severe corrosion of ICs and BOP components) to TSP-1 stacks and multi-stack cores. Alternatively, the oxygen can be diluted with steam, CO_2, or activity reduced via applying a vacuum.

In this project, a fresh 75-cell TSP-1 stack (X-260) from HTAS was tested in steam electrolysis for >3000 hour. The stack was operated first galvanostatically at -63 A for 500 hours, then potentiostatically at thermoneutral voltage (1.3 V cell voltage) for 2500 hours. In both periods the sweep gas on the oxygen electrode side was switched between pure oxygen and no sweep gas. The change of sweep gas has no influence on the stack degradation behavior. It was thus concluded that TSP-1 stacks operate quite fine with the "no sweep" condition. Another objective of the test was to maintain temperature control (see Figure 11). In the first 600h the stack was operated in constant current mode (i.e. galvanostatic mode, I = -63A) and the average stack temperature was set to 725 °C. When the average cell voltage exceeds the thermo-neutral voltage due to degradation, the outlet temperature increases. The furnace temperature was then lowered in order to maintain an average stack temperature of 725 °C. These operation conditions was stopped at 600h as the temperature difference between inlet and outlet became too high. After this period it was decided to operate the stack at thermo-neutral in potentiostatic mode (Constant potential at E_stack = 95V). It can be seen that the temperature profile was held pretty stable during this part of the experiment.
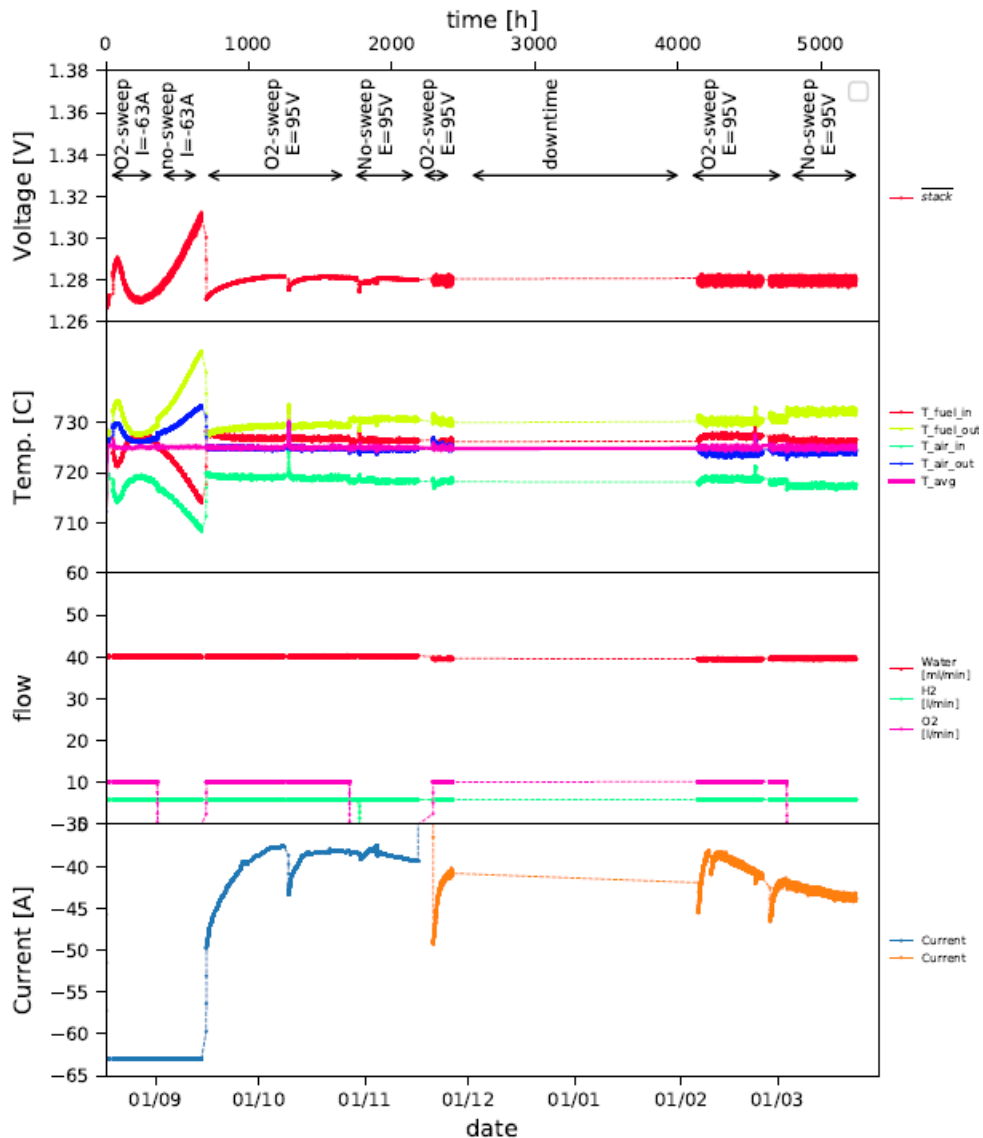
rig47,X260,75-cells,steam,-electrolysis,C:/Users/jehq/47test022/python_script/04_EC_H2O_vs_O2_63A_3.py

Figure 11. Overview plot of the stack testing.

WT2.2 – Multi-stack SOEC core

This task was devoted to the development of multi-stack SOEC core for future integration with the biomass gasification process. For most applications, the gas production capacity of a single SOEC stack is not sufficient and several stacks need to be operated simultaneously. Instead of equipping each stack with its own oxygen-side and fuel-side heaters, large benefits in terms of cost and system simplicity can be achieved if several stacks are supplied with heat and gas using an integrated system equipped with heat exchangers. The SOEC Core combines all the components (the stacks, heaters, heat exchangers, gas lines) that are subjected to high temperatures during system operation. In addition to the SOEC stacks, other components in the Core such as heaters and heat exchangers will be subjected to harsh conditions during system operation, especially when

subjected to pure O_2, very high levels of steam, or CO_2. Therefore, the useful lifetime and relevant failure mechanisms of these Core components need to be evaluated.

In this project, an SOEC-CORE test with two TSP-1 stacks (U-100 and U-101) was running with the aim to demonstrate >1 year operation of an SOEC Core to complete the milestone M2.2 (*Long-term testing of an SOEC Core for a period exceeding one year completed*). The stacks were operating in CO_2 electrolysis (CO_2/CO mixture on the fuel side, CO_2 flush with minor amount of air on the oxygen side). The CORE was operated for approximately 9 kh with stable operation at -70A. The O_2 concentration in the oxygen outlet with these conditions was 16%.

The average cell voltage per stack as a function of time is shown in Figure 12. After changing to -70A operation and correcting the inlet temperature slightly, the stacks start to activate. This is normally observed with this stack generation. Between 1000 – 5000h there was no observable degradation on the stacks. After 5000h the system experienced several trips and thermal cycles. Some of these trips were related to the test facility and were unfortunately harmful to the stacks. Nevertheless, the average total degradation during the test was 0.5% V/kh, which is a very good result. The low degradation is partly explained by gas cleaning to remove Sulphur in the CO_2 feed to the fuel electrode. A **few ppb** Sulphur has a detrimental effect on the degradation of the stacks[1,2]. There is a Sulphur guard installed with commercial HTAS gas impurity adsorbents on this specific test rig, which successfully solved the Sulphur impurity contribution to the overall degradation.
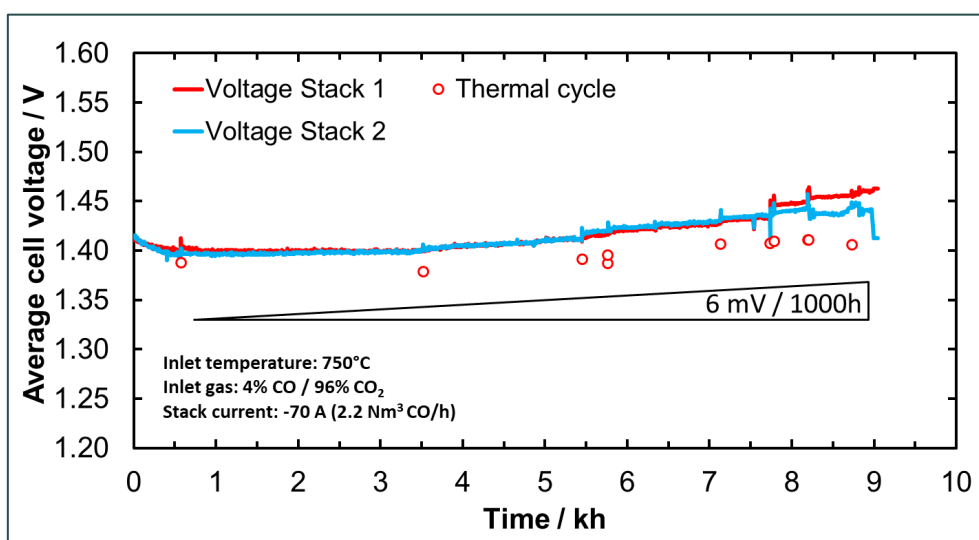

Figure 12. Average cell voltage per stack for the SOEC CORE test (P51-006) containing the stacks U-100 and U-101. The stacks were operated in CO_2 electrolysis with an inlet temperature of 750 ºC. The first 500h was a run-in period at -50A and subsequently at -70A.

Within the entire project period, the SOEC-Core was operated for >13100h. The stack U-100 was operated over the entire period, whereas the stack U-101 that failed after 9 kh of testing and was replaced with a new fresh stack and the test restarted at the same operating point as before.

WP3 – Pyrolysis reactor and gas cleaning

This WP aimed at designing, building and extensively testing a new pyrolysis reactor for handling different biomass feedstocks. The work was very successful in all aimed tasks and resulted in a brand new pyrolysis technology. The design has awaken a significant commercial interest and Stiesdal Fuel Technologies A/S is – in close collaboration with DTU KT – upscaling and commercializing the technology now. Stiesdal Fuel Technologies and DTU is continuing the work initiated in the EP2Gas project in a newly started EUDP-supported

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[1] S.D. Ebbesen, M. Mogensen, J. Power Sources, 193(1), 349-358 (2009)

[2] T. Skafte, P. Blennow, J. Hjelm, C. Graves, J. Power Sources, 373, 54-60 (2018)

project (64021-1114 - SkyClean 2 MW Process Development and Industrial Demonstration), where the current pyrolysis system will be upscaled, further tested and will pave the way for a full-scale pyrolysis plant, while bio-oil and syngas upgrading will be investigated in detail.

