Final report

1.1 Project details

Project title	Ny metode til opgradering af biogas (UPGRADE)
Project identification (program abbrev. and file)	Upgrade file 2016-1-12449
Name of the programme which has funded the project	ForskEl
Project managing company/institution (name and address)	Danish Power Systems ApS (DPS) Egeskovvej 9c 3490 Kvistgård
Project partners	Elplatek DTU-Energy DTU-Mechanics
CVR (central business register)	17913301
Date for submission	31-july 2019

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1.2 Short description of project objective and results

The UPGRADE project has aimed at proof of concept on cost efficient purification of biogas, as well as a new technology for direct conversion of CO_2 in biogas to methane with reduced energy consumption.

Gas purification system-units have been designed and tested on both synthetic and real biogas. Purification to acceptable levels of H_2S has been achieved, both in lab-scale purification of synthetic gas and in larger scale of real biogas. Further a reliable model has been established for the purification process, enabling further parameter optimisation.

Direct conversion of CO_2 in biogas to methane has been proven with high selectivity at 300 °C and 8 Bar. A liquid phosphate electrolyte is retained in a porous, reinforced membrane, and an electrocatalytic electrode is made from non-noble metal. Further, formation of DME, methanol and other higher hydrocarbons is shown to be possible.

UPGRADE-projektet har til formål at eftervise et koncept om omkostningseffektiv rensning af biogas samt en ny teknologi til direkte konvertering af CO_2 i biogas til metan med et reduceret energiforbrug.

Enheder til gasrensningssystemer er designet og testet på både syntetisk og reel biogas. Oprensning til acceptable niveauer af H2S er opnået, både ved rensning af syntetisk gas i laboratortiet og i større skala af reel biogas. Der er endvidere etableret en pålidelig model af rensningsprocessen, hvilket muliggør videre parameteroptimering.

Direkte omdannelse af CO_2 i biogas til metan er blevet påvist med høj selektivitet ved 300 ° C og 8 Bar. En flydende phosphatelektrolyt tilbageholdes i en porøs, forstærket membran, og en elektrokatalytiske elektrode er fremstillet af ikke-ædelmetal. Endvidere er dannelse af DME, methanol og andre højere carbonhydrider vist at være mulig.

1.3   Executive summary

A large and promising potential for contributing to the national environmental agenda lies within efficient utilisation of biogas, in particular if the present fraction of CO_2 can be upgraded to methane of a quality suitable for injection in the existing gas grid. The project Upgrade has set out to develop a new two-step concept for this, involving electrochemical gas purification and direct electrochemical methanisation (co-electrolysis) of the carbon dioxide. The gas purification technology has been developed and successfully demonstrated in conjunction with a biogas facility at at Nature Energy Midtfyn. The co-electrolysis upgrade of CO_2 to methane has been successfully established and demonstrated in laboratory scale at present.

1.4   Project objectives

The objective of the project is to develop a new concept for direct electrochemical methanisation (co-electrolysis) of the carbon dioxide contained in biogas, for upgrading to natural gas. The proposed concept can reduce the energy consumption with 20% compared to today's State of the Art (H_2 production by electrolysis and subsequent methanisation). The concept is furthermore expected to reduce the demands to the degree of purification of the raw biogas before methanisation very considerably.

The above objectives are deconvoluted into a series of technical challenges, forming the WP's of the project:
- Develop and document a process for initial purification of biogas (CH_4, CO_2 and ppm-ppb impurities)
- Construct and validate a test reactor for the co-electrolysis (design point: 8 Bar, 300 °C)
- Establish and test a membrane concept for the co-electrolyzer (molten phosphate salt contained in porous matrix)
- Establish and test electrode materials for the co-electrolyzer (metal or metal-supported structures with suitable performance)

- Test or demonstrate purification and co-electrolysis (run experimental purifier and co-electrolyzer on synthetic and real biogas)

The project consortium has proven to be well composed and fully integrated in the project execution. Sharing of samples and results have been dynamic, and fast adaptions have been made. Due to personal conditions (illness) among key staff and issues regarding permissions and preparations for installation and commissioning of the purification unit on the biogas-plant, the demonstration and purification activities were delayed, and a 6 month extension of the project has been granted. This extension allowed for real life test and validation of the purification processes on biogas at Nature Energy Midtfyn along with detailed analysis of the gas and thus provided proof of concept as well as valuable data for further development of the purification model.

4 of the 5 Deliverables and 4 of the 6 Milestones has been fully achieved as planned, whereas 1 Deliverable and 1 Milestone has been reached on a proof of concept/pilot scale individually but not in integration for the two technologies. The remaining 1 Milestone has been reached individually by the gas purification technology and not by the co-electrolysis technology, however this is considered a minor deficit as compared to other similar milestones.

1.5 Project results and dissemination of results

Initial purification of the biogas
Biogas is inherently polluted with various gasses and particulates which has to be removed. The most problematic compounds are S-containing, predominantly H_2S. An overview diagram of the developed technology is graphically presented in Figure 1. The set-up resembles the commercial gas scrubbing systems, the catalysts and liquid, however, differs greatly from commercial systems as additional cleaning processes are incorporated. The reactor has been constructed using corrosion resistant materials due to the gasses and chemicals being handled. The piping is made from standard PP and PMMA, where the PMMA is used for visual purposes, as to allow inspection of the system while operating. The technology is called 'electroscrubbing' and refers to the fact that an electrochemical cell is connected to the scrubber to oxidize active species for sulfur removal. Therefore an electrochemical cell was also part of the setup, initially consisting of two carbon electrodes.

Focus from this project have been to make sure the purified biogas quality is high enough for direct conversion by electrolysis. To demonstrate this, a biogas purification unit Figure 1 was constructed to experimentally purify biogas. Furthermore, a thermodynamic model was developed to confirm and enhance the capability of the purification technology.
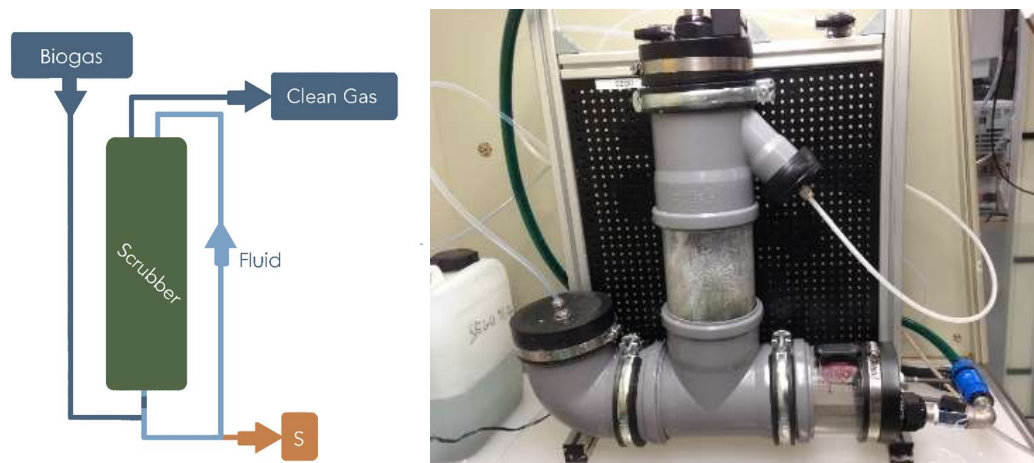

