Final Report

1.1 Project details

Project title	BioCat 3, System Control and Integration	
Project identification (program abbrev. and file)	P2G-Biocat 3, Project 12 563	
Name of the programme which has funded the project	EUDP	
Project managing company/institution (name and address)	Electrochaea.dk ApS Chr M Østergaardsvej 4A DK-8700 Horsens	
Project partners	Electrochaea.GmbH Semmelweisstrasse 3 82152 Planegg Germany DTU, Department of Chemical and Biochemical Engineering Søltofts Plads, Building 228 Dk-2800 Kongens Lyngby	
CVR (central business register)	3387 3956	
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1.2 Short description of project objective and results (600-800 characters)

Dansk

Resterende risici i kommercialiseringen af Electrochaea-teknologi til biometanering til Power-2-Gas er blevet behandlet på pilotanlægget i Avedøre. Et styresystem på højt niveau er blevet designet, varmeudvekslings- og udgangsgasrensningsstrategier er implementeret, driftsformer og overgange mellem disse tilstande er valideret. Et stærkt samarbejde med DTU resulterede i en vellykket model af processen. Der er demonstreret langvarig drift med biogas eller CO2 som kulstofkilde og afsluttet med injektion af gas af høj kvalitet produceret ved biometanering i det danske gasnet. Metoder til at reducere omkostninger gennem næringsstofog biokatalysatorgenvinding er med succes testet. Hindringer for kommerciel udnyttelse af denne teknologi i det danske lovgivningsmiljø anerkendes og skal løses. Anlægget har tiltrukket mange besøgende, der er interesseret i udsigterne til strøm til gas.

English

Remaining risks in the commercialization of Electrochaea technology of bio-methanation for Power-2-Gas have been addressed at the pilot plant in Avedøre. A high-level control system has been designed, heat exchange and outlet gas purification strategies have been implemented, modes of operation and transitions between these modes have been validated. A strong collaboration with DTU resulted in a successful model of the process. Long-term operation has been demonstrated with biogas or CO_2 as Carbon source, and concluded by injection of high quality gas produced by bio-methanation into the Danish Gas grid. Methods to decrease costs through nutrient and biocatalyst recovery have been successfully tested. Obstacles to commercial fruition of this technology in the Danish regulatory environment are recognized and need to be addressed. The plant has attracted many visitors interested in the prospects of power-to-gas.

1.3 Executive summary

The P2G-BioCat 3 project aimed at lowering the remaining risks to commercialization, at establishing standards for control and integration, and at identifying in the Danish power and gas markets the economic conditions necessary to attract capital investment for implementation of power-to-gas (P2G) at grid scale in Denmark. The one-year project, with reduced scope from the original application, has provided many benefits to furthering the commercial application of P2G in the Danish market and worldwide and provided valuable learnings in design and operation of a P2G plant. It allowed Electrochaea to de-risk the technology and develop industry standard design and operating documentation, which previously was not possible due to the limited experience. Many of the learnings from BioCat 3 have been presented across several continents, further developed Electrochaea's process and led to the development of an informed front-end engineering package which was used successfully in a subsequent project where an automated second generation P2G plant was built.

WP-1: A mechanistic model has been developed by DTU to describe the biomethanation reactor at the Avedøre wastewater treatment plant (WWTP). The main biological and physicochemical processes in the biomethanation process have been modelled using the Anaerobic Digestion Model No 1 (ADM1) extended with: i) an improved aqueous phase description, ii) a mass transfer formulation to consider gas flows as inputs and iii) metabolic water production through a hydrogen balance. The results are satisfactory since the proposed approach successfully predicts CO₂, CH₄, H₂, pH and metabolic water production for different modes operation (biogas or CO2 as carbon feed).

WP-2: A high-level expert system, which collects information from the electrolysers, the biological process, the gas injection and the electricity supplier, was designed to control the system according to different modes of operation: optimization of the electricity cost mode, power regulation mode, and frequency regulation mode. The scheme shown below controls the operation of the plant with respect to the percent of maximum capacity required and takes into account the process limitations. High-level controls to automatically start, ramp-up or

shut-down the plant have been designed, as well as specific low-level controllers of key functionalities, such as the gas feed system or the chemical dosing.



Figure 1. Control cascade for operation of the Power-to-Gas plant.

WP-3: As the methanation process produces metabolic water in the reactor, the liquid in the reactor needs to be continuously drained to maintain a constant level, which incurs additional operating costs because nutrients and biocatalyst are washed out of the reactor and discharged into the drain. The nutrient dosing system was re-engineered to maximize the biocatalyst concentration and the use of nutrients, and tests of water filtration were completed at a Danish solution provider's test facility. Reactor liquid was collected from the BioCat plant and subjected to filtration treatment. Two major objectives were experimentally determined: the viability of the biocatalyst after recycling through the filtration unit was not significantly altered, and in a simulation of in situ water formation it was found that the concentration was not changed by more than 2%. These results demonstrate that filtration treatment has the potential to significantly reduce the costs for nutrient addition to the reactor, and that the biocatalyst remains viable. Further testing in the presence of gas flow is required for final evaluation of the method.