The reactor planning and design was initiated in 2018, where the main operation principles were established. A 100kW pilot-scale pyrolysis reactor was designed, and was configured with a recirculation mechanism that utilizes the produced gas as the heating medium for the conversion of biomass (Figure 13). Dry biomass is fed at the top of the reactor and is processed through the fixed bed updraft reactor to at least 500 ºC at the grate. The produced biochar is discharged beneath the grate, while the gas flows to the top and exits through a hot filter. After filtration, the bio-oil is extracted in a - patent pending - bio-oil condensation train. Part of the residual syngas is then recirculated via a blower and fed to a heat exchanger, after which it is led to the bottom of the reactor and from there passing through the fuel bed in the upwards direction. By configuring the system in this way, it is possible to produce an undiluted syngas free of N_2, scale the system, integrate a variety of heat sources to achieve high energy efficiency. The novel pyrolysis reactor design scheme of the final system structure can be seen in Figure 13 and the development of the system can be followed in pictures of Figure 14.
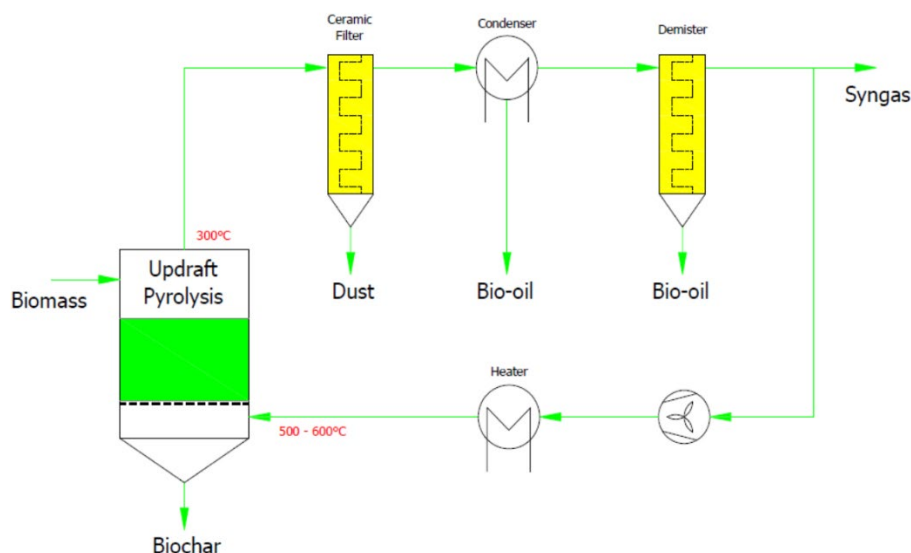
Figure 13. Updraft pyrolysis reactor design scheme.

Figure 14. Development of the construction of the updraft pyrolysis reactor at DTU-KT, Campus Risø.

The milestones regarding the pyrolysis unit design, construction and testing, even with different alternative fuels have been fulfilled and the pyrolysis gas was characterized. A gas cleaning system (partial oxidation reactor – POX) has been installed and tested with the produced producer gas. The system has also been optimized for the collection of the solid residue of pyrolysis – biochar and the volatiles from the gas as bio-oil. All these efforts are mirrored in the reached milestones of WP3.

The finalized pyrolysis system was functioning automatically by the year 2020, with operation control (temperature/pressure/bed height measurement and ventilator operation), except manual biomass feeding and char removal and it showed stable operation with good performance for multiple hours. The pyrolysis unit has also been integrated with the existing gas handling and gas cleaning facilities at Risø (hot gas filter and torch), which includes being coupled side streams to the downstream partial oxidation (POX) reactor for gas cleaning, SOEC equipment and bio-oil extraction and upgrading equipment. The pyrolysis setup has been tested with multiple biomass feedstocks, including wood chips, straw pellets and biogas fiber pellets. The system was also tested without the POX reactor, where side streams of the hot pyrolysis gas were led to a bio-oil extraction unit and a catalytic bio-oil upgrading unit. When the milestone M3.5 was reached in 2021, DTU KT has implemented a number of improvements in the system, including automized char removal, electric tracing of the removal system and piping to avoid condensation, temperature profile measurement and measuring the influence of temperature on system performance. Besides this, a number of fuels have been tested in the improved system and the products, gas, volatiles and char have been characterized in detail and possible uses of the products in different applications have been evaluated.

Gas composition with using different biomass feedstocks

The main gas components have been characterized in the produced gas from the updraft pyrolysis unit. Significant differences can be seen in the contents of CO, H_2 and methane of the gas, when wheat straw and biogas fiber pellets are pyrolyzed (Table 2).

Table 2. Gas composition from pyrolysis of wheat straw and biogas fiber pellets. Results are showed without considering N_2 in the gas.

Compound in gas (vol%)	Wheat straw pellets	Biogas fiber pellets
CO	26	14
H_2	9	20
CO_2	46	51
CH_4	15	11
Other hydrocarbons	4	4

Pyrolysis process evaluation in repeated experiments

Repeated experiments (with varying tar condensation parameters) were performed with the tested fuels and Figure 15 and Figure 16 summarize the mass and energy balances of the system, with focus on the pyrolysis products, syngas, bio-oils (tars) and the solid residue, biochar. It can be seen in the figures that the results are well repeatable, although some deviations appear for example in the syngas contents.
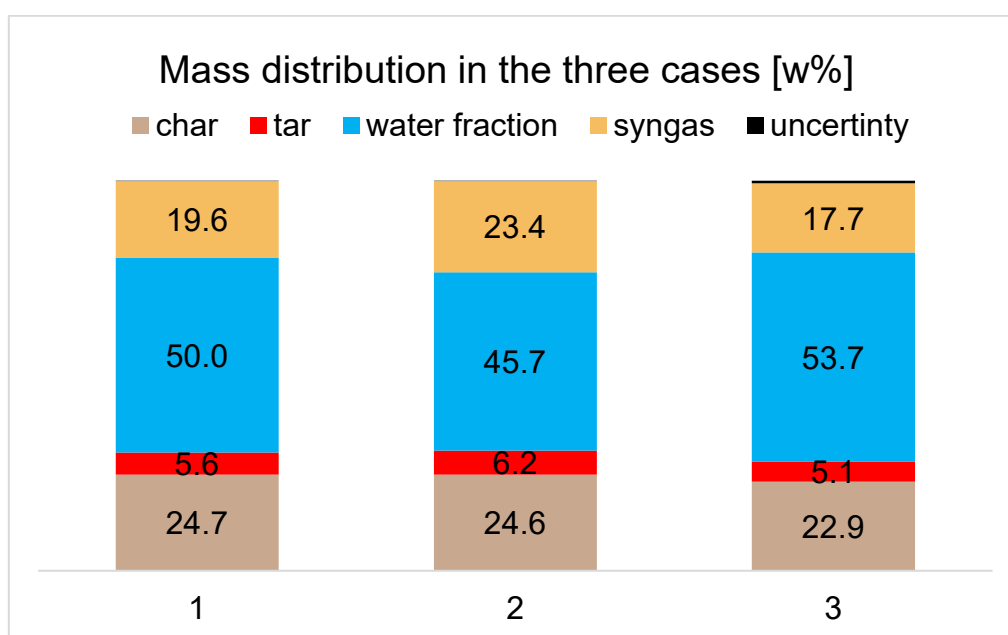
Figure 15. Mass balance of pyrolysis experiments on wheat straw.
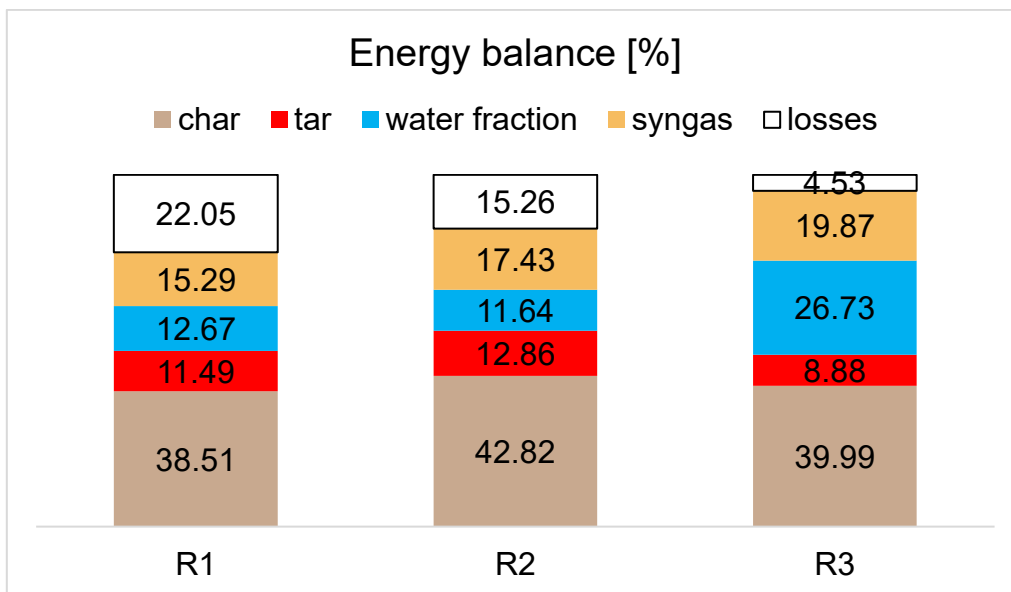
Figure 16. Energy balance of pyrolysis experiments on wheat straw.

WP4 – Integration of SOEC and gasification

The original project description put a lot of focus on coupling biomass pyrolysis with an SOC (SOEC/SOFC) stack setup, where the two systems are coupled and work in continuous operation. However, due to recent developments in biomass pyrolysis and following processes using the products of pyrolysis gave the basis that DTU KT requested modifications on the focus of WP4. Hence, this WP put more emphasis on pyrolysis oils (bio-oils) and biochar that can be used as a carbon capturing agent and used in soil applications. During the pyrolysis process volatiles in the produced pyrolysis gas would be condensed into a bio-oil that would be upgraded to a green fuel oil, whereas the residual gas after bio-oil separation, would still be utilized. The gas quality is suitable for further upgrading to a green gas and produce methane. The needs for hydrogen addition should be defined for the methane production. Besides bio-oil and green gas production, biochar for carbon sequestration, carbon storage would be separated and applied by Danish farmers on their fields.