Figure 1 The electrocatalytic gas cleaning system (SEGO). Gas and liquid is mixed over a catalyst and combined with electrochemical treatment of the mixture

Different purification techniques have been tested in this unit by varying the active chemical compounds used for purification. Finally, the combination of an electroscrubber and an activated carbon filter was chosen as the most promising (**Deliverable 1, MS1)**. For the electroscrubber, different active compounds were tested, however, only the halides had sufficient regeneration for applications. Activated carbon is a very good and well known sulfur removal technology that suffers from being too expensive and generating toxic waste. This technology is thus only used as a police filter, i.e. in case the electroscrubber malfunctions.

In the figure below, synthetic gas compositions in and out of the purification system is presented, with a) and b) presenting data for a packing height of packing material of 2.1 cm and with c) and d) representing data for a packing height of 5.3 cm. The packing was made from regular pp packing rings. For both experiments, it is observed in Figure 2a) and c) that the CO_2 content leaving the system is lower than the CO_2 content entering the cleaning unit. This is likely due to the CO_2 being dissolved as carbonate in the electrolyte. While the system was quickly saturated with H_2S before the experiments were initiated, the carbonate content of the liquid would require additional time to reach equilibrium. The removal of CO_2 from the model biogas appears to increase with a gas flow as evident from Figure 2c). However, no such tendency is observed in Figure 2a). The H_2S removal is observed in Figure 2b) and d) to decrease with increasing gas flow. This is expected, as a higher gas flow allows for shorter reaction time (space velocity) inside the scrubber unit.
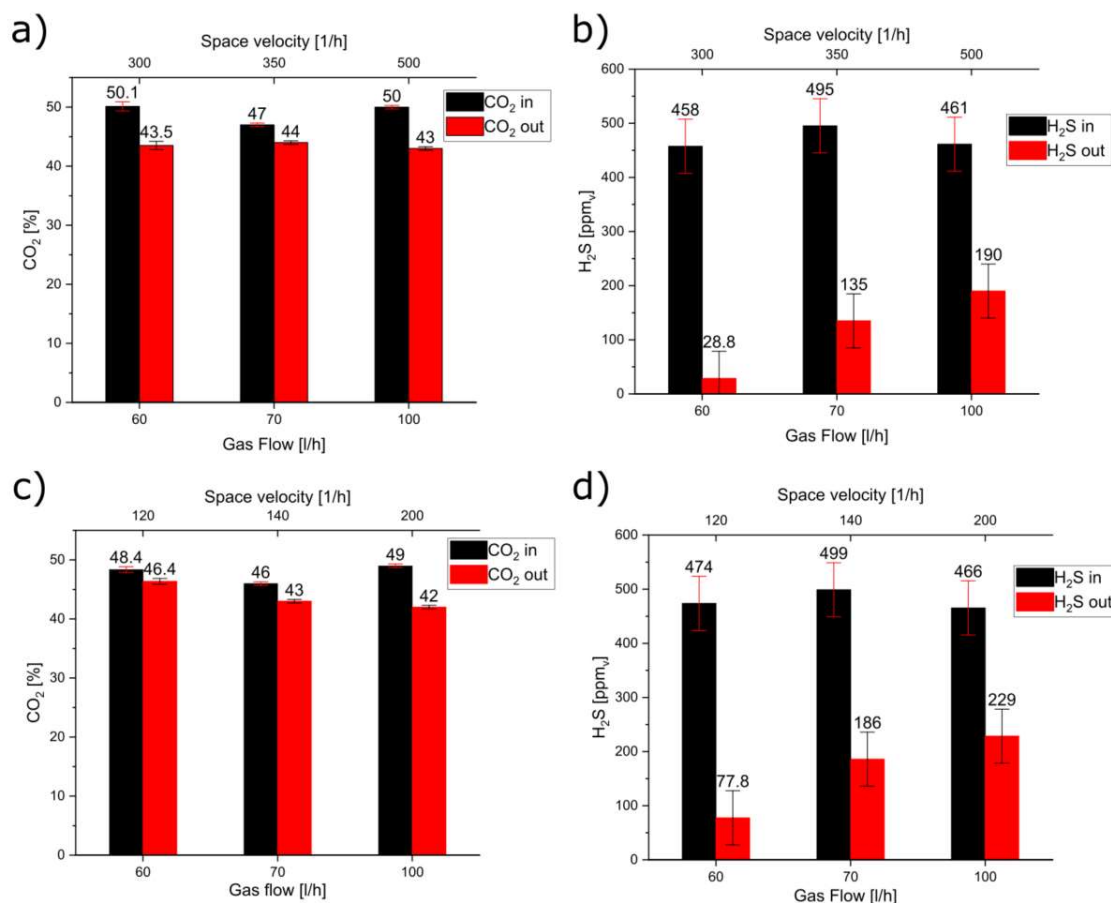

Figure 2: Gas compositions as a function of total gas flow. a) and b) show the content of CO_2 and H_2S, respectively, in and out of the 2.1 cm tower, while c) and d) show the CO_2 and H_2S, respectively, for the 5.3 cm tower. Overall, a small amount of CO_2 is observed to be absorbed in the liquid inside the cleaning unit. It is evident that H_2S is removed to a large degree and that the removal rate is observed to be dependent on the gas flow as a smaller gas flow lowers the H_2S concentration.

The results from the SEGO unit showed that the developed purification process can be used with different electrolytes and remove H_2S in synthetic biogas down to non-detectable limits. By operating the unit with higher currents it was possible to remove H_2S down to non-detectable limits. MS1.

Real biogas test and analytical procedures

The SEGO unit is built to be compatible with real biogas and be installed in a biogas-plant and be integrated with downstream-electrolysis units. However, as an opportunity opened up, it was decided to establish the SEGO technology in an upscaled version of the purification process and utilize part of an already existing biogas purification set-up which is constructed under the MeGa-StoRE project. This was done in order to take advantage of the apparent synergies between the closely related processes as this set-up was already connected on-site to a real biogas-stream. See Table 1 below for details.

Table 1: Display of gas purification systems in and between the projects Upgrad and MeGa-Store.

Upgrade	MeGa-Store
- Development of purification process (WP1) - Modelling of purification process (WP1) - Construction and test of purification Lab Unit (SEGO) with possibility of using various purification processes (various chemicals) (Del. 1, MS1) - Lab scale testing of synthetic biogas - Incorporation of SEGO technology into existing biogas-unit on-site	- Laboratory tests for scaling purposes - Construction and testing of process - Connection of pilot-plant on-site

Composition analysis on raw and pre-cleaned biogas was measured at Nature Energy Midtfyn, April 2019. The biomass from this site consists primarily of 75% manure from cattle, pigs and minks. The rest of the biomass originates from organic industrial waste and energy crops [1].