WP-4: During the BioCat 3 project, the heat exchange system was redesigned to automate the heat exchange system and to export the heat generated both by the electrolyzer and the bioreactor with increased robustness. In collaboration with Biofos, the heat exchange system has been modified to adjust the distribution of pressure and available flow in the water loop of the wastewater treatment plant that is used as a heat sink. This modification allows a more flexible operation of the different heat sources on site, which is fundamental when dealing with the P2G plant since it has intermittent operation.

WP-5: Further improvements to plant operation were implemented to demonstrate the commercialization potential of such a plant. As Electrochaea's technology has a high tolerance to contaminants usually found in biogas or biogas-derived CO₂ sources, the plant does not include any pre-treatment steps. Therefore, the gas collected at the outlet of the reactor can contain contaminants preventing its injection into the Danish gas grid. These contaminants may include hydrogen sulfide, ammonia, or volatile organic compounds. Additional gas purification stages have been added to the plant to assure the stability of the gas quality when either biogas or CO₂ feed gas is provided to the reactor. A combination of demister and contaminant filters provides the police filter to produce a polished gas cleaned of gas contaminants and with a low water content, allowing further post-treatment to produce a dry gas with relative composition in methane, hydrogen, and carbon dioxide compatible with the Danish gas grid. During the BioCat 3 project, two post-treatment approaches have been successfully tested independently and in combination: gas membranes able to preferentially extract excess hydrogen and CO₂ from the produced gas, and a pressure swing gas drier. The gas quality has been checked regularly at the plant and the conformity of the gas with the grid specifications has been verified on gas samples analyzed by an independent laboratory.

WP-6: The BioCat 3 project was characterized by ~1500 hours of operation and six experimental campaigns carried out between December 2017 and September 2019. During this operation, strategies were further defined to run a robust biomethanation process. Modes of operation that can be implemented in automated plants, as defined in WP-2, were tested and validated, including operation for extended periods of time and transitions between different operating modes. Within the November 2018 experimental campaign some problems were encountered with nutrient dosing and biocatalyst performance. These challenges promoted further optimization of the process. In addition, the plant was run to provide information for the ETV (Environmental Technology Validation) and for gas grid injection. A major goal to inject methane into the Danish gas grid was met in September 2019. Injection at a flow of 20 Nm³/h of renewable Natural gas at the HMN injection site occurred, demonstrating the commercial application of the BioCat P2G plant and the maturity level of the technology.

WP-7: During BioCat 3, development of the business case for P2G was foremost. Evaluation of the obstacles for P2G in the current framework showed that current regulations favor a unidirectional connection between the power grid and the gas grid. Yet, P2G requires bi-directional connection between the gas and power grid. Regulations of the Danish power grid do not favor a technology that stores the energy from power into another form of energy, a gaseous fuel. Obstacles have arisen when direct connections to adjacent renewable energy sources, such as windmills or photovoltaic panels, are sought. Grid related fees are being charged at a full rate and options to connect directly to the transmission grid are also limited by grid operators.

Obstacles have also arisen inhibiting good connection with the gas grid. CH₄ produced by biomethanation does not qualify for subsidies under the current regulatory support environment. Moreover, in order to connect a P2G plant to the gas grid, a significant investment must be made for the injection point and operational costs should be paid by the P2G plant operator, but ownership of the injection asset remains with the gas grid operator. Finally, grid entry charges apply to a P2G operator, which decreases the profitability of the business case.

WP-8: The BioCat plant in Avedøre, Denmark has been used effectively for dissemination of technical and economic information about Power-to-gas systems. There has been a great deal of interest in the plant. Since the beginning of the granting period, more than 40 presentations have been made in 13 countries, and more than 200 people from 100 different organizations have taken a tour of the plant, including representants of Danish institutions eager to understand better the challenges and opportunity of integrating Power2X technology in the Danish energy system. One of the achievements of BioCat 3, the first injection of renewable methane onto the Danish gas grid, has recently been featured in several news articles.

1.4 Project objectives: Description of project and execution

1.4.1 Background

The P2G BioCat 3 Project was modified from Forskel proposal 2017-12563; the original proposal, submitted in Sept 2016, was for a four-year project. The scope of this funded project was reduced to one year. This one-year project had a reduced budget.

1.4.2 Project evolution: Project goals and objectives

The P2G-BioCat 3 project aimed at lowering the remaining risks to commercialization, at establishing standards for control and integration, and at identifying in the Danish power and gas markets the economic conditions necessary to attract capital investment for implementation of power-to-gas (P2G) at grid scale in Denmark.

1.4.2.1 Timeline and execution management of major plant modifications Some of the milestones with regard to major plant modifications were challenging to meet in the reduced time frame of the Biocat 3 project. Goals that were re-evaluated are:

- Agitator replacement. Obtaining higher mixing energy in the reactor was of interest as the existing agitator was not capable of providing enough energy for high flow rates. The basic engineering and execution planning was completed with the provider of the replacement agitator (Nordic Engineering). The lead time and scope of works was also defined. It was determined that the lead time and execution work duration would allow less than 3 months of testing the replacement agitator. It was also determined that other existing plant constraints would challenge running at these very high flow rates. As a result of these complications, it was decided to cancel this work.
- Mass flow control system. It became clear that the mass flow control could be improved to be more stable at higher flow rates. The engineering for this work was completed, however due to time restrictions, it was not possible to implement the revised system.
- Post processing unit assessment. The post processing package, to include additional gas quality improvement measures to ensure gas quality, was an ambitious project. This work allows a wider operating range while still meeting grid requirements. The works were completed but the time to completion was longer than anticipated. This meant that the test time for validation of the design and evaluation of the results was limited.