WP4 focused on ensuring high quality bio-oil condensation from the system and besides, making sure that the produced syngas is free of contaminants that would hinder further methane synthesis. This WP also put emphasis on necessary gas cleaning methods (e.g. active carbon filter) followed by careful characterization of the gas, and the amount of hydrogen needed for the process to upgrade the gas.

The integration of the pyrolysis unit and the gas cleaning system was finalized in the fall of 2019 and in October 2019, test of gas cleaning with the POX reactor and oxygen from the SOEC stack was performed using hot pyrolysis gas from the updraft pyrolyzer. The POX reactor consists of a chamber with a fixed char bed where the pyrolysis gas is let through and oxygen is added for partial oxidation of the tar compounds (large organic molecules C_{6+}) with the purpose of cracking the molecules into smaller molecules, mainly to CO and H_2.

Gas cleaning with the integrated POX/SOEC-system
Pyrolysis gas from the updraft pyrolysis unit was gasified in a partial oxidation (POX) reactor that was supplied with oxygen from an SOEC stack. During the POX reactor operation, the outlet gas composition was analyzed for hydrocarbons and tar-compounds (PAH's and phenols) using gas collection bags and solid phase adsorbtion (SPA) tubes, respectively. The composition of the collected gas bag samples were analyzed with a multichannel GC-FID system and the results are shown in Table 3. The composition unfortunately lacks CO

analysis. This is a problem because CO surely is one of the biggest constituents in syngas. The total gas components are 56 % (v/v) so CO is potentially up to 46 % (v/v).

Table 3. Gas composition of the gasified pyrolysis gas after gas cleaning in the POX reactor. The same sample was analyzed 3 times and in one analysis, the H_2 level was measured 10.2% but there was no signal in the other analyses.

Compound	% (v/v)
C_{6+} (hydrocarbons)	0.002
methane	0.01
ethane	0.009
ethene	0.03
propane	0.001
propene	0.01
other hydrocarbons	0.005
CO_2	35.86
Nitrogen	8.65
Hydrogen	10.22
Oxygen	1.50

The integration of the SOEC stack oxygen worked as expected and it gives a syngas that is very low in nitrogen, and therefore less diluted than when air is used in the POX reactor. This makes the syngas more valuable. The tar contents were evaluated by taking SPA samples and analyzing for the most common polycyclic aromatic hydrocarbons (PAH's) and phenols. The results show that the sum of all PAHs is calculated at 22, 26 and 25 mg/m^3 at three different sampling times, where the most abundant PAH is phenanthrene in the samples and a very low amount of phenol was found. The results were comparable with those found in an earlier study of the research group (Ravenni et. al. Fuel Processing Technology, 210, 106546, 2020) and it was concluded that the POX reactor has the desired effect of cracking most tar-compounds into light gases, and thereby clean the gas and proves the efficiency of the technique.

Bio-oil and biochar collection from the updraft pyrolysis unit and bio-oil properties

A condensation system was established for the volatiles to collect them as bio-oils. Bio-oil condensation is done in multiple condensation fractions, where a heavy tar and a water-rich phase are separated. The bio-oil condensation unit and biochar separation have been heavily tested, especially with wheat straw as fuel. Figure 17 shows the scheme of the reactor and the condensation systems.
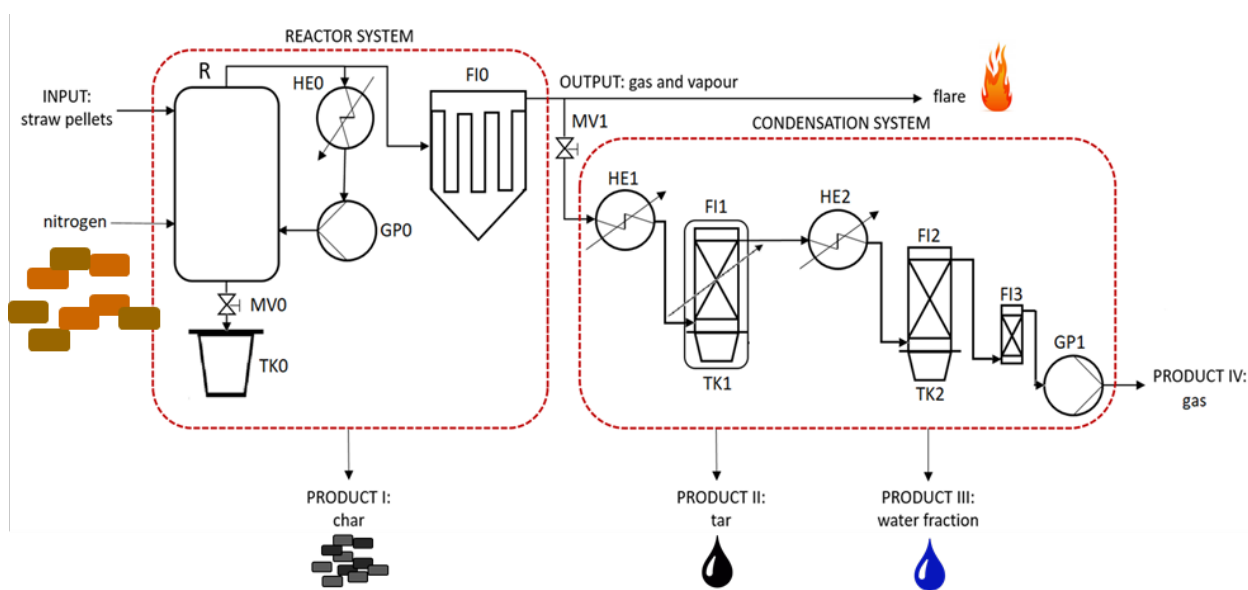

Figure 17. Scheme of the updraft pyrolysis reactor and the bio-oil condensation system.

The characteristics of the produced bio-oil are summarized in Table 4. The oils were produced via pyrolysis of wheat straw and the oil quality is compared to standards of different fuel oils. It can be seen that oil upgrading is necessary, as the oil produced and condensed from the reactor show high acidity – too high oxygen content, which needs to be reduced.

Table 4. Bio-oil properties from wheat straw pyrolysis.

Property	Unit	tar R1	tar R2	tar R3	ISO 8217	EN 16900	ASTM D6751
density	[kg/m^3] at 15 °C	1477	1330	999	max 975	max 1300	-
kinematic viscosity	[mm^2/s] at 40 °C	2786	2824	842		max 125	max 6
	[mm^2/s] at 50 °C	1207	1251	353	max 80		
LHV	[MJ/kg]	31.4	31.4	29.3	-	min 14	-
CCAI	/	1327.1	1179.8	860.7	max 860	-	-
water content	[w%]	0.66	1.75	1.78		max 30	
	[vol%]	0.97	2.32	1.78	max 0.5		max 0.05
ash content	[w%]	0.01	0.02	0.02	max 0.07	max 0.25 wb	-
sulfur content	[w%]	0	0	0	max 0.1	max 0.1 db	max 0.0015
Acid Number	[mg KOH/g]	40.84	34.94	52.68	max 2.5	-	max 0.5

Catalytic upgrading of the producer gas has also been tested from the updraft pyrolysis system, with using wheat straw as biomass fuel. The pyrolysis temperature was ~600 °C. The catalytic reactor was filled with 100 g of Na-Al$_2$O$_3$ and was operated at 530 °C (Figure 18).
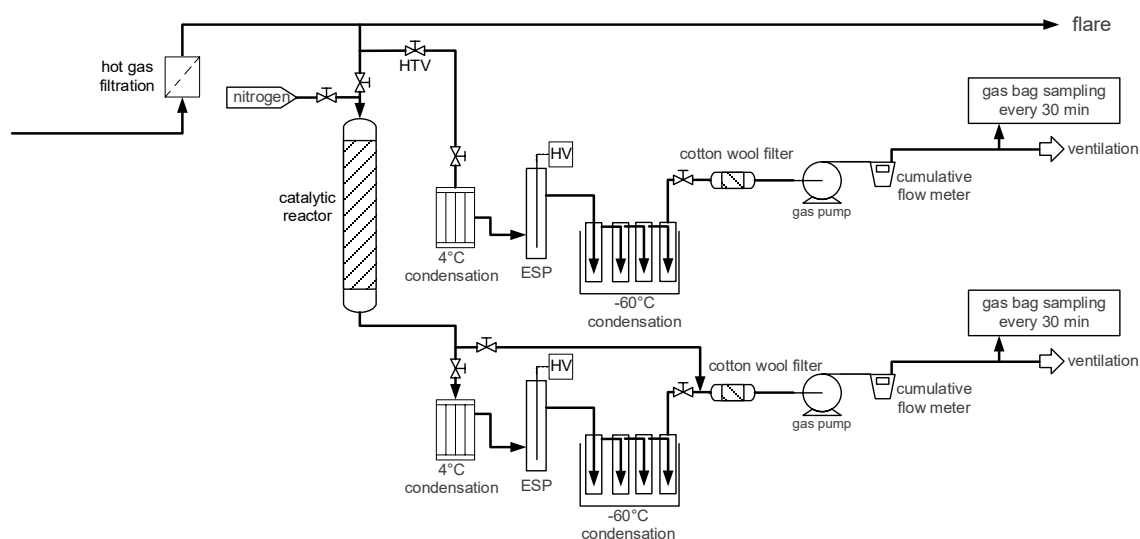

Figure 18. Test rig with two parallel condensation trains for condensation of tars and dry gas sampling.

The results of the gas composition analyses are presented in Table 5. The non-condensable gas after catalytic treatment showed a lower N$_2$ concentration of 9.6 vol.% N$_2$ during the initial 60 min of operation, while the N$_2$ concentration was measured to be ~14 vol% during the last 15 min. This shows that a higher production of other light gases occurred over the catalyst, thereby reducing the concentration of inert N$_2$. The reducing environment (high levels of CO and H$_2$) and the high levels of CH$_4$ could provide a suitable atmosphere for hydrodeoxygenation, and further tests in this direction, e.g. by using Pt-promoted TiO$_2$ catalysts is expected to yield oils with increased concentration of aliphatics.