The biogas composition was measured using a mobile high-resolution multi-component FTIR analyser (atmosFIR, Protea Ltd.). The FTIR analyser was calibrated for CH_4, CO_2, and H_2S concentrations up to 70 vol%, 50 vol%, and 5000 ppm respectively. Additionally, the analyser also measures siloxanes, ammonia and water.

Raw and pre-cleaned biogas composition results of two batches are presented in Table 2 and Table 3. Average and standard deviations of the analysed biogas of each batch are shown in the tables. Two sets of analysis were carried out: batch 1 and 2. These were performed 10 minutes apart. The variation from batch 1 to batch 2 show clearly how fluctuating the gas composition were. The numbers given exemplify the analysis performed. In reality a continuous analysis over a prolonged period of time should be carried out, in order to characterise the efficiency of the sulphur-removal technology.

From the tables it can be concluded that the average content of methane and CO_2 in the raw and pre-cleaned biogas are ~59% and ~39% respectively. An average level of 1110 ppm H_2S is seen in the raw biogas. After the desulfurization process the H_2S content is below the detection limit of the analyser as seen in Table 3. The detection limit of the analyser is 50 ppm, however, it is expected that the actual H2S concentration is lower than 50 ppm. External analysis is required for confirmation. An external analysis was performed by DGC and found that the H_2S content in the cleaned gas was below their detection limit of 0.5 ppm. This is a general observation for all analysis performed at Nature Energy Midtfyn.

The overall conclusion is that the applied technology is very efficient in the removal of H_2S from the biogas (**Deliverable 5 & Milestones MS5 & MS6 (for purification)**).

Based on the testing, 70-100 kW of electrical power is required for removal of H_2S from a 10 MW biogas plant, corresponding to 1500 Nm^3/h.

Due to the variability in the gas composition it cannot be determined from these measurements, whether the sulphur-removal technology has an impact on the removal of siloxanes.

Table 2: Composition of Raw biogas measured at Nature Energy Midtfyn.

Component	Unit	Conc.	Std.dev	Conc.	Std.dev
Batch no.			1		2
Pentamethyldisiloxane	ppm	0.3	0.013	0.36	0.147
Hexamethyldisiloxane	ppm	0.86	0.067	0.79	0.053
Hexamethylcyclotrisiloxane	ppm	n/a	n/a	n/a	n/a
Octamethyltrisiloxane	ppm	0.84	0.003	0.95	0.060
Ocatmethylcylclotetrasiloxane	ppm	0.57	0.007	0.73	0.040
Decamethyltetrasiloxane	ppm	0.66	0.000	0.62	0.020
Decamethylcyclopentasiloxane	ppm	0.65	0.017	0.41	0.050

Dodecamethylpentasiloxane	ppm	0.19	0.000	n/a	n/a
Dodecamethylcyclohexasiloxane	ppm	0.14	0.000	n/a	n/a
Trimethylsilanol	ppm	0.72	0.003	1.24	0.040
Ammonia	ppm	0.19	0.010	0.1	0.020
Hydrogen Sulphide	ppm	1144	1.86	1091	5.12
Carbon Dioxide	%	39.3	0.057	38.9	0.123
Methane	%	59.1	0.443	59.5	0.097
Water	%	0.33	0.000	0.36	0.007
Total siloxane	ppm	4.2	0.087	3.85	0.160

Table 3: Composition of cleaned biogas measured at Nature Energy Midtfyn.

Component	Unit	Conc.	Std.dev	Conc.	Std.dev
Batch no.		1		2	
Pentamethyldisiloxane	ppm	n/a	n/a	0.4	0.370
Hexamethyldisiloxane	ppm	0.14	0.200	1.08	0.320
Hexamethylcyclotrisiloxane	ppm	n/a	n/a	n/a	n/a
Octamethyltrisiloxane	ppm	1.07	0.120	1.03	0.050
Ocatmethylcylclotetrasiloxane	ppm	1.03	0.383	0.83	0.517
Decamethyltetrasiloxane	ppm	1.59	0.120	1.43	0.067
Decamethylcyclopentasiloxane	ppm	2.29	0.377	0.97	0.590
Dodecamethylpentasiloxane	ppm	0.04	0.033	0.09	0.087
Dodecamethylcyclohexasiloxane	ppm	0.03	0.037	0.06	0.063
Trimethylsilanol	ppm	0.78	0.353	0.2	0.210
Ammonia	ppm	0.25	0.043	0.18	0.057
Hydrogen Sulphide	ppm	n/a	n/a	n/a	n/a
Carbon Dioxide	%	39.1	0.153	38.6	0.180
Methane	%	59.1	0.153	59.3	0.157
Water	%	0.35	0.003	0.35	0.007
Total siloxane	ppm	6.2	0.870	5.89	0.583

Thermodynamic modelling of an oxidative biogas cleaning system

A detailed modelling study of the desulfurization process of removing H_2S from biogas using active chlorine was performed using the Extended UNIQUAC model.

The purpose is to create a calculation basis in order to perform a more fundamental understanding of the chemical processes in the sulfur-removal technology. The system investigated was the complex electrolyte system containing CH_4-Cl_2-CO_2-H_2S-H_2SO_4-NaCl-HClO-HCl-H_2O.

The Extended UNIQUAC model is a Center for Energy Resources Engineering (CERE), DTU inhouse model, which is implemented as a stand-alone model, but it can also be used with a Microsoft Excel interface. It has previously shown to be very capable similar type of chemical systems [2].

The Extended UNIQUAC model is an activity coefficient model consisting of three terms accounting for the surface area and the volume of the molecules. But it also accounts for the interaction between the ionic species in a solution. The interaction, the surface, and the volume parameters in the model are fitted to literature data by minimizing the sum of squared residuals of each data point. The model contains a good coverage of the parameters for the binary and ternary systems CO_2-H_2O, CO_2-NaCl-H_2O, NaCl-H_2O, Na_2SO_4-H_2O and H_2S-H_2O [3]–[5]. However new chloride derived species needed to be included in the model in order to describe the oxidative biogas cleaning system. The model parameters were determined from binary and ternary vapour-liquid equilibria (VLE) and solid-liquid equilibria (SLE) data of the systems such as Cl_2-H_2O, CH_4-H_2O, and H_2S-NaCl-H_2O.