1.4.3 Project risks

Throughout the project there have been several risks, some of which are related to resources and some are inherent to compressing a four-year project into a one-year time frame.

1.4.3.1 Non-reliable availability of CO₂ on site

Successful operation of a P2G plant is dependent on a reliable source of CO_2 . The BioCat P2G plant receives CO_2 from a biogas upgrading plant that was not under the control of Electrochaea. During the BioCat 3 grant period, the upgrading system suffered a series of malfunctions and periods of low performance. We suffered one failed experimental campaign due to lack of CO_2 , at the same time incurring full staffing costs for the majority of the campaign period. It is understood that the priority of the upgrading plant is to inject biogas into the gas grid, and not to support Electrochaea in obtaining a CO_2 stream. This is fully accepted, and the operators of the upgrading plant have been supportive throughout the project.

1.4.3.2 Difficulty to locate an affordable commercial offer for a nutrient recovery system Because of the high-specificity of the project, constraints of the filtration system and the relatively small size, on-shelf solution could not apply and suppliers had difficulties to provide a system at a cost compatible with the current budget. Since the principal goal for the project was to understand the cost and performance of nutrient recovery on the overall system, we have been able to establish a solid cost basis from the engineering, planning and cost quote. We have in fact been able to find a vendor and complete lab scale testing of nutrient recovery technologies. We have not had sufficient time in the BioCat 3 project to complete a physical implementation. The information obtained has been valuable for planning and could be implemented in a future phase of BioCat.

1.4.3.3 ETV Certification

Due to the delays caused by equipment failure, we started the ETV certification process later than expected. The process normally takes three months to complete, and this was reinitiated in July 2019. The planning for the ETV validation was completed, and tests were initiated in September 2019. The final results will be issued too late to be included in this report.

1.4.4 Overview of Project Execution

Project execution followed a general approach of incremental plant modifications followed by intensive test campaigns where specific experiments were executed to validate the

modifications, data and experience feed-back were collected and analyzed to support the next modifications and operation phase.

1.4.4.1 Project challenges

The modification of the agitator to be able to operate across a broader range of flows was recommended to be cancelled due to too long delivery times and likely cost overruns. Changes to the mass flow control system to enable testing over a wide range of gas flows were designed but not implemented as these tests would have been possible only with the wider range of mixing energies available with the modified agitator assembly. Absences of this capability did not impact the overall goals of the project but will have some impact on our ability to predict performance and capital costs outside of the current operating design. We believe this information can be recovered in a subsequent project in which the agitator and mass flow modifications can be implemented with sufficient operational flexibility for robust testing of the operating envelope enabled by these changes.

Delays in scheduling operational testing on site at Avedore have occurred due to the unstable operations of the biogas upgrading facility in Avedore. As a result, we accelerated the schedule for some of the plant modifications to take advantage of site downtime. Negative consequences include additional travel and personnel costs to EC GmbH, for personnel brought to site during unexpected down time, and a somewhat compressed timeline for operating campaigns at the end of the year.

1.4.5 Outlook & benefits of the project

The BioCat 3 project provided valuable learnings in design and operation of a P2G plant. It allowed Electrochaea to de-risk the technology and develop industry standard design and operating documentation, which previously was not possible due to the limited experience.

Many of the learnings from BioCat 3 have been presented across several continents, further developed Electrochaea's process and led to the development of an informed front-end engineering package which was used successfully in a subsequent project where an automated second generation P2G plant was built.

A first benefit has been to accumulate hours of operations, both with biogas or CO_2 as Carbon source, allowing Electrochaea to gain long-term experience and to standardize and eventually automatize the entire operation of the plant. The extended operation also allowed developing training material for operators of future commercial plants.

Additionally, the further development in modeling, process design, with the addition of gas polishing and gas post-treatment units, process operation with the functional description of automated operation modes and transitions have strengthened the robustness of the plant and supported the design of standardized engineering package backed by experience for the development of commercial projects.

Finally, the better integration of the heat exchange and the encouraging results of preliminary tests on nutrient recovery support an optimization of the operation costs, by adding revenue streams through the exchange of heat or by reducing the costs of nutrient supply.

1.5 Project results and dissemination of results

The BioCat 3 Project resulted in significant advances in bringing the operation capabilities to commercial application status. Briefly, the following have been successfully completed. A mechanistic model predicting CO_2 , CH_4 , H_2 , pH and metabolic water production has been tested. Control cascades, states of operation, and transitions have been determined allowing three operational goals that are not mutually exclusive: renewable gas producer, and power or frequency regulating agent. A test has been made to re-engineer the nutrient dosing system to reduce costs of chemical and biomass production. Improvements have been made on the plant for the heat exchange system and outlet gas purification.