Table 5. Gas composition (as measured) before and after catalytic upgrading of the pyrolysis gas from wheat straw pyrolysis.

gas composition (as measured)						
	RAW 0-30 min	CAT 0-30min	RAW 30-60 min	CAT 30-60min	RAW 60-75 min	CAT 60-75min
C$_6$+	0.02	0.0	0.05	0.0	0.04	0.0
Methane	13.80	13.6	13.75	13.7	12.97	12.9
Ethane	2.37	2.4	2.38	2.4	2.23	2.2
Ethene	1.22	1.3	1.10	1.2	0.95	1.0
Propane	0.49	0.5	0.52	0.5	0.49	0.5
Propene	0.79	0.9	0.77	0.8	0.69	0.8
n-Butane	0.07	0.1	0.08	0.1	0.08	0.1
trans-2-Butene	0.07	0.1	0.08	0.1	0.07	0.1
1-Butene	0.12	0.1	0.12	0.1	0.11	0.1
Iso-butylene	0.08	0.1	0.08	0.1	0.08	0.1
cis-2-Butene	0.06	0.1	0.07	0.1	0.06	0.1
CO$_2$	41.10	40.6	40.30	40.0	37.58	36.5
Nitrogen	10.4	9.6	10.3	9.6	15.2	13.6
CO	20.06	19.5	19.61	19.4	17.99	17.7
Hydrogen	9.36	11.3	10.74	11.9	11.45	14.5

When looking at the properties of the collected liquids, it appears striking, that the bio-oil yield hardly decreased after catalytic treatment (see Table 6) even though a clear deoxygenation (and therefore oxygen removal of CO/CO$_2$/H$_2$O from the liquid-range organics) was obtained. However, this can be explained by ketonization, i.e. C-C coupling of acids during deoxygenation for this catalyst as was previously observed. Furthermore, this likely resulted in a more favorable phase separation between the oil and aqueous phase. Despite the clear carbon losses to gas and coke by the vapor upgrading, the remaining organics are less polar, and therefore dissolve less in the water-rich phase. As an example, acetic acid and propionic acid are fully miscible in water, whereas its ketonization products butanone and pentanone only have a limited solubility in water of ~30 g/L.

Table 6. Key properties of the condensed liquid products; yellow = phases-separated aqueous phase; green = phase-separated oil phase.

Properties of collected liquid				
	untreated tars		tars treated with Na-Al$_2$O$_3$ (500 °C)	
	aqueous phase	oil phase	aqueous phase	oil phase
moisture content [wt%]	85.3	12.2	93.6	4.0
wt% N (d.b.)	n.d.	2.4	n.d.	1.7
wt% C (d.b.)	53.6	71.3	51.6	77.7
wt% H (d.b.)	n.d.	8.3	n.d.	8.6
wt-% O (d.b., by diff.)	n.d.	**18.0**	n.d.	**11.9**
HHV (d.b.) [MJ/kg]	n.d.	32.8	n.d.	36.0
HHV (w.b.) [MJ/kg]	n.d.	28.8	n.d.	34.6
H/C	n.d.	1.39	n.d.	1.32
O/C	n.d.	0.19	n.d.	0.11
effective hydrogen index	n.d.	0.92	n.d.	1.03
TAN [mg KOH/g]	n.d.	29.7	n.d.	4.6
revaporization efficiency [wt-% d.b.] at 350 °C	n.d.	91.5	n.d.	98.1

The moisture content and the acidity (TAN) of the condensed oil decreased from 12 wt% and 30 mg KOH/g to 4 wt% and 4.6 mg KOH/g, which shows a clear improvement in the oil properties. It is noteworthy that the TAN of the raw pyrolysis oil obtained from this slow pyrolysis test is in a similar range to previously collected oil from a LT-CFB gasifier with pyrolysis temperature 630-670 °C.

Contaminants in the pyrolysis gas

The produced pyrolysis gas was studied for compounds that would hinder the methanation process, by poisoning the applied, Ni-based catalysts. In this regard, the content of sulfur compounds is important to monitor in the gas. The sulfur measurements from wheat straw pyrolysis (Table 7) revealed that the H_2S and sulfide concentrations are quite significant and should be reduced to be able to apply the produced pyrolysis gas in a methanation setup.

Table 7. Sulfur measurements in the produced gas from wheat straw pyrolysis.

Sulfur content (ppm)	Sample 1 time 13:40	Sample 2 time 14:00	Sample 3 time 14:20
H_2S	>100	>100	>100
COS	>8	>8	>8
CS_2	0.12	0.12	0.13
Dimethylsulfid	>8	>8	>8
Methylmercaptan	7.4	7.5	7.6
Ethylmercaptan	4.8	4.9	5.2
N-propylmercaptan	2.05	2.01	2.13
Methyl isopropyl sulphide	>8	>8	>8
2-methylthiophen	2.49	2.33	2.58
3-methylthiophen	1.39	1.34	1.44
Unknown S	2.14	2.16	2.22

WP5 – BOP and energy system modelling

This work package involves two work tasks. In WT5.1, the complete TwoStage Electro-Gasifier was analyzed using thermodynamic modelling. In WT5.2, analyses of most suitable scale and way of integrating large scale P2G (or P2F) plants into the future Danish energy system was conducted.

WT5.1 – BOP modelling

DTU MEK has performed thermodynamic modelling and analysis on a system for flexible production of green methanol. The main idea behind the system is to integrate the electric grid with the production of green fuels using biomass. This includes the power-to-X concept, but also enables the system to produce power from biomass to the grid when renewable power from wind and solar is not available. Further operating modes are included so that the system can also operate without power consumption or production producing bio methanol. The system is named the flexible system and is based on using the so called TwoStage Electro-gasifier to generate syngas for methanol synthesis. The possible operating spectrum of the system is illustrated in Figure 19.
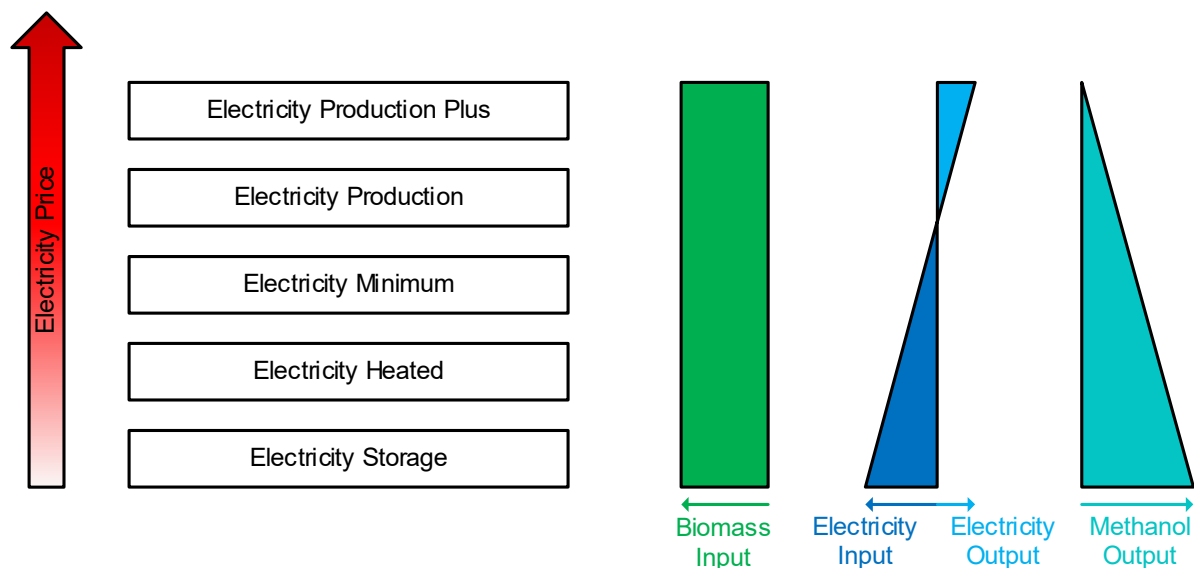
Figure 19. Operating spectrum of the flexible system with respect to the electricity price. The figure also shows the names of five distinct operating modes.

The difference between the five operating modes are mainly due to the way the SOC is operated (electrolysis mode, fuel cell mode or heated mode) but also the way the char gasifier is operated (air injection or electric heated). The different ways the Electro-gasifier can be operated can be seen in Figure 20 below. The fifth operating mode (electricity production plus) is where the syngas is used for electricity production (not used for methanol production).