Figure 3 shows a comparison between calculated and experimental Cl_2 partial pressures data in the temperature range 10 to 40°C. Overall the extended UNIQUAC calculates the binary Cl_2-water system with an absolute average relative deviation (AARD) of 0.87. The model result shows a very good resemblance between calculations and experimental data. The characteristic non-ideal curvature at low pressure is well modelled using the principles of hypochlorite dissociation. The binary CH_4-water system is depicted in Figure 4 as function of the total pressure (bar). Again, the model predicts the literature data well in the temperature range 10 to 25°C and total pressure up to 120 bar with an AARD of 0.28. Figure 5 illustrates the modelling results versus the experimental data for H_2S in NaCl solutions of ~4 and ~6 mol/kg water respectively. As seen in the figure the model calculates the solubility of H_2S in 4 mol NaCl/kg water at temperatures up to 80°C and total pressure ranging between 0.05 to 60 bar well. Increasing the NaCl concentration to 6 mol/kg water results in a higher deviation between the model prediction and the experimental data. But still, the modelling is quite acceptable.

The chemical system is very complex and there is a lack of data availability for certain subsystems in the sulfur-removal process. For this reason, there is a potential to optimize certain molecular interaction parameter, particularly for H_2S mixtures and more complex systems containing multiple low-pressure gases. Said that, the current modelling is acceptable and can be used to validate the sulfur-removal technology.
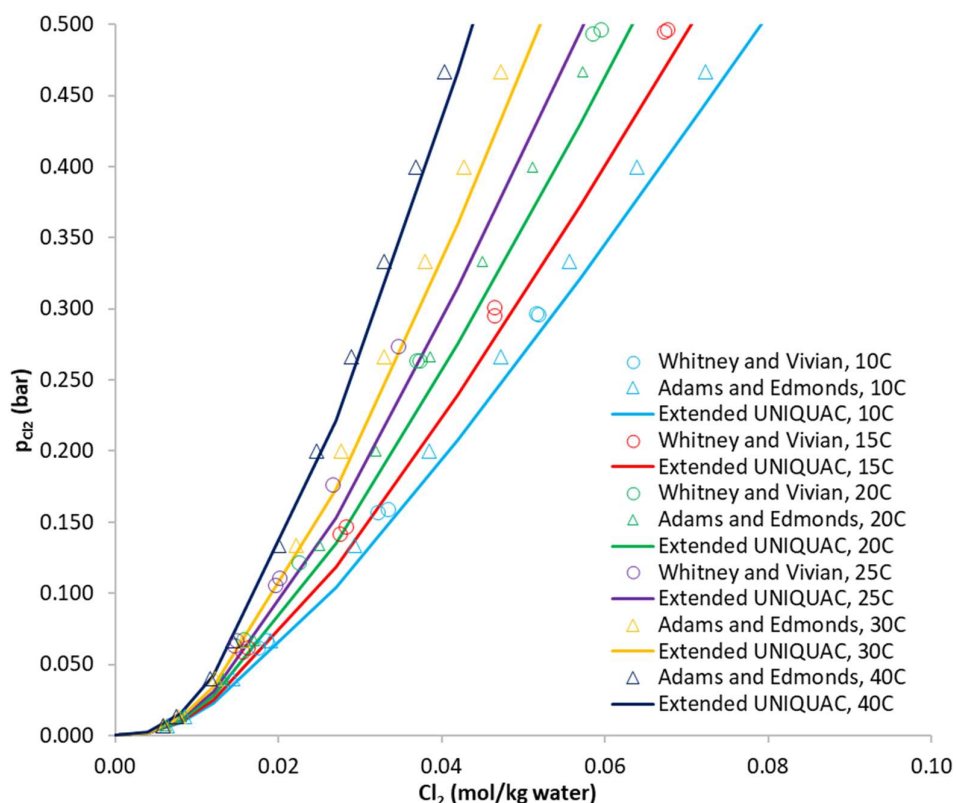

Figure 3: Cl_2-water system in the temperature range 10 to 40°C. Lines are the Extended UNIQUAC. Circles and triangles are literature data obtained from Whitney and Vivian [6] and Adams and Edmonds [7].
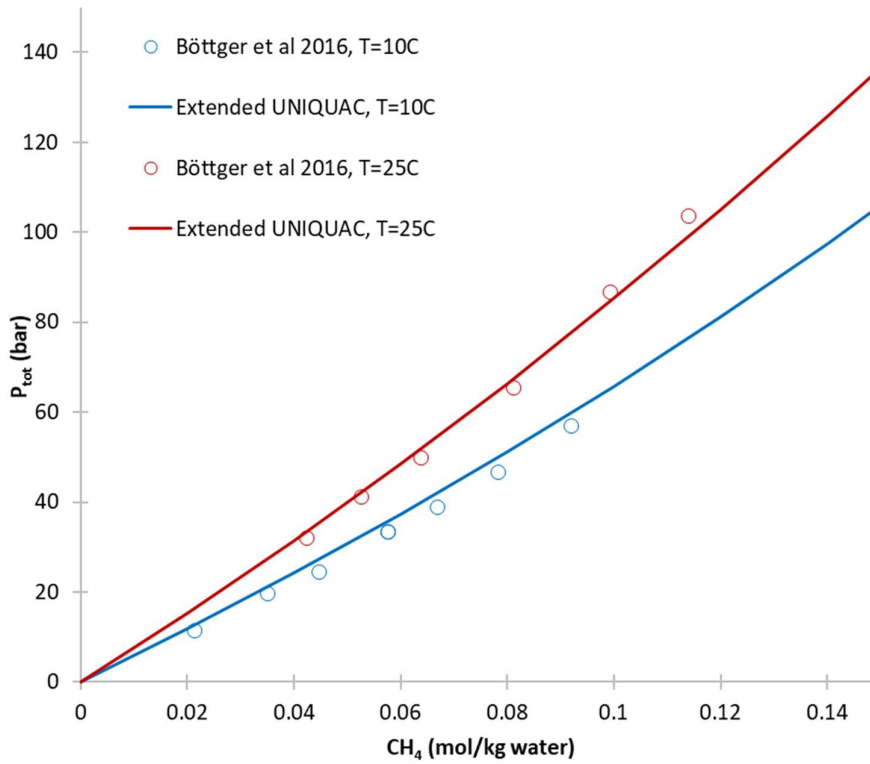
Figure 4: CH4-water system in the temperature range 10 to 25°C. Red color indicate 25°C. Blue color represents 10°C. Lines are the Extended UNIQUAC. Circles are the literature data obtained from Böttger et al. [8].
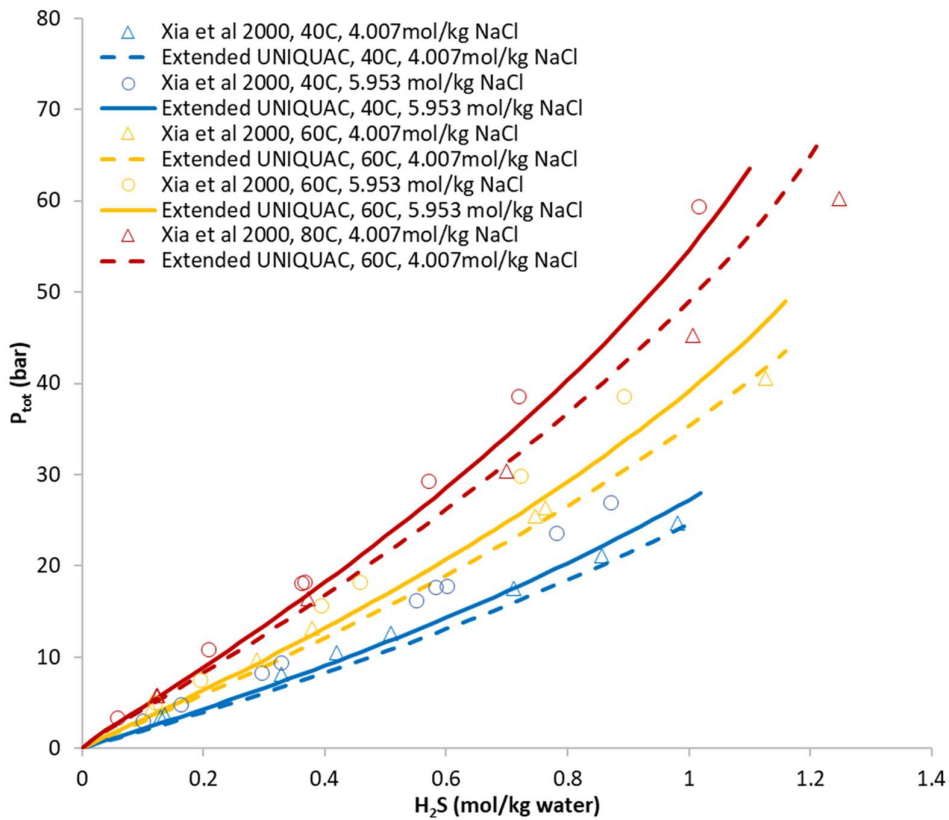