The BioCat 3 project was characterized by ~1500 hours of operation and 6 experimental campaigns carried out between December 2017 and September 2019. The main objectives of these campaigns were to further define the strategies to run a robust biomethanation process.

Obstacles to commercialization in the Danish regulatory framework have been characterized and recommendations solidified.

1.5.1 **WP-1**: Development of a predictive model and control policies (Industrial research with academic partner)

A mechanistic model has been applied to describe the biomethanation reactor at the Avedøre wastewater treatment plant (WWTP). The main biological and physico-chemical processes in the biomethanation process are modelled using the Anaerobic Digestion Model No 1 (ADM1) extended with: i) an improved aqueous phase description, ii) a mass transfer formulation to consider gas flows as inputs and iii) metabolic water production through a hydrogen balance. The model is coded in the c. language and can be simulated in the MatLab/Simulink platform. The proposed approach is tested using a two data sets: (DS#1) a 28 day-time-series from an anaerobic digester unit (5/31/17- 6/27/17) and (DS#2) a 4-day time-series from a biogas plant (20/11/2018-24/11/2018). Mass balances (steady state) for COD, C, H and N are used to verify the model continuity and avoid leaks. Simulation results (dynamic state) show that the model is capable to reproduce CO2, CH4 and H2 conversion processes within the reactor. Good resemblance between simulated and experimental pH values reveals that the proposed approach correctly describes weak acid base chemistry. Finally, the model states that 1.6 kg H2O (produced).m3 N CO2 (treated).

The main biochemical processes are based on the Anaerobic Digestion Model No 1 (ADM1) (Batstone et al., 2002). The framework proposed by Flores-Alsina et al. (2015) is used to describe aqueous phase (weak acid base chemistry) reactions. Mass transfer between the liquid and the gas phase is described for selected compounds ($i = G_{CO_2}$, G_{CH_4} and G_{H_2}). The transport rates are formulated as a function of the difference between the saturation concentration and the actual concentration of the gas dissolved in the liquid (Batstone et al., 2012). For this particular case, the default reactor flux implementation was reformulated to account for gas flows that are included in the inputs to the bioreactor (Batstone et al., 2002). The last modification is related to the biogenic water production. The latter is rather relevant in systems with mainly hydrogenotrophic methanogenesis (archaea driven). Here, the sourcesink approach is used described in de Gracia et al. (2006), closing the H balance assuming H2O as state of reference (Figure 1).



Figure 1. Overview of the full-scale system implemented in the Avedøre wastewater treatment plant. Inputs to the system are: 1) CO₂/CH₄ outflow from the AD system, and 2) H₂ coming from the electrolyser system. Outputs to the system are biogas stream (CO₂/CH₄/H₂) and a liquid stream resulting from the metabolic H₂O production.

1.5.1.1 Steady state simulations, mass balances and continuity verification for DS#1 Assuming a bioreactor volume (Vreactor) of 5 m3 (Vliq = 3 m3 and Vgas = 2 m3), operational temperature (Top) of 60 °C, operational pressure (Pop) of 9 bar, VSS = 20 g/m3 and ADM1 default parameters, the model provides the following simulation results (Table 1). The figure below shows the COD, C, H, and N distribution entering and leaving the reactor (normalized to 1) (Figure 2). Around 55 % of the incoming COD is associated to CH4 (the remaining 45 %

is linked to H2). In the effluent almost (> 95%) all the COD is allocated to CH4. The remaining COD is part of H2 in the off-gas and biomass + cell degradation products in the effluent resulting from the archaeal activity. Regarding influent C balance, 55% stays in CH4 and 45% in CO2. Similar to the previous case, all the leaving C is part of CH4 (> 95%). The other fraction is CO2, biomass and degradation products. H is part of influent CH4 (45%) and H2 (55%). After the reactor, H is part of CH4 (70%) while the remaining part is metabolic water production (30%), which makes the reactor to overflow. Finally, all the N entering and leaving the reactor is associated with media composition (100%).

Component	IN	OUT	
CH ₄ (m ³ .d ⁻¹)	19.18	31.59	
CO ₂ (m ³ .d ⁻¹)	12.78	0.1	
H ₂ (m ³ .d ⁻¹)	52.44	1.4	
Total gas (m ³ .d ⁻¹)	84.52	33.1	





Figure 2. Normalized mass balance before and after the bioreactor for COD, C, H and N for DS#1.

1.5.1.2 Dynamic simulations for DS#1

The figure below depicts the dynamic influent profiles for DS#1 (Figure 3). It is important to notice that the electrolyser is operated to maintain optimal stoichiometric conditions between CO2 and H2. Input CO2 and CH4 have a constant ratio of 1.5. Simulation results (solid lines) show that the proposed approach is capable of reproducing (dotted lines) the main biological (hydrogenotrophic methanogenesis) and mass transfer phenomena (gas dissolution and stripping) occurring in the reactor (see CH4, CO2 and H2 % of the output biogas composition represented in Figure 4). The pH reveals the correct description of the weak acid-base chemistry model. Finally, the model predicts a quantity of 1.4 kg H2O (produced).m3 N CO2 (treated) as result of the metabolic activity.



Figure 3. Dynamic influent profiles for $CO_2(a)$ and $H_2(b)$. Notice that constant stoichiometric ratio (c) between a and b (the electrolyser is operated accordingly) (DS#1).