The thermodynamic modeling of the Electro-Gasifier showed an input to output efficiency between 91.5% and 94.3%, comparable with the biomass-to-syngas conversion efficiency of the conventional TwoStage Gasifier. The partial oxidation with air, used to provide heat to the char gasifier in the electricity production mode, introduces nitrogen in the syngas (~11 vol.%): this affects negatively the downstream methanol synthesis. In the other modes, the produced syngas is nitrogen free and suitable for an efficient gas-to-liquid conversion. The ash collected at the bottom of the fluid bed contains only carbon (80 wt.%) and ash, representing a loss of ~4% of the input biomass LHV. An analysis on the reactivity at the top of the char gasifier demonstrated that the electricity storage mode represents the most critical operation, due to the simultaneous high and low fractions of H_2 and H_2O, respectively.
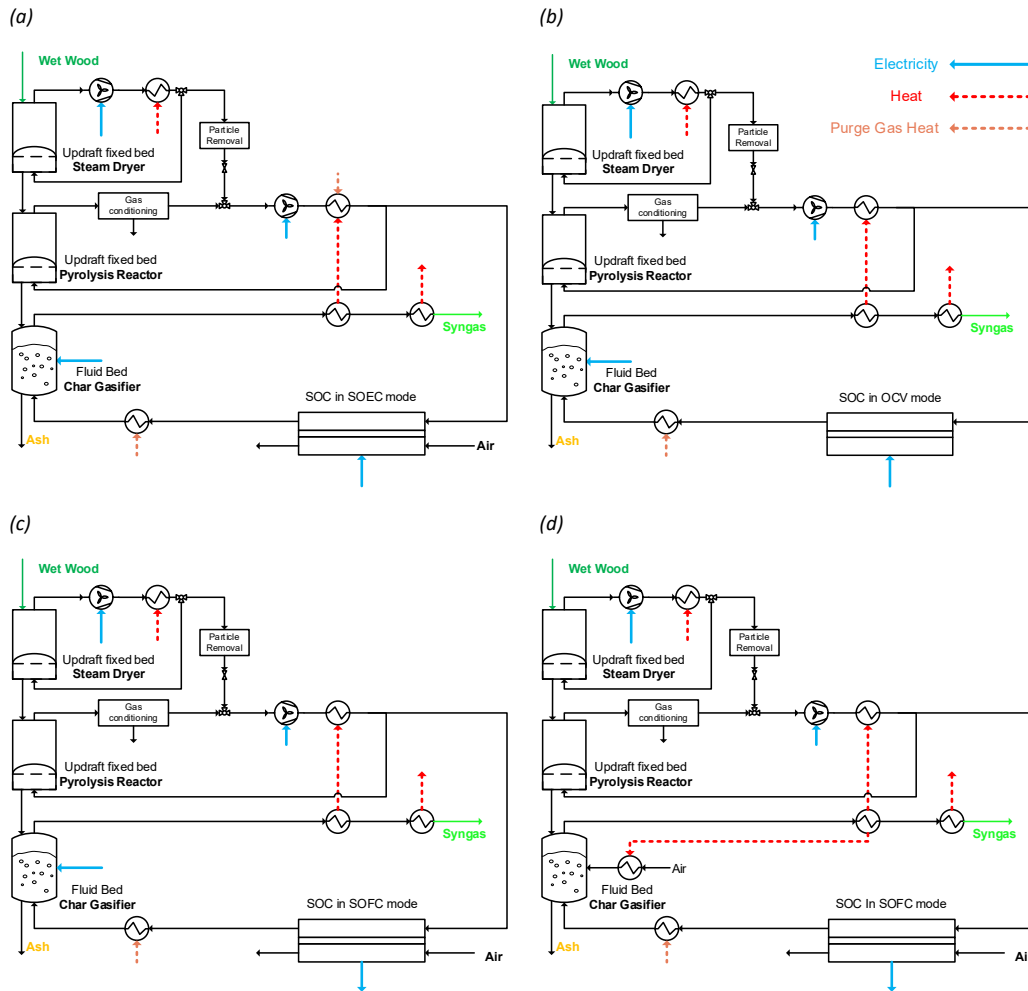
Figure 20. The four operating modes of the TwoStage Electro-Gasifier: (a) electricity storage mode, (b) electricity heated mode, (c) electricity minimum mode and (d) electricity production mode.
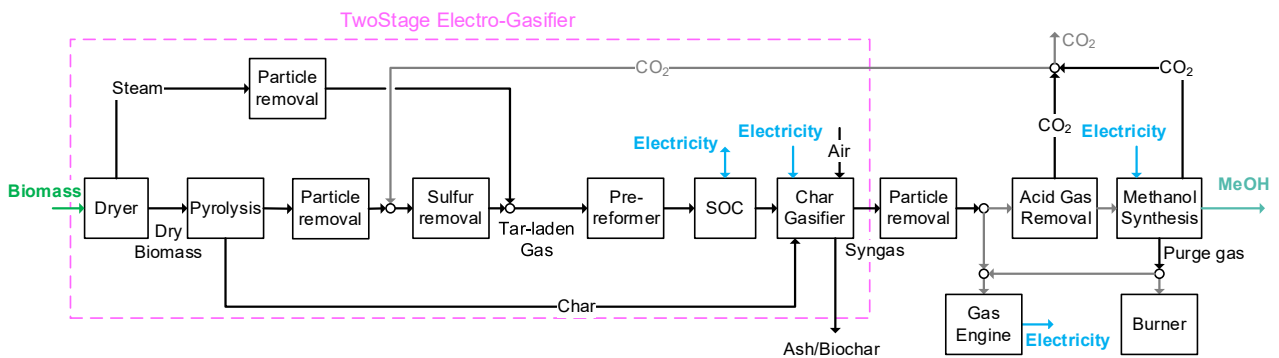
Figure 21. Schematic flowsheet of the complete system for biomass conversion to methanol based on the Electro-Gasifier.

The complete methanol production system is shown in Figure 21. The system can be gradually adjusted between the modes, thus creating a spectrum of possible operating points. When the SOC acts as electrolysis cell, CO_2 is recirculated from the acid gas removal and the topping column back to the SOEC. This increases the electricity consumption and the carbon conversion (up to 92%), and consequently the methanol yield.

The system efficiencies ranges from 70% at very low electricity price to 37% when producing only electricity (Table 8). The system outperforms previous solutions for methanol synthesis from biomass gasification in

terms of efficiency, in addition to the flexibility that allows to operate no matter the electricity price. The SOC operates at 850 °C with current densities ranging from -1 to 0.40 A/cm^2. The SOC benefits a low fuel utilization factor UF in both SOEC and SOFC mode (31-35%), which should prevent equilibrium carbon formation when combined with a sufficiently high *H/C* ratio (6.4-7.5).

Table 8. Energy flows and efficiencies for the five operating modes (LHV, dry basis).

	Electricity storage (ES)	Electricity heated (EH)	Electricity minimum (EM)	Electricity production (EP)	Electricity production plus (EPP)
Input [MW]					
Dry biomass	100.00	100.00	100.00	100.00	100.00
Electric power	83.18	29.90	17.98	-	-
Syngas [MW]	159.74	111.54	90.52	84.18	84.18
Output [MW]					
Methanol	129.13	90.40	74.84	36.50	-
Electric power	-	-	-	7.88	36.98
Efficiencies [%]					
Efficiency[a]	70.5	69.6	63.4	44.4	36.98
Biomass to MeOH	129.1	90.4	74.8	36.5	-
Carbon efficiency	91.9	64.7	52.5	26.4	-

[a] Efficiency is calculated as the input to output efficiency.

A comparison of the system based on the Electro-Gasifier with alternative solutions was published in Paper 13 (see below). It showed that: (1) the Electro-Gasifier guarantees the highest efficiency and carbon conversion; (2) the Electrically heated TwoStage gasifier is comparable with the Electro-Gasifier, enabling a safer operation of the SOC on tar-free gas; (3) the bubbling fluid bed with tar reformer has a slightly lower carbon conversion (biomass to methanol) and efficiency, mainly due to a lower carbon conversion inside the fluid bed; (4) the pressurized entrained flow gasifier represents the weakest solution as torrefaction is used before grinding process, and the released volatiles are not used. Possible solutions to increase the potential of the entrained flow gasifier are to skip the torrefaction step and instead grind woodchips, or using volatiles from torrefaction for a chemical quench.

A techno-economic analysis of methanol production units based on the Electro-Gasifier has also been performed. The system is compared with two single-mode production units, to investigate potential advantages of the flexible unit. One of the single-mode methanol production units is represented by the electricity storage single-mode of the flexible unit. The other single-mode solution is a more conventional layout obtained by coupling the TwoStage gasifier and steam electrolysis. The single-mode facilities are conceived to produce biofuel only from biomass feedstock and renewable electricity. The flexible production unit has the highest capital cost, followed by the electricity storage single-mode unit and the conventional unit (Figure 22).
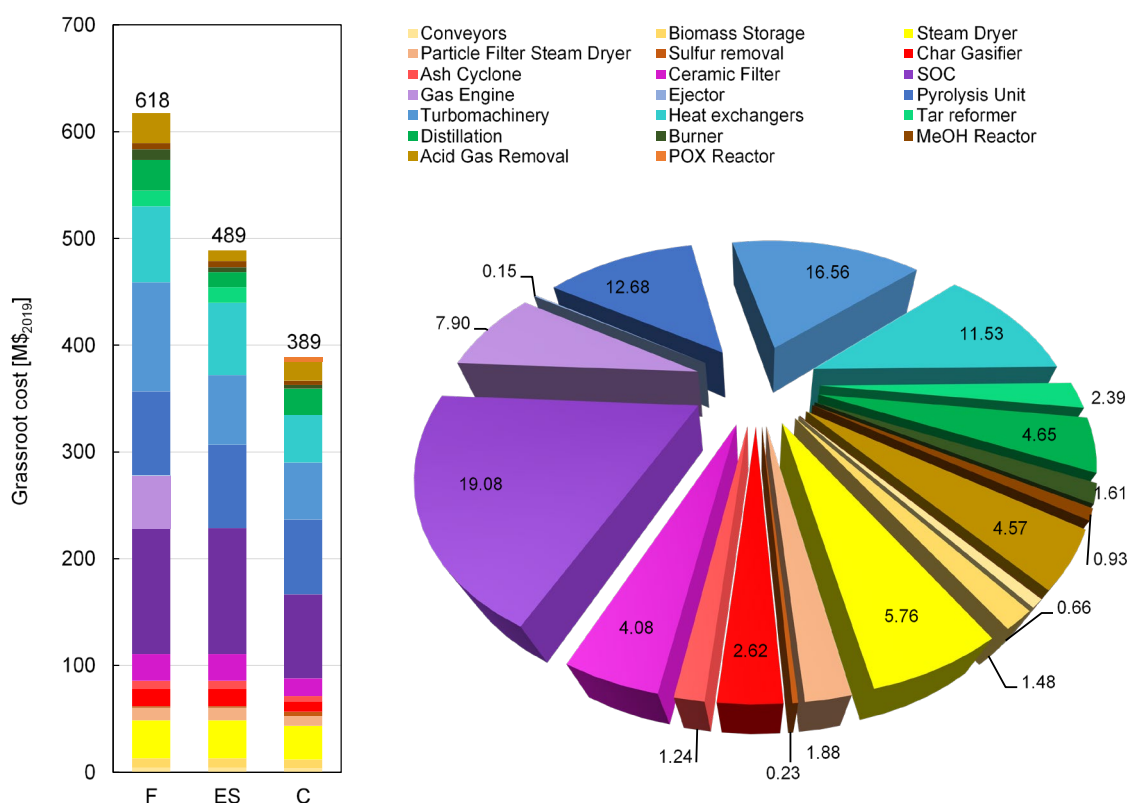
Figure 22. (left) Absolute grassroot costs for the flexible (F), electricity storage (ES) single-mode, and conventional (C) single-mode production units. (right) Percentage grassroot cost distribution for the flexible production unit.