Figure 5: H2S-NaCl-water system in the temperature range 40 to 80°C. Red color indicate 80°C. Blue color represents 60°C. Yellow color represents 40°C. Dotted and full lines represent the calculated values at 4.007 and 5.953 mol NaCl/kg water respectively. Circles: represent literature data obtained from Xia et al. [9].

A test system for co-electrolysis

The co-electrolysis test system Figure 6, Figure 7 has undergone several improvements during the project, and two design versions are established. Materials for components of the system has been tested and an adequate solution is established.

Initially an active area of 1.2 cm^2 was established, while adequate sealings were unresolved and an external pressure bearing enclosure was required. Other initial technical challenges include stable evaporation of water and pressure balancing of the two electrode compartments. During 2018 the active area was increased to 7 cm^2, as 40 mm electrolyte tablets and 30 mm electrode structures were established (see below).
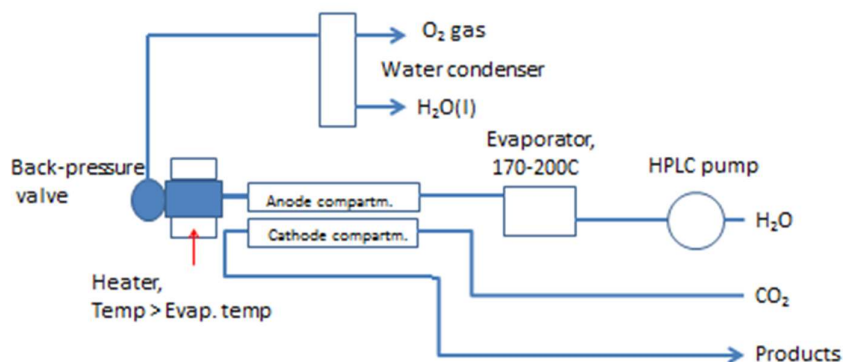

Figure 6 Schematic test system for co-electrolysis at elevated pressure and temperature.
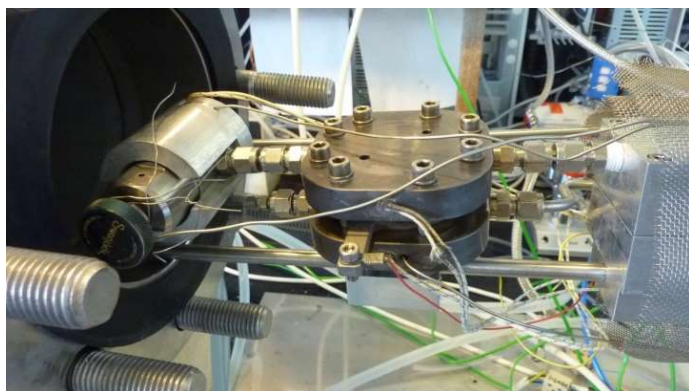

Figure 7 From left: external pressure enclosure, heated pressure regulator, steel housing for compression of the electrochemical cell under test, and gas/steam supply.

The project work concludes that brass is a suitable housing material, whereas stainless steel must be used for the flow plates providing gas manifolding and electrical contact to the electrodes. Further the stainless steel must be coated with Tantalum on the oxidant (anode) side to avoid corrosion. In addition, porous current collecting layers introduced between flow plates and electrodes. Here carbon based felt and Ta-coated stainless steel felt are applied, respectively. Ru has been tested and found very promising as well, although reported problems with water reactions in PEM systems should be considered before further use. Sealing materials for the cell with sufficient mechanical and electrical properties to provide leak-tight sealings as well as electrical insulation has been tested extensively among polybenzimidazole (PBI from DPS), PEEK, Polyimide and other relevant materials. An adequate solution is finally identified in a bilayer structure composed of polyimide ("Kapton") and a graphite-based sealing material ("Papyex"). Using these the exterior pressure enclosure will be obsolete.

A large amount of electrochemical tests has been conducted in the mentioned test systems (**Deliverable 2**), which is capable of operating at 350 °C and up to 15 Bar. It is verified that various relevant electrodes and membrane solutions can be tested with adequate leak control and sufficient sensitivity to characterize materials properties (**Milestone MS2**). Furthermore the 7 cm^2 system is evaluated to be adequate for experiments on membrane integrity.

Development of electrolyte (membranes) for the co-electrolyser

Development of suitable membranes include a number of requisitions, leading to a design where an active electrolyte-material (protonic conductor, initially thought to be CsH_2PO_4- or $K_2H_2PO_4$-based and molten at operating conditions), a porous structure defined by a filler material (initially proposed to be $Sn_2P_2O_7$) to withhold the molten electrolyte and a "reinforcing structure" to give the electrolyte handling strength.

The initial work on $K_2H_2PO_4$ was first supplemented with mixtures of $K_2H_2PO_4$ and $KHCO_3$, and then later replaced by LiH_2PO_4 with additions of $LiPO_3$ and H_2O, as the fundamental conductivity was demonstrated to be at least an order of magnitude above that of $Cs_2H_2PO_4$. The carbonate system was eventually discontinued as a match with a suitable filler to contain the melt was unsuccessful.