Figure 4. Full-scale measurements versus model predictions for selected operational variables: effluent CH₄ (a), H₂ (b), CO₂ (c), outflow gas (d), pH (e), reactor liquid volume (f) and metabolic water (g) for #DS1

The feasibility of ADM1 was tested to predict the behavior of the full-scale bio-catalytic methanation reactor currently in operation at the Avedøre WWTP. The results are satisfactory since the proposed approach successfully predicts CO_2 , CH_4 , H_2 , pH and metabolic water production

1.5.1.3 References

Batstone et al., (2002). Anaerobic Digestion Model No. 1. *IWA Scientific and Technical Report No. 13*. London, UK: IWA Publishing.

Batstone et al., (2012). Towards a generalized physicochemical framework. *Water Science & Technology*, 66(6), 1147-1161.

Flores-Alsina, X et al., (2015). Water Research. 85, 255-265.

de Gracia M., et al., (2006). Water Science & Technology, 53(1), 225-24

1.5.2 **WP-2**: Definition of the software and hardware architecture for the Expert System (Industrial Research)

The goal of WP-2 was to design a high-level expert system which collects information from the electrolysers, the biological process, the gas injection and the electricity supplier. The information is used to define hardware for interconnects, and software parameters needed to control the system according to different modes of operation:

- optimization of the electricity cost mode
- power regulation mode
- frequency regulation mode

1.5.2.1 Introduction

A power-to-gas (P2G) plant is typically connected to several interfaces: the electrical grid (or a local electricity producer), the gas grid, a source of CO_2 and a heat consumer, each coming with its own constraints on the design and dynamic operation of the plant. Additionally, the P2G system is composed of two main units of operation, the electrolyzer and the methanation reactor, both having their own dynamic and operation constraints. Therefore, the design and hierarchy of control loops and setpoints needs to be designed to satisfy both.

1.5.2.2 Power-to-gas control cascade

P2G plants differ from many industrial plants as they operate dynamically; they must start, ramp-up or down their capacity usage, and stop on demand and with different time constraints. Therefore, several process states have been defined.

State	Description
Sleep	No operation is expected for the next days (heavy maintenance). Plant is allowed to cool down, power input is minimized.
Standby	Plant operation is expected shortly. System is maintained in conditions allowing an immediate transition to operation.
Operation	Plant is operating. Capacity usage of the process can fluctuate depending on external request or process limitations.

Specific control sequences are designed to transition in sequence from one state to another.

Transition	From	То	Description
Warm up	Sleep	Standby	Reactor temperature and pressure are adjusted to setpoints compatible with process start-up.
Start up	Standby	Operation	Gas flows are initiated, and plant is brought to the requested capacity usage.
Shut down	Operation	Standby	Gas flows are stopped, controls to maintain pressure and temperature in a range compatible with operation are maintained.
Parking	Standby	Sleep	Setpoints for temperature and pressure are set to safe values. Most controllers are disabled.

Start-up and ramping of an alkaline electrolyzer, such as the one used at BioCat, typically offer a response time in a range of 3 to 15 minutes. Start-up and ramping of the biological methanation system are in a range of 5 to 15 minutes, depending on the conditions. As hydrogen storage is typically avoided or minimized, which is the case at BioCat, the methanation system is the only outlet for hydrogen. Therefore, the methanation system is the process setting the speed and amplitude of changes to the operating conditions.

The figure below illustrates a control cascade (Figure 5). When a request is given to alter the operation loading-rate, defined as a % of maximum capacity, the following points must be considered:

- Observed process limitations can change the requested loading-rate to a lower value.
- A setpoint of CO₂ feed flow (in Nm³/h) is determined based on the corrected loadingrate.
- A setpoint for the carbon mass-flow control is determined based on the volumetric CO₂ feed-flow request and the current composition of the carbon feed. Composition of the carbon feed can be altered by variation in the primary source of CO₂ (for example biogas) and/or by return flows from the gas post-processing.
- A setpoint for the hydrogen mass-flow control is determined based on the volumetric feed-flow of CO₂ and the objective for the H₂:CO₂ ratio in the gas mixture supplied to the reactor.
- The dosing of additives is controlled according to the reactor loading-rate.

Process limitations are controlled continuously. Typical process limitations are:

- Current hydrogen production is lower than the requested amount (for instance the electrolyzer is still ramping up production to match the request or has met another process limitation).
- Current availability of carbon feed is lower than the requested consumption (for instance biogas storage has hit a low level or the capacity of the upgrading plant has met another process limitation).
- Performance of the methanation reactor has altered and lower feed flows are required to restore process performance.
- Temporary congestion of the gas grid limits the amount of gas that can be injected
- Capacity to export heat or oxygen produced by the system is temporarily limited, therefore the profitability of the plant is reduced for high flows.

Designed as such, the P2G system presents only one entry setpoint, which is a loading-rate of its maximal capacity.



Figure 5 – Control cascade for operation of the Power-to-Gas plant.