The fuel production costs have been analyzed based on real and projected electricity prices in Denmark (data retrieved from Energinet.dk). The fuel production cost was decomposed to identify the major cost factors, which resulted to be the electricity cost and the biomass feedstock price (Figure 23). The Minimum Fuel Selling Prices (MFSPs) were computed through a Discounted Cash Flow Rate of Return (DCFROR) analysis. In order to generate profit and reduce the payback period, it is necessary that the actual bio-methanol selling price is above the MFSP. The profitability analysis showed that it is generally difficult to identify a generally most-competitive solution. The conventional unit generally offers the lowest MFSPs and shortest payback periods. However, the electricity storage single-mode solution is usually more competitive at current bio-methanol sell-ing prices. In addition, the electricity storage single-mode ensures a larger annual methanol throughput (+25% compared to the conventional solution). The larger methanol production is the real objective of methanol pro-duction plants based on biomass thermochemical conversion, as this ensures a better exploitation of the car-bon stored within the biomass, which is the scarce resource. In this perspective, it is relevant to introduce supportive incentives to support and reward those methanol production facilities guaranteeing an enhanced overall carbon conversion from biomass to methanol. In case of supportive policies, the electricity storage single-mode would definitely be the most competitive solution. The flexible production unit does not seem competitive compared to the electricity-storage single-mode. MFSPs for the conventional and electricity stor-age single-mode are usually below the actual bio-methanol selling price range, while this is not always true for the flexible production unit. MFSP and MeOH production costs are generally higher than production cost of methanol for solutions not involving solid oxide electrolysis (SOC) – using WGS units instead. However, the methanol production from the same biomass feedstock is usually doubled when using SOC. Lastly, price of bio-methanol will likely always be higher than for fossil-methanol.
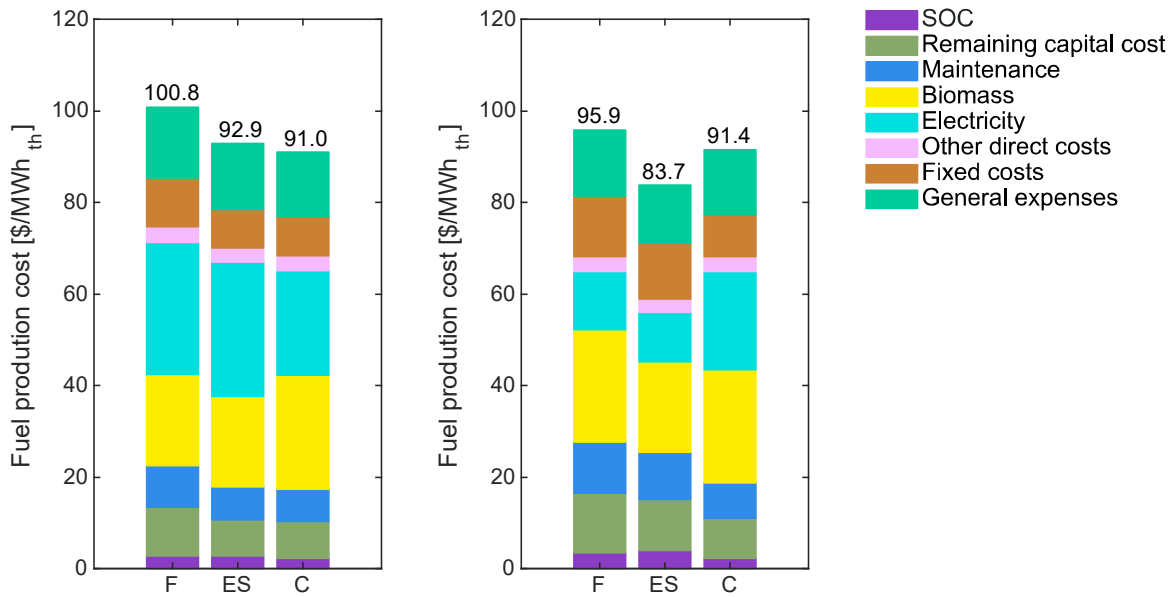
Figure 23. Methanol production cost or Minimum Fuel Selling Prices (MFSPs) and distributions for the flexible (F) electricity storage (ES) and conventional (C) methanol production units. (left) scenario 2019, (right) scenario 2040. The SOC share included also the cost associated with the replacements.

From a societal or TSO perspective, the flexible system will avoid the construction of a backup power plant, whose size corresponds to the maximum power produced by the flexible system. An analysis was performed on the MFSP of the flexible system, by subtracting the cost of a natural gas backup power plant with carbon capture, as this corresponds to an avoided cost for society and the TSO. The analysis showed that, by accounting for the societal benefit of the flexible system, the system ensured MFSPs e.g. in the range 82-97 $/MWhth in scenario 2019, or in the range 62-83 $/MWhth in scenario 2040. In this situation, the flexible system is generally more competitive than the single-mode facilities.

WT5.2 – Energy system modelling

In the WT5.2 Energy System Modelling, three focused approaches were conducted during the project period. The summary of the results is provided below and has been adapted from the research publications.

Energy System Modelling (see Paper 21 for details)

Energy system modelling of the role of the biomass gasification routes in the energy system was carried out. The hour-by-hour energy system analysis considered both Danish (DK) and European (EU)100% renewable energy system in year 2050. The modelling was carried out in the EnergyPLAN software. The reference systems were then compared to the alternative scenarios where renewable fuel production pathways from the reference systems were displaced by pathways using solely PtX fuels by biomass gasification + H_2 route (bio-electrofuels) or solely PtX fuels based on CCU route (CO_2-electrofuels). This approach focuses only by displacing liquid or gaseous hydrocarbons and does not interfere with electrification of the transport from the reference energy systems (EU and DK). The end-fuels considered are methanol, methane and Fischer-Tropsch liquids.

The European model was based on the European Commissions' one of the most ambitious scenarios - 1.5 TECH model. The model was converted to the EnergyPLAN model and calibrated with the similar boundaries as the Danish model, allowing for 10% of the excess electricity production and minimizing it by reduction of variable renewable energy sources. Both models are designed as closed systems that are balanced by gas fired power-plants in case of lack of renewable power production. In the transport sector, the personal vehicles, light-duty vehicles and rails are electrified (80-90%), busses and heavy-duty road transport use a mix of

drivetrains, batteries, fuel cells, liquid and gaseous fuels. Marine and aviation are supplied with fuel mix based on biofuels, electrofuels and some fossil fuels. Offset of fossil fuels used is done by implementation of carbon capture and storage (CCS). The Danish model is based on the Smart Energy System model that maximized the synergies between energy grids and energy storages, by providing robust energy system with high degree of flexibility enabled by cross-sectorial integration. In comparison the European model is less detailed on the transport sector and is originally based on the evolution of the traditional fossil-based system and therefore lacks the utilization of excess heat and has less electrolysis. This enables to test the impact of the same technology on the two types of energy system designs.

The considered end-fuels were replacing another transport fuel in the reference scenarios either through the bio-electrofuel pathway or through the CO_2-electrofuel pathway, both pathways having three sub scenarios, as follows and as illustrated in Figure 24.

- Methanol for heavy-duty road and maritime transport, while aviation utilizes jet fuel produced through the methanol-to-kerosene synthesis (HydroMeOH scenarios).
- Fischer-Tropsch liquids to produce diesel for heavy-duty road transport and shipping combined with jet fuel for aviation (HydroFT scenarios).
- Liquefied methane (LMG) as fuel for heavy-duty road transport and shipping, while aviation uses jet fuel produced through the gas-to-liquids process (HydroGTL scenarios).

This analysis highlighted that bio-electrofuels or PtX fuels produced via biomass gasification route enhance the utilization of renewable electricity and reduce the overall energy system costs in comparison to CCU route fuels. Interestingly this route also shows that the overall biomass consumption in the system would be even higher without the biomass gasification even though these fuels are still biomass intensive. However, CO_2 electrofuels can complement bio-electrofuels depending on biomass and CO_2 source availability.
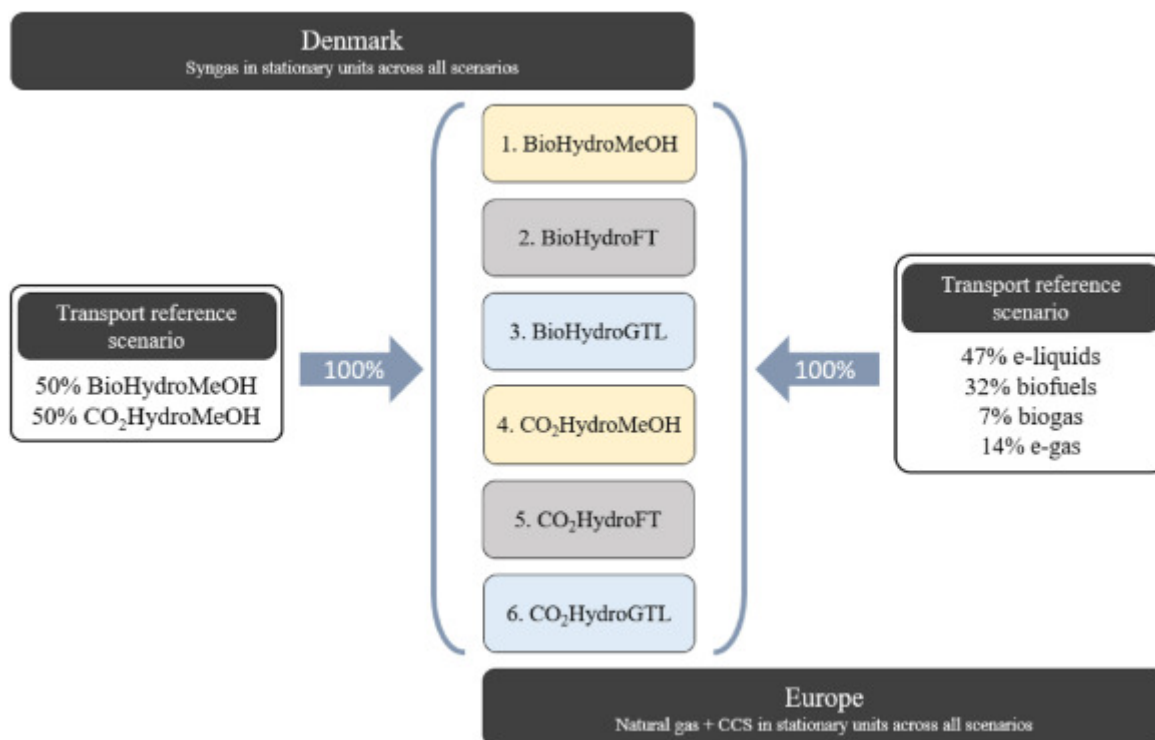

Figure 24. The six 'extreme' scenarios in the transport sector produced as bio-electrofuels or CO_2-electrofuels.

Potential Niche Markets, Regulatory Framework and Incentive Structures of P2X (see Paper 22 for details)

As a part of WT 5.2, analysis of strengths, weaknesses, opportunities, and threats (SWOT) of Power-to-X in Denmark was conducted to further investigate niche markets and suggestions for incentive structures and public regulation to push the development of this technology. Originally it was planned to conduct this work with a Power-to-X workshop with Danish actors, scheduled for 24th of March 2020, with 35 participants that have signed up for the event. Due to the COVID-19, the workshop had to be cancelled, therefore the data gathering has been adapted to the situation and study was redesigned to a two-stage empirical study where four main expert groups were involved (i) academia, (ii) public authorities, (iii) energy providers/network operators, and (iv) technology producers. Individual experts from academia (i) were chosen based on their number of publications on P2X or related topics that are listed in the literature database Scopus. The Danish practitioners (ii–iv) were chosen according to their actual involvement or keen interest in P2X projects.