In addition, fundamental studies were conducted and published on conductivity in the MH_2PO_4 system, as well as melting temperatures and decomposition properties which both depend significantly on the water vapor pressure, which is new, Figure 8.
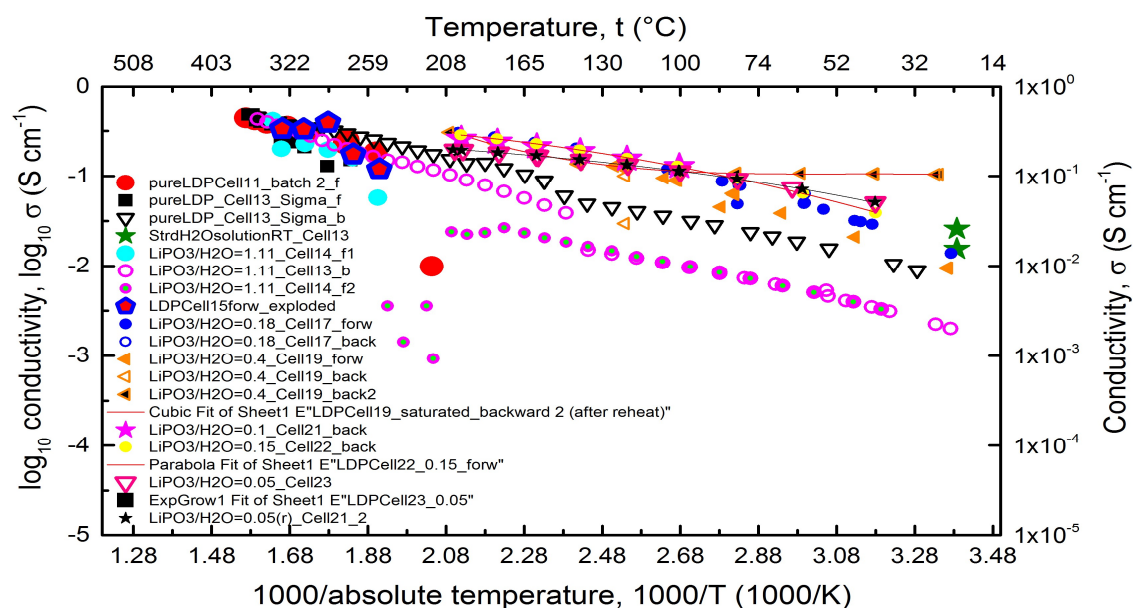

Figure 8 Conductivity measurements on LiPO4 molten salts

The filler material has been varied between $Sn_2P_2O_7$, ZrO_2 and SiC of different grades and granularities. α-SiC with a distributed PSD in the 100-1000 nm range is the most promising candidate, with good retention properties at an acceptable volume fraction. The ZrO_2 material should be avoided as it interacts with CsH_2PO_4 and forms a zirconium phosphate.

The reinforcement material has been varied quite a bit. Felts with ceramic/glass fibers are tested but found to be incompatible with a pressing method (see below). These include ZrO_2 fibers, SiO_2 and "Pyrex" fibers.

Nano-spun fibers of PBI seem suitable, however the "felt structure" of such fibers must be very well controlled and the impregnation with electrolyte/filler very careful, to avoid lamination and consequently limited beneficial effect. Work to optimize this has been done but has been terminated as results were not sufficiently promising.

Figure 9 Ø42 mm electrolyte disk consisting of CsH2PO4 with α-SiC filler

The primary small-scale manufacturing method for electrolyte discs has been based on creating a dispersion of electrolyte and filler material, impregnating this into a reinforcement structure and pre-pressing the disk to preliminary structure. This structure is later hot-pressed to melt the electrolyte materials and hence create a final shape with little or no porosity to avoid gas crossover, Figure 9. Selection of solvents and pressing parameters appear critical, and disks cannot readily be produced below a thickness of 1mm, which sets limits to materials cost and resistive losses in the electrochemical cell. The initial pressing step is also responsible for rejecting the ceramic/glass fibers in the membrane, as these are mechanically impaired by the process. An alternative exists in impregnation of a ZrO_2 fiber "paper", but both cost and challenges with homogeneous impregnation in combination with thickness limitations make this path less attractive.

As a more process oriented and scalable approach, the first pressing step has been replaced by a casting procedure, where the reinforcing material is replaced with a dissolved PBI, which will then upon drying form a porous network around particles of electrolyte and filler Figure 10. The approach appears successful, although it has not been tested in the setup during the project period. Diameters of >100 mm and thicknesses approaching 100 microns has been demonstrated.

Figure 10 Cast electrolyte, containing CsH_2PO_4 and SiC filler. Ø >100 mm

During the project more than 100 electrolyte membranes has been produced and evaluated. Many of these fail in an indirect leak test (density measurement), which has spawned an effort to consider a "self-repair" mechanism. Work on this introducing $CsH_5(PO_2)_4$ and H_3PO_4 has not been concluded.

Consequently, the most promising system identified for membrane is LiH_2PO_4 with additions of $LiPO_3$ and H_2O, using α-SiC with a distributed PSD in the 100-1000 nm range (**Deliverable 3, Milestone MS3**). These are dispersed in solvent and tablets are demonstrated by impregnation into PBI nanofiber felt for reinforcement, followed by drying and pressing at room temperature and 2000 kg/cm^2. A scalable casting proposed using dissolved PBI in the process.

Development of electrodes for the co-electrolyser

Work on active electrodes for the co-electrolyzer has exclusively been on the cathode materials, as these determine the selectivity and activity of the reactions between protons from the

electrolyte and CO_2 from the biogas. The choice of stable reference for the anode side has been 5 mg/cm^2 IrO_2, deposited by spraying with a PBI binder on Ta-coated stainless steel felt.

During the project the production of and studies on electrodes has been extensive. More than 100 electrodes have been produced, comprising Ni and Cu metal foams, Ni pressed powder, carbon felt paper, stainless steel felts and electrochemically formed coatings on these structures by Au, Au/Co, Ru, Cu, Co, Pt, Ni and Ni-Ga alloy as well as Mo by CVD. Later especially Cu-Zn (Brass) alloys has also been deposited electrochemically on stainless steel felt and tested.
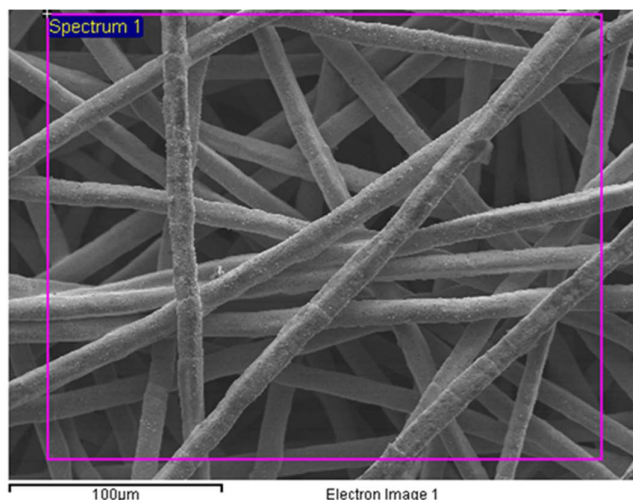

Figure 11 Carbon felt with electroplated metal catalyst

Cu has been excluded due to incompatibility with the phosphate electrolyte.