1.5.2.3 Power-to-gas integration control

The P2G system can typically be operated:

- As a renewable gas producer, modulating its operation profile according to the price of power purchase.
- As a power regulating agent, able to stop or start its operation at the demand of the power regulating entity.
- As a frequency regulating agent, able to modulate its power consumption to support the control of the frequency on the electrical grid.

These three operational goals are not mutually exclusive, as the operation can maximize the gas production (e.g hours of operation and loading rate) and still accept a request for grid balancing.

1.5.3 **WP-3**: Reuse of drain water and nutrient recycling (Experimental Development)

The main goal of WP-3 was to re-engineer the nutrient dosing system to maximize the biocatalyst concentration and the use of nutrients. The nutrients and some biocatalyst are washed out of the reactor and discharged into the sewer, which increases the operating costs of the technology. In the amended Phase 3 project, Electrochaea designed and provided a cost estimate, a HAZOP plan and installation plan for the recycling system.

1.5.3.1 Introduction

Due to the water formation during methanation, nutrients and biocatalyst are drained from the reactor and discharged into the sewer, which is required to maintain the volume of the reactor. This loss of reactor contents represents a real cost to the project and contributes to normal operating costs for the technology. In the Phase 3 project, Electrochaea has completed a technology evaluation and selection process, and performed preliminary experimental tests with the reactor liquid to evaluate the suitability of nutrient recovery with the BioCat process.

1.5.3.2 Technology selection

A design and cost analysis of different technologies for biomass and nutrient recycling was performed. Based on the results of this analysis, a filtration technology has been selected allowing the retention of the biocatalyst, the recovery and recycling of nutrients. Technology has been chosen to allow an easy and cost-effective process integration and to minimize the on the biocatalyst. A supplier able to offer equipment in the scale applicable to the BioCat system and in the scale of commercial projects has been selected and offered to do preliminary testing with the BioCat reactor liquid. The test allowed an experimental evaluation of the separation performance and to assess potential negative effects on the biocatalyst by the filtration treatment.

1.5.3.3 Preliminary testing

To perform the preliminary tests, reactor liquid was collected from the BioCat plant and subjected to filtration with the supplier test unit. During the testing, two major objectives were experimentally addressed:

- Determine biocatalyst viability after recycling through the filtration unit.
- Simulation of *in situ* water formation by performing diafiltration to estimate the separation performance.

Biocatalyst viability. To test biocatalyst viability, the reactor liquid was subjected to the filtration for one hour with continuous recirculation and recombination of both the retentate and the permeate stream from the filtration unit. Before and after the test, a sample of reactor liquid was collected and the viability and performance of the biocatalyst within these samples was assessed at a later date in Electrochaea's laboratory. These tests showed no effect in terms of growth behavior and methanation capacity of the biocatalyst.

It was concluded that the filtration had no effect on the biocatalyst and could be applied to the BioCat process. However, due to the setup of the test unit, no feed gases (CO_2 , H_2) could be applied to the culture and therefore no methanation was present during testing. The effect of the filtration on methanation *in situ* has not yet been evaluated.

Separation performance. To determine separation performance, the water formation by methanation and the removal by filtration was simulated by running the system as a diafiltration process. Specifically, for every liter of water removed by the filtration, 1 liter of fresh water was added to the reactor liquid. This process was continued, until the entire reactor liquid volume had been exchanged once. Before and after this test, samples of the liquid were collected to monitor the recovery efficiency of the filtration. Specifically, the concentration of various nutrient salts in the treated sample before and after water removal by filtration were analyzed. For all relevant components, the relative concentration change was below 2 % (Figure 6), resulting in a recovery efficiency of >98%. These results demonstrate that the filtration technology has the potential to significantly reduce the costs for nutrient addition to the reactor.



Figure 6. Relative concentration change in the reactor liquid after one volume exchange by filtration in diafiltration mode.

In summary, the results of the preliminary testing highly support the implementation of filtration for nutrient and biocatalyst recovery and recycling for the BioCat system. Additional testing will be required to evaluate the performance under real process conditions *in situ*.

1.5.4 **WP-4**: Industrial ecology: Re-engineer and design the temperature control system. (Experimental Development)

1.5.4.1 Introduction

Integration of the P2G plant with the site can increase its environmental benefit and provide additional revenue. The heat generated by the electrolyser and the methanation process can be used on site, for example, to heat the biogas reactors operated by Biofos and to pre-heat the amine solution of the biogas upgrading system. To enable and demonstrate the long-term synergy between the methanation system processes and the WWTP and biogas upgrading processes, a new temperature control system coupled with an integrated heat transfer system has been designed.

The Biocat P2G plant has two main heat sources: the electrolyzer and the methanation reactor. The electrolyzer generates heat from the power inverters that deliver continuous current to the cell stacks and at the cell stacks as part of the electrolysis process. The heat generated by electrolysis is evacuated through the cooling of the electrolyte and the cooling of the produced gases. The electrolyte cooling loop represents a heat source at 60 C with a power up to 120 kW for a 600 kW electrolyser. Heat is also generated in the methanation reaction which occurs in the bioreactor and must be exported. It represents a potential heat source of 96 kW for a 600 kW system, typically at a temperature of 55 C.