First empirical round was based on expert interviews to identify the SWOT-factors, where eleven actors were interviewed. Interviews were transcribed and qualitative content analysis was conducted to identify commonly mentioned SWOT-factors. The outcome of the analysis were 4 factors for each of SWOT categories (see Table 9). In the second round, experts were asked to judge the relative importance of the SWOT factors. Based on the identified SWOT-factors an online survey has been created and sent in May 2020 to 67 experts from the targeted groups of which 28 completed it. Response rate was therefore 41.8%. The results of the survey were analysed by using the Analytic Hierarchy Process (AHP) method according to Saaty[3]. In addition to SWOT-factor analysis, additional qualitative statements on potential niche markets as well as on regulatory framework and incentive structures were included in the second part of the survey. Experts were asked to assess their level of agreement with 24 statements on a seven-level Likert scale.

Table 9. SWOT-factors identified by first round of expert interviews.

	Positive	Negative
	Strengths	**Weaknesses**
Internal	Sa: P2X improves system flexibility	Wa: P2X lacks cost competitiveness due to electricity price and electrolysis CAPEX
	Sb: P2X enables sector coupling	Wb: P2X lacks upscaling and manufacturing production capacity
	Sc: P2X provides a large spectrum of end-products that are compatible with existing infrastructure and equipment	Wc: P2X technologies have low production efficiency
	Sd: P2X contributes to decarbonize parts of transport sector not suitable for direct electrification	Wd: P2X technologies are immature and have short lifetime (electrolysis)
	Opportunities	**Threats**
External	Oa: The European Union ambitious climate targets support further expansion of renewable energy.	Ta: Competitive technologies are more visible and economically attractive
	Ob: Consensus on limited biomass availability and the need to minimise its use	Tb: Uncertainty upon fuel market readiness or support schemes.
	Oc: Existing district heating networks can benefit from excess heat from the P2X processes.	Tc: Rising electricity prices
	Od: Denmark is a P2X knowledge hub.	Td: Uncertainty on the climate agenda due to external shocks such as the COVID-19 pandemic

The results (as an illustration in Figure 25 shows answers by practitioners) show that positive factors are considered more important than their negative counterparts, with the only difference in the order assigned to them, the academics stress factors from the strengths category as the most important and practitioners' opportunities. The experts see the potential developments and current frameworks in the surrounding system, in which technology is to be implemented, is more important than the technology-inherent factors. Both expert groups point to Denmark being a P2X knowledge hub as a driver for this technology, both locally but also as being a knowledge exporter. P2X could be seen as a new industrial success story in Denmark due to the

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[3] Saaty, T.L. Decision Making for Leaders: The Analytic Hierarchy Process for Decisions in a Complex World; RWS Publications: Pittsburgh, PA, USA, 1999

strong industrial environment, wind developments, and already high share of renewable electricity in the energy system. Danish experts agree that the main contribution for P2X technology should be its application in the transport sector, as a solution for the decarbonisation of the aviation and shipping sectors as well as long-haul road transport. Even though more consistency is under the Strength and Threats category, the Opportunities and Weaknesses categories indicate some disagreements between two expert groups. While industrial experts are concerned about the absence of cost competitiveness, in connection with the uncertainty upon fuel market readiness or support schemes, academics are pointing towards the lack of the production capacity and current technological development status. Finally, both expert groups highlight the need for improving the current regulatory framework to enable the faster deployment of this technology.
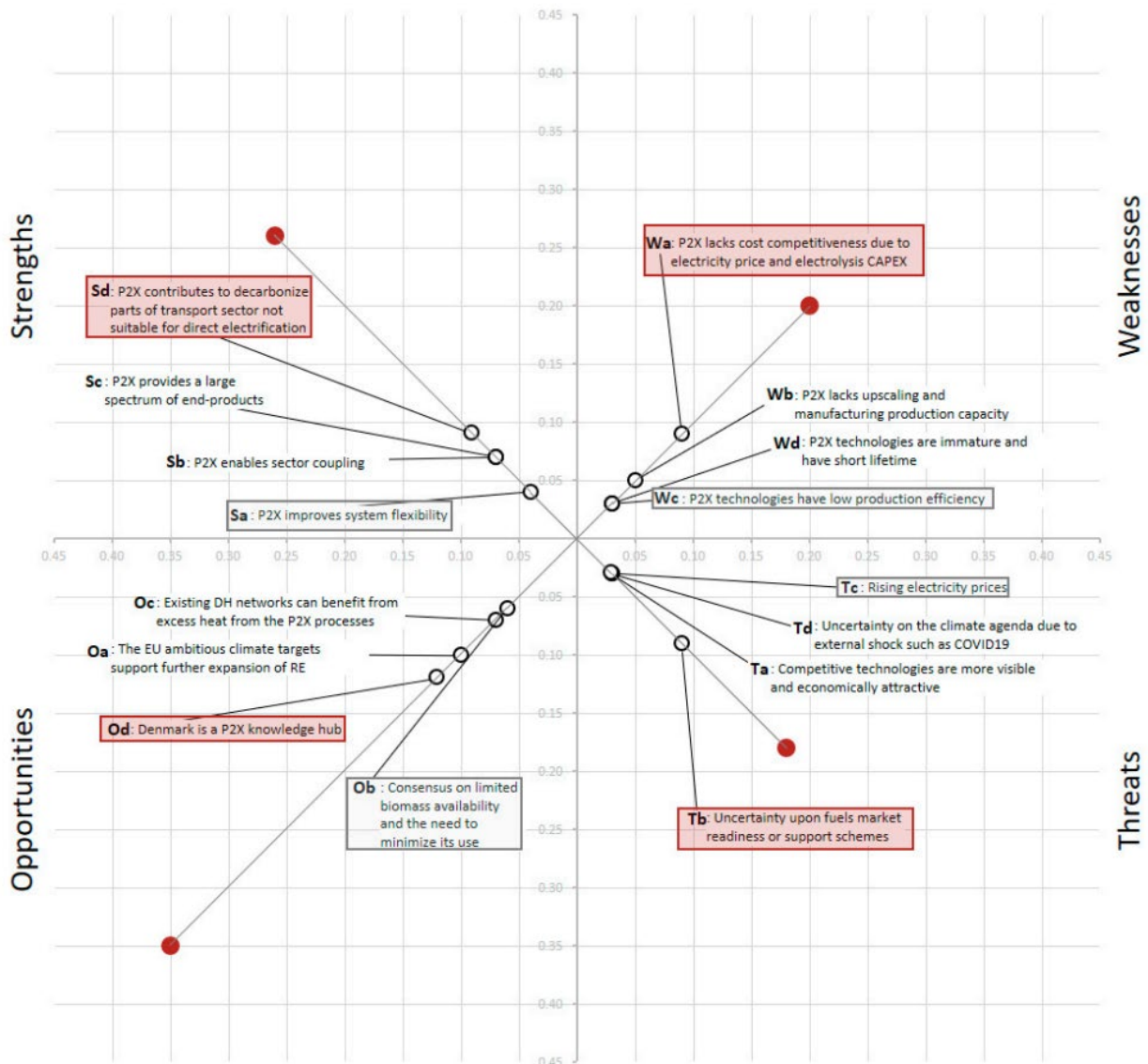
Figure 25. Illustration of integrated SWOT-AHP analysis results for practicioners. The highest importance in the field is market in yellow, and the lowest in grey.

The experts highly disagree that there are enough public funding opportunities for P2X. This is also in line with the SWOT-AHP results, where experts agree that there is a need for further funding and support schemes to outset the implementation of this technology, most importantly for innovation markets. The experts highly agree that P2X fuels need to meet a mandatory low carbon footprint to contribute to reductions of carbon emissions.

This is in line with different types of P2X and especially targets the origin of carbon source for carbon based P2X products. Targeting P2X towards specific markets could enable faster deployment, and experts point towards aviation fuels and shipping to be the most attractive markets. Another possible application is in the chemical industry to displace fossil-based products.

Incentive structures for Power-to-X and e-fuel pathways
Lastly, review of the current incentive structures for PtX and electrofuels pathways was conducted including the updates in the main aspects of the legal framework in the European Union from 2019 to mid-2021 related to Power-to-X: support schemes, specific targets, and potential barriers. The problematization of different terminologies used in the legislation has been highlighted. Current legislative framework is using many cross-terms such as Power-to-X (PtX), Power-to-liquid (PtL), Power-to-gas (PtG), Renewable fuels of non-biological origin (RFNBO), Recycled carbon fuels (RFC), hydrogen-derived synthetic fuels, alternative fuels and electro-fuels.

The results show growing interest and slow market entrance of electrolysis and push from the different actors and regulatory parties to establish solutions that will enable faster upscaling. However, it is visible from the National Energy and Climate Plans and hydrogen strategies that the most emphasis is still on hydrogen as end-fuel for personal vehicles or power-to-gas. It seems that only few countries have implemented legal frameworks facilitating diverse PtX pathways without focusing solely on hydrogen, and Denmark being one of them having a dedicated PtX strategy rather than hydrogen strategy. The recent advances in the EU legal framework and some MSs show early signs of policies changing towards more substantial focuses on e-fuels and recognition of the role these fuels could have in the decarbonisation of the transport sector. It is visible that there are tendencies for agreeing where electrofuels should be applied and which fuels should meet the demands in aviation, marine and long-haul road transport supported by initiatives such as FuelEU Aviation Initiative and FuelEU Maritime Initiative. However, the supporting infrastructure schemes will arrive earliest in 2025, which could have an impact on the rolling out of these technologies. Finally, the holistic approach that would result in reliable roadmaps and strategies for PtX and electrofuels could enable a more stable and predictable legislative framework for investments and consider the future benefits and need for these technologies.

It has been identified that Denmark is currently leading in announcing and planning the big scale projects.

Dissemination

The results obtained in this project were generated and presented as research papers, theses, and/or conference presentations, as listed below:

Research paper:

1. M. Chen, R. Küngas, J. J. Bentzen, S. Molin, P. Blennow, K. Norrman, "Post-mortem analysis of a 25-cell solid oxide electrolysis stack operated for 9000 hours"; pp. B1506 in Proceedings of the 13th European SOFC & SOE Forum 2018, Lucerne, Switzerland, 2018.
2. X. Tong, P. V. Hendriksen, A. Hauch, and M. Chen, "Development of Solid Oxide Electrolysis Cells for Hydrogen Production at High Current Densities", *ECS Transactions,* **91** 2433-2442 (2019). https://doi.org/10.1149/09101.2433ecst
3. R. Küngas, P. Blennow, T. Heiredal-Clausen, T. Holt Nørby, J. Rass-Hansen, J. B. Hansen, and P. G. Moses, "Progress in SOEC development activities at Haldor Topsoe", *ECS Transactions,* **91** 215-223 (2019). https://doi.org/10.1149/09101.0215ecst
4. S. Ovtar, X. Tong, J. J. Bentzen, K. T. S. Thyden, S. B. Simonsen, and M. Chen, "Boosting the performance and durability of Ni/YSZ cathode for hydrogen production at high current densities via decoration with nano-sized electrocatalysts", *Nanoscale,* **11** 4394-4406 (2019). http://dx.doi.org/10.1039/C8NR07678B
5. X. Tong, S. Ovtar, K. Brodersen, P. V. Hendriksen, and M. Chen, "A 4 × 4 cm^2 Nanoengineered Solid Oxide Electrolysis Cell for Efficient and Durable Hydrogen Production", *ACS Applied Materials & Interfaces,* **11** [29] 25996-26004 (2019). https://doi.org/10.1021/acsami.9b07749
6. M. Trini, P. S. Jorgensen, A. Hauch, J. J. Bentzen, P. V. Hendriksen, and M. Chen, "3D Microstructural Characterization of Ni/YSZ Electrodes Exposed to 1 Year of Electrolysis Testing", *Journal of The Electrochemical Society,* **166** F158-F167 (2019). https://doi.org/10.1149/2.1281902jes
7. G. Butera, S. H. Jensen, R. Ø. Gadsbøll, J. Ahrenfeldt and L. R. Clausen, "Biomass Conversion to Methanol Integrating Solid Oxide Cells and Two-Stage Gasifier: Effects of Carbon Dioxide Recirculation and Pressurized Operation", Chemical Engineering Transactions, vol. 76, p. 1177-1182, 2019. https://doi.org/10.3303/CET1976197
8. M. Chen, K. Cheng, H. Xu, L. Zhang, M. Trini, S. D. Angelis, and P. V. Hendriksen, "Modeling of microstructure evolution in solid oxide cells"; pp. A0905 in *14th European SOFC & SOE Forum 2020*, Lucerne, Switzerland, 2020.
9. X. Tong, Y. Xu, Đ. Tripković, P. V. Hendriksen, W.-R. Kiebach, and M. Chen, "Promotion of oxygen reduction and evolution by applying a nanoengineered hybrid catalyst on cobalt free electrodes for solid oxide cells", *Journal of Materials Chemistry A,* **8** 9039-9048 (2020). https://doi.org/10.1039/D0TA02979C
10. X. Tong, P. V. Hendriksen, A. Hauch, X. Sun, and M. Chen, "An Up-scalable, Infiltration-Based Approach for Improving the Durability of Ni/YSZ Electrodes for Solid Oxide Cells", *Journal of The Electrochemical Society,* **167** 024519 (2020). https://doi.org/10.1149/1945-7111/ab6f5c
11. X. Tong, S. Ovtar, K. Brodersen, P. V. Hendriksen, and M. Chen, "Large-area solid oxide cells with La$_{0.6}$Sr$_{0.4}$CoO$_{3-\delta}$ infiltrated oxygen electrodes for electricity generation and hydrogen production", *Journal of Power Sources,* **451** 227742 (2020). https://doi.org/10.1016/j.jpowsour.2020.227742
12. M. Trini, A. Hauch, S. De Angelis, X. Tong, P. V. Hendriksen, and M. Chen, "Comparison of microstructural evolution of fuel electrodes in solid oxide fuel cells and electrolysis cells", *Journal of Power Sources,* **450** 227599 (2020). https://doi.org/10.1016/j.jpowsour.2019.227599
13. G. Butera, S. Fendt, S. H. Jensen, J. Ahrenfeldt and L. R. Clausen, "Flexible methanol production units coupling solid oxide cells and thermochemical biomass conversion via different gasification technologies", Energy, vol. 208, 2020. https://doi.org/10.1016/j.energy.2020.118432
14. G. Ravenni, Z. Sárossy, S. Sanna, J. Ahrenfeldt, U. B. Henriksen, "Residual gasification char applied to tar reforming in a pilot-scale gasifier: Performance and evolution of char properties for perspective cascade uses", Fuel Processing Technology, 210, 106546, 2020. https://doi.org/10.1016/j.fuproc.2020.106546

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17. X. Sun, Y. Liu, P. V. Hendriksen, and M. Chen, "An operation strategy for mitigating the degradation of solid oxide electrolysis cells for syngas production", Journal of Power Sources, 506, 230136 (2021). https://doi.org/10.1016/j.jpowsour.2021.230136

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19. M. Chen, X. Tong, and S. Ovtar, "Lessons Learned from Operating a Solid Oxide Electrolysis Cell at 1.25 A/cm^2 for One Year", *ECS Transactions,* **103** [1] 475-486 (2021). http://dx.doi.org/10.1149/10301.0475ecst

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<u>Thesis:</u>
1. Giacomo Butera, PhD thesis, "Techno-economic analysis of methanol production units coupling solid oxide cells and thermochemical biomass conversion via the TwoStage gasifier", Technical University of Denmark, 2021. https://doi.org/10.1016/j.fuproc.2020.106718

2. Andrea Sainz Mapes, Master thesis, "Polygeneration of bio-oil and synthetic natural gas (SNG) based on biomass pyrolysis and water electrolysis", Technical University of Denmark, 2021.

3. Lidia Benedini, Master thesis, "Production and characterization of bio-oil from pyrolysis", Technical University of Denmark, 2021.

<u>Conference presentation:</u>
1. Peter Stanley Jørgensen, "Characterization of Three Dimensional Transport Networks in a Long-Term Tested Solid Oxide Electrolysis Cell", oral presentation at the 4th International Congress on 3D Materials Science (3DMS) 2018, Copenhagen (Denmark), June 10-13, 2018.

2. Janet Jona Bentzen, "Post-mortem analysis of a 25-cell solid oxide electrolysis stack operated for 9000 hours", oral presentation at the 13th European SOFC & SOE Forum 2018, Lucerne (Switzerland), July 3-6, 2018.

3. Xiaofeng Tong, "Strategy for enhancing stability of solid oxide electrolysis cells at high current density", poster presentation at the 13th European SOFC & SOE Forum 2018, Lucerne (Switzerland), July 3-6, 2018.

4. Xiaofeng Tong, "Development of Solid Oxide Electrolysis Cells for Hydrogen Production at High Current Densities", poster presentation at the 16th International Symposium on Solid Oxide Fuel Cells (SOFC-XVI), Kyoto, Japan. September 8-13, 2019.

5. Rainer Küngas, "Progress in SOEC development activities at Haldor Topsoe", oral presentation at the 16th International Symposium on Solid Oxide Fuel Cells (SOFC-XVI), Kyoto, Japan. September 8-13, 2019.
6. Ming Chen, "Modeling of microstructure evolution in solid oxide cells", oral presentation at the 14th European SOFC & SOE Forum 2020, Lucerne, Switzerland, October 22-23, 2020.
7. Iva Skov, "Incentive structures for Power-to-X and e-fuel pathways for transport in EU and Member states", oral presentation at the 16th Conference on Sustainable Development of Energy, Water and Environment Systems, October 10-15, 2021 Dubrovnik, Croatia.
8. M. Chen, "Lessons Learned from Operating a Solid Oxide Electrolysis Cell at 1.25 A/cm^2 for One Year", oral presentation at the 17th International Symposium on Solid Oxide Fuel Cells (SOFC-XVII), July 18-23, 2021, Online.

6. Utilisation of project results

A number of good results have been achieved in the current project. The results obtained by DTU Energy, in particular improvements in performance and durability of SOEC cells, improved understanding of degradation mechanisms, and fruitful degradation mitigation strategies will be transferred to HTAS. These results also form the basis for the necessary further research and development at DTU Energy. The improved understanding of degradation behaviour at the SOEC stack and CORE level obtained by HTAS will be utilized in their further development of the SOEC technology. The brand new pyrolysis technology developed by DTU KT has awaken significant commercial interests. Stiesdal Fuel Technologies in close collaboration with DTU KT is upscaling and commercializing the new technology now. DTU is continuing the work initiated in EP2Gas in a newly started EUDP-supported project (64021-1114 – SkyClean 2 MW Process Development and Industrial Demonstration), where the current pyrolysis system will be upscaled, further tested and will pave the way for a full-scale pyrolysis plant, while bio-oil and syngas upgrading will be investigated in detail.

7. Project conclusion and perspective

The key outcome of the project can be summarized as the following:

- SOEC cells with enhanced performance and improved long-term durability, showing a low degradation rate of 20 mV/kh at -1.25 A/cm^2 with actual demonstration over years.
- A phase field model capable of modelling the 3D microstructure evolution of the Ni/YSZ electrode under different conditions.
- A confirmation that the SoA HTAS stacks (TSP-1) operate quite fine with no sweep gas to the oxygen electrode side.
- Demonstration of the multi-stack SOEC-CORE via a >13000h test, with a degradation rate of only 0.5%/kh at the CORE level during the first 9 kh.
- A brand new pyrolysis reactor for handling different biomass feedstocks designed, built and successfully tested.
- Successful integration of pyrolysis, SOEC and gas cleaning, ensuring high quality of syngas for further methane synthesis.
- An analysis of the TwoStage Electro-Gasifier system with regard to system efficiency and fuel production cost, in comparison with the competing technologies.
- An SWOT analysis of Power2X in Denmark, pointing to Denmark being a P2X knowledge hub and highlighting the need for improving the current regulatory framework to enable the faster deployment of the technology.

The good results achieved in the current project will form the basis for the necessary further research and development at DTU and AAU. More importantly, they will be transferred to the industry (HTAS, Stiesdal Fuel Technologies, etc.) to accelerate the actual technology development and commercialization. Stiesdal Fuel Technologies is upscaling and commercializing the new pyrolysis technology developed by DTU KT. HTAS is accelerating the development of SOEC technology in the coming years to accommodate the increased interest and to future mature the SOEC technology for the growing commercial markets. The increased focus on the "green transition" has put Power-to-X much higher on the agenda, both technically as well as politically. This bodes well for the technologies developed and demonstrated in this project. With Denmark's ambitions of 70% decrease in CO_2 emissions by 2030, it is essential that all available technologies are used. The results obtained in the series of ForskEL and EUDP projects including the current project played a key role in achieving the development targets necessary for commercialization of the Danish SOEC and Power2X technologies.

8. Appendices