Initial Ni electrodes from pressed powder has shown ability to produce methane, Figure 12, Figure 13. At 300 – 340 °C and 8 Bar using CsH_2PO_4- or $K_2H_2PO_4$-based electrolytes, this cell has demonstrated ability to produce mixtures of methane, water, hydrogen and carbon monoxide, and in some cases with high selectivity almost entirely methane and water (**Milestone MS4, Milestones MS5 & MS6 (for Co-electrolysis)**). Water may partly be due to leakage from the anode compartment. At very low current density the voltage is approx. 0.9V, less than the potential for water splitting at this temperature (1.1V). Furthermore, voltammetry on this electrode in CO2 show reduction at lower potential than H2 evolution, indicating clearly that formation of methane is electrocatalytic and direct, not via formation of H2 and a Sabatier-process.
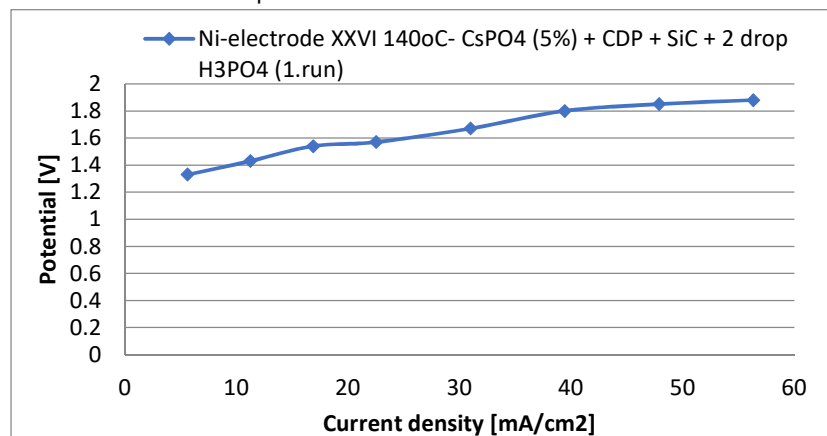

Figure 12 Polarisation curve at 300 °C and 8 Bar. Ni-based cathode with MH2PO4 electrolyte in SiC matrix and using an IrO2 based anode.
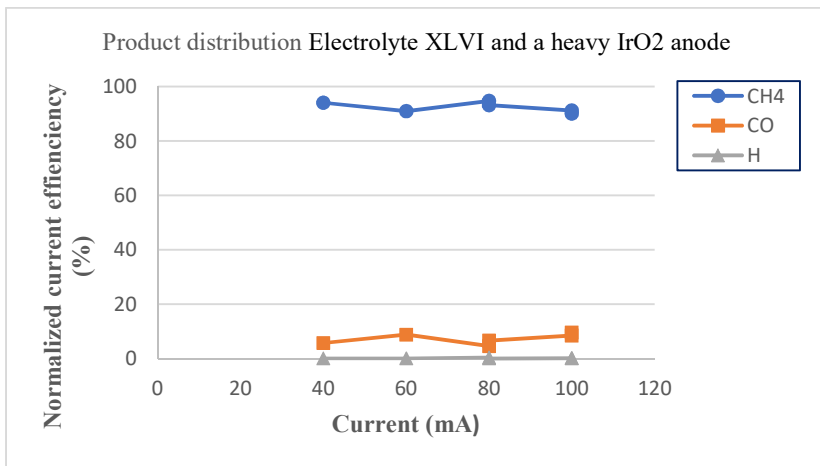
Figure 13 Selectivity at 300 °C and 8 Bar. Ni-based cathode with MH2PO4 electrolyte using an IrO2 based anode.

An experiment where the produced methane has been quantified by GC analysis has indicated a Faradaic (electron) efficiency of 70%. It is unclear where the remaining 30% are consumed, but trace elements produced in parallel processes and short circuit leakage might be considered and should be quantified further.

Also a single test using a Ni-Ga alloy powder in a pressed electrode has produced methane selectively. This has not been pursued further due to the promising results on pure Ni.

It has further been attempted to clarify whether the technology has potential for producing other (higher) organic molecules than methane. Using a cathode made of Cu-Zn (brass) alloys electroplated on a stainless steel felt and exposed to specific heat treatments, the electrolysis test has produced a mixture of methane, hydrogen and dimethyl ether (DME), methanol, a third unidentified product as well as traces of (presumably) acetone.
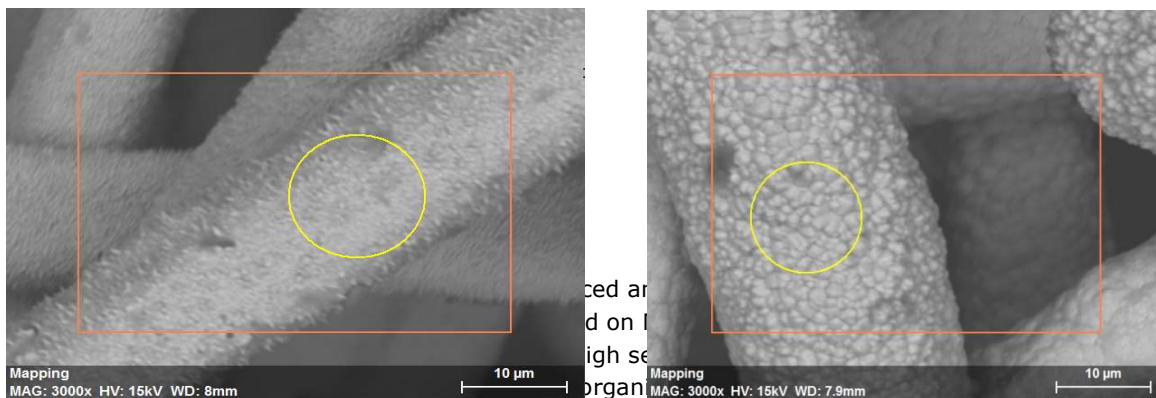

Figure 14 Brass electroplated onto stainless steel felt, 17 and 45% Zn, respectively. Color markings indicate EDX element analysis areas.

demonstrating ability to restart cells without performance loss, which is very reassuring as the electrolyte phase changes could be suspected to be critical in a technological application.

Also, it has not been feasible within the project to bring the co-electrolyzer technology to a risk and maturity level where integration with the above gas purification equipment has been evaluated as sensible. Consequently, **Deliverable 5 and Milestones MS5 and MS6** has been approached separately for the two technologies, and whereas gas purification (individually) has successfully achieved all objectives, the co-electrolyzer has individually achieved **Deliverable 5 and MS5, but not MS6**. It is however evident from the work and data above that MS6 could have been achieved with no expected difference in results to **Milestone**

MS5. The integration of the two technologies however is presently hindered by different levels of maturity.