1.5.4.2 Heat exchange system

At the end of the Biocat 2 project, only the heat generated by the bioreactor was exported. During the completion of the Biocat 3 project, the heat exchange system was redesigned to meet the main objective: to automate the heat exchange system to export the heat generated both by the electrolyzer and the bioreactor with increased robustness. In collaboration with Biofos, the heat exchange has been modified to adjust the distribution of pressure and available flow in the water loop of the wastewater treatment plant that is used as a heat sink. This modification allows a more flexible operation of the different heat sources on site, which is fundamental when dealing with the P2G plant since it has intermittent operation. An additional heat exchanger was installed to exchange the heat produced by the cooling of the electrolyte.

The figure below (**Error! Reference source not found.**) shows the power at the heat exchanger of the bioreactor and the power at the electrolyser as it relates to the flow of CO_2 that is delivered to the inlet of the reactor. The modifications to the heating exchange system enabled a more stable operation of the cooling loop of the bioreactor and increased the value of the heat by more than 100%, by exporting between 6 to 7 kWh per Nm³ of CO₂ that was reacted into methane by the reactor.



Figure 7 – Heat exchange and carbon feed flow.

1.5.5 WP-5: Improvements to move from a pilot to a demonstration plant (Experimental Development)

1.5.5.1 Introduction

At the end of the BioCat 2 project, Electrochaea had validated the performance of the scaled-

up implementation of the biomethanation technology, yet several modifications and improvements needed to be carried out to reach industrial standards and grid specifications. These objectives included implementation of gas purification strategies and improved weather proofing.

1.5.5.2 Gas purification strategies

As Electrochaea's technology has a high tolerance to contaminants usually found in biogas or biogas-derived CO_2 sources, the plant does not include any pre-treatment steps. Therefore, the gas collected at the outlet of the reactor can contain contaminants preventing its injection into the Danish gas grid. These contaminants may include hydrogen sulfide, ammonia, or volatile organic compounds (VOC). Additional gas purification stages have been added to the plant to assure the stability of the gas quality when either biogas or CO_2 feed gas is provided to the reactor. A filter to remove any excess H_2S still present in the gas product after the biological reaction was installed to insure the production of a gas with concentrations of contaminants compatible with grid injection. To minimize the potential for contamination of the product gas or downstream equipment with biological material, a foam trap was installed in series with the H_2S filter. The gas quality has been checked regularly at the plant and the conformity of the gas with the grid specifications has been verified on gas samples analyzed by an independent laboratory.

The production of a sweet gas, cleaned of corrosive contaminants, allows subjecting the gas to further post-treatment to achieve a water content and a relative composition in methane, hydrogen, and carbon dioxide compatible with the Danish gas grid. During the BioCat 3 project, two post-treatment approaches have been successfully tested independently and in combination: gas membranes able to preferentially extract excess hydrogen and CO_2 from the produced gas, and a pressure swing gas drier.

1.5.5.3 Weather proofing

In addition, several minor plant modifications have been carried out on the different process stages to improve its robustness and tolerance to changing weather conditions. The most sensitive equipment has been containerized (Figure 8), offering better control on their environment; it also proves to reassure visitors that it is possible to erect a fully weather proofed plant, in line with constraints of the Danish climate.



Figure 8. Containerized gas post-processing unit.

1.5.5.4 Result

After commissioning and testing of all modifications, stable operation with a high level of performance has been demonstrated and repeated and stable productions of a product gas meeting the specifications of the Danish gas grid has been achieved.

1.5.5.5 Quantification strategy for operation with Biogas

When the methanation plant uses biogas as a carbon source, the resulting product gas contains

two methane fractions, which despite being chemically perfectly identical, have different legal status: the bio-methane which was initially present in the biogas, is deemed renewable based on the feedstock used for its production, whereas the electro-methane should be deemed renewable based on the origin of the electricity used to produce the hydrogen. As the ratio between the two kinds of methane cannot be analytically determined at the injection site, it is necessary to include process inputs.

Electrochaea, Energinet.dk and HMN have recently (January 2017) agreed on the certification process for injection of biomethane into the Danish gas grid. The biomethane initially present in the biogas will be quantified at the entry point of the methanation reactor, and the electromethane produced by methanation will be determined by substracting the biomethane fraction from the total methane flow. The scheme still requires validation by Energistyrrelsen.

As a general outcome of the work package, the Biocat P2G plant has been improved to shift from demonstration of the technology to demonstration of the industrial maturity of the process design.

1.5.6 **WP-6**: Commissioning, start-up and operation (Experimental Development)

The BioCat 3 project was characterized by ~1500 hours of operation and 6 experimental campaigns carried out between December 2017 and September 2019. The main objectives of these campaigns were to further define the strategies to run a robust biomethanation process.

1.5.6.1 Stability of operation at different flow rates

The first campaign of BioCat 3 was performed in March and April 2018. The major goal of this campaign was to test the long-term stability of the process at several different flow modes. At each flow mode, the goal was to maintain for 72 hours a selected series of parameters in a range of \pm 10% of their average value, before changing to the next mode. Additionally, a new chemical dosing strategy was assessed during this campaign. The goal of the campaign was to establish if the new dosing strategy allows operation of the process at constant conditions at two specific operational modes.

1.5.6.2 Testing sequences to evaluate modes of automated operation

From May to June 2018, in order to understand the challenges, limitation and current state of the art of the BioCat plant, a series of sequences or modes of operation were defined by Electrochaea's Denmark, Development and Engineering Teams for an automated start-up, shutdown and recovery of the system. The goal of this campaign was to test and determine if these sequences are valid for automated and unattended operation of the BioCat system.

In summary, the following test sequence was performed three times:

- Start-up: Start of the system according to the start-up sequence
- Nominal 15: Operation at "Nominal 15" for 24 hours ramp up to "Nominal 30"
- Nominal 30: Ramp down to "Nominal 15"
- Shut down: Shutdown of the system
- Cold standby: Leave the system at Cold Standby for at least 6 hours

1.5.6.3 Validation of operational modes

In November of 2018, the campaign had four major objectives: maximal possible performance, post-processing unit test, validation of the recovery mode and fine-tuning of the startup procedure. Since the biocatalyst present in the reactor was not performing well, the system was freshly inoculated. Beforehand, the reactor will have to be drained and cleaned. The inoculation and ramp-up were performed as done in campaign 3, with the difference that flows were ramped until the system was not able to reach full conversion anymore or once the maximum electrolyzer capacity had been reached. The start-up sequence simulation was already performed within campaign 3 but had to be tested again after a change in chemical dosing strategy.

1.5.6.4 Post processing unit commissioning

To finalize the downstream gas polishing and injection readiness of the BioCat plant in Avedøre, purification membranes and gas drier needed to be commissioned and tested during dynamic operation. To address this scope, Electrochaea's Denmark and Engineering Team have defined sequences and a logic for PPU operation considering permeate recirculation in the carbon-feed.

The initial timeframe proposed were 3 weeks and the goals of this BioCat campaign were:

- System enabling after shut-down of approximately 3 months and biocatalyst reactivation.
- PPU membrane break-out and PPU operation/characterization/dynamic operation
- Gas drier commissioning

During this session, the PPU and gas drier were commissioned. Further work was identified in order to reach injection quality; some more work was required to achieve the desired function of the gas drier.

1.5.6.5 Environmental Technology Validation and Gas Injection

The last campaign of BioCat 3 was performed in September 2019 and had as objectives: to document specific performance claims for the Environmental Technology Verification (ETV) with data collected across agreed protocols, and to commission the connection to the injection station.

Within one week of continuous operation, the stable production of a gas compatible with the Danish gas grid was demonstrated the connection to the injection station was commissioned and eventually gas was injected at a flow-rate of 20 Nm³/h over a period of 24 hours. After the successful injection, the rest of the verification protocol agreed with the independent verifying body was implemented, demonstrating performance of the plant treating pure CO2 or raw biogas, with static or dynamic operation profiles (fast start-up and ramps)

1.5.7 **WP-7**: Business case development

1.5.7.1 Obstacles for P2G in the current framework conditions

Power-to-Gas bi-directionally connects the gas and electricity grid. Current regulations favor a unidirectional connection between the gas grid and electricity grid. To enable Power-to-Gas functionality, significant adjustments to the regulatory framework are required to permit the profitability of Power-to-Gas business cases.

1.5.7.2 Obstacles from the power grid

Currently, the Danish power grid disfavors technologies that convert power into other forms of energy like gaseous or liquid fuels. Obstacles have arisen when direct connections to adjacent renewable energy sources, such as windmills or photovoltaic panels, are sought. Grid related fees are being charged at a full rate and options to connect directly to the transmission grid are also limited by grid operators.

1.5.7.3 Obstacles from the gas grid

When using the carbon dioxide from biogas to produce methane, several obstacles arise for P2G. Methanized CO_2 does not qualify for subsidies under the current regulatory support environment. Moreover, in order to connect a P2G plant to the gas grid, a significant investment must be made for the injection point and operational costs should be paid by the P2G plant operator, but ownership of the injection asset remains with the gas grid operator. Finally, grid entry charges apply to a P2G operator, which decreases the profitability of the business case.

1.5.7.4 Recommendations for future regulatory framework in Denmark

During the development of a new support scheme for renewable gases, it is recommended to take into consideration the following aspects:

• Reservation of a pool of funds for methanation gas produced from excess CO₂ from the energy agreement available 240 mill DKK for biogas and P2X gases.

- Integrate into the New Gas Strategy the reduction of CO₂ from second generation biogas upgrading
- Exempt P2X technologies from TSO and DSO charges for energy storage schemes.
- Enable the use of adjacent renewable sources for P2G.
- Enable the emission of certificates for Guarantees of Origin and green gas certificates from methanized CO₂
- Guarantee in the implementation of the RED II Directive the recognition of methanized gas as 100% renewable to enable the access to subsidies.

As it can be seen in Error! Reference source not found., under current conditions the operation of a P2G plant is not profitable because the generation of revenues from gas at natural gas prices are not enough to cover the cost of operating the plant.

Table 2. Example of a 10 MW plant operating under current conditions without heat or oxygen sales

Assumptions:		
Capex Methanation + Electrolyzer	DKK 93.4 million	
Operating hours	8760	
Electricity price	DKK 512	
Gas price	DKK 111	

Results:	
Discount rate	8%
IRR (20)a	n/a
NPV (