Project evaluation and outlook

The developed gas purification concept was established in terms of purification units that proved to be efficient in cleaning synthetic and real biogas - even with different electrolytes - on both lab-scale and industrial scale. A valuable model was developed to predict the behaviour of the system.

Overall, the biogas purification met the project objectives of obtaining gas with very low levels of H2S, and the results from the pilot plant testing were very promising. In addition to this, the power consumption of the purification technique makes it comparable in OPEX with the cheapest available technology, while the other aspects of the cleaning, CAPEX, cleaning ability and no addition of oxygen, makes the new technology better than the competitors.

DTU-MEK strongly expect to continue working with the developed purification technology in future projects, as the initial results are very encouraging but further development is required in order to fully demonstrate and validate the technology on an industrial level. The results are so positive that they are already currently being used as background information in connection with new project applications in this field.

The additional development of a model describing the gas purification is a strong tool for optimisation in the expected work ahead for commercialisation.

The ambitions set to make a proof of concept on direct reduction of CO_2 to methane by co-electrolysis has been fulfilled. A functional solution on the materials level is established, with further potential for improvement by electrode geometry, materials tuning and operational conditions. Very good selectivity for the desired reaction has been established. Also processing of the electrodes and electrolyte are established on laboratory scale, with a positive outlook to industrialisation. Here existing competencies at Elplatek and DPS seem appropriate for production of electrode and membrane.

A surprising extra result of the project work has been realisation of direct reduction of CO_2 to form fractions of DME, methanol and traces of other higher-than-methane organic compounds. This poses perspectives way beyond the planned production of methane, into production of valuable industrial chemicals.

What has not been achieved for co-electrolysis is firm data on attainable electrical efficiency, limits to current density and durability. Also, the applied anode will likely have to be replaced with a more commercially suitable material. The next steps towards commercialisation of the technology would require development work including these steps.

The project outcome on co-electrolysis is an important step ahead with good results. These results are necessary but not yet sufficient for commercial evaluation and planning of a business case.

Overall the project has been successful on the levels of technology proof of concept, as well on establishing a set of preferred chemicals and an operative procedure for both technology branches. Furthermore, the gas purification technology has been demonstrated in conjunction with an industrial plant in real conditions and show promising cost perspectives. The achieved maturity of co-electrolysis has not allowed a similar level of evaluation, as was planned. Neither technology can at this time claim actual or forecast increased turnover, exports, employment. However, both technologies have a very positive fit with both national and international trends and objectives in renewable energy and biomass, as should be pursued further from the results achieved.

IPR and Dissemination of the project:
PA DK201770669 – patent application Denmark: Niels J. Bjerrum, Erik Christensen, Irina Petrushina, Aleksey Nikiforov, Rolf W. Berg "Method and apparatus for methane production"

R. Neerup, S. N. B. Villadsen, K. Thomsen and P. L. Fosbøl, "Thermodynamic Modelling of an Oxidative Biogas Cleaning System using the Extended UNIQUAC Model", Trondheim CO2 Capture, Transport and Storage Conference (Trondheim CCS Conference), Trondheim, Norway June 17 - 19, 2019 - (Poster)

A. V. Nikiforov, R. W. Berg and N. J. Bjerrum, "Vapor pressure and specific electrical conductivity in the H_2O-LiH_2PO_4-$LiPO_3$ system – A novel electrolyte for water electrolysis at ~225-400 °C", Ionics, September 2018, Volume 24, Issue 9, pp 2761–2782 (link)

A. V. Nikiforov, "Specific electrical conductivity in solid and molten CsH_2PO_4 and $Cs_2H_2P_2O_7$ – a potentially new electrolyte for water electrolysis at ~225-400 °C", 1st International Conference on Electrolysis Copenhagen (ICE2017), 12-15 June 2017 (Poster)

A.V. Nikiforov, I. M. Petrushina, E. Christensen, R.W. Berg, N. J. Bjerrum, "Voltammetric study of one-step electrochemical methane production during water and CO2 co-electrolysis in molten CsH_2PO_4", Renewable Energy, Volume 145, January 2020, Pages 508-513 (link)

1.6 Utilization of project results

The successful and cost-effective removal of H_2S in the purification process is a vital step in the effort of using catalytic upgrading of biogas as a mean to achieve energy policies objectives. The results from this project will substantially increase the market potential for catalytic upgrading of biogas as the near complete purification opens up otherwise unrealistic possibilities of implementing biogas in a wide range of renewable energy concepts where both price and purity of the gas is essential.

The rights to the gas cleaning technology is currently being owned by Elplatek, however, three different companies (2 Danish and 1 international) have shown interest in obtaining the rights. For future commercial reasons these companies will not be named, although it can be said that all three market and operated equipment on several Danish biogas plants.

The current plan is to develop the gas purification further in separate projects that will focus only on this aspect and convey the results to relevant industries and drastically broaden the potential use of the technology. The developed thermodynamic model and the validation of the model carried out in the current project will be very valuable in this regard as it will enable important predictions without having to obtain costly and not readily accessible experimental data.

The co-electrolysis of CO_2 to methane or other higher hydrocarbons in one step is a potentially very strong competitor to existing multistep technologies for CO_2 activation as a green energy carrier and power-to-X. At present the technology is owned by DTU, and the technology has not yet reached a level allowing discussion of commercial perspectives.

1.7 Project conclusion and perspective

The developed purification techniques for biogas as proof-of-concept was indeed successful. It was clearly demonstrated that it is possible – in a cost effective process - to purify the gas and bring down the H2S contamination to the very low levels that are essential in order utilize the biogas for further upgrading and/or synthetization into more energy dense fuels. The cost-efficiency of the process and the obtained purity of the gas will in combination be a most convincing argument and a strong motivation for the energy industry to increase the implementation of biogas

as powerful tool in the effort to meet the ambitious energy policies put forward in recent years.

The developed thermodynamic model and purification process is already being used as a foundation for further gas-cleaning projects, where the idea is to incorporate more components into the model and get more experimental data to support and validate it. Furthermore the plan is to upscale the process to an industrial level and in this regard the model will be a valuable tool in the design and development phase.

The co-electrolysis of CO_2 to methane or other higher hydrocarbons has been proven and suitable materials for the reactor are identified. This will pave the way for further development to qualify the technology for demonstration and commercial applications within biogas upgrade, CO_2 reduction, green fuels and power-to-X.

The results from this project and coming projects will potentially have a remarkably impact on the value of biogas as a renewable energy resource.

Annex

Links to dissemination
https://www.sintef.no/Projectweb/TCCS-10/
https://link.springer.com/article/10.1007%2Fs11581-017-2420-3
http://www.ice2017.net/conference/ice2019
https://www.sciencedirect.com/science/article/pii/S0960148119309036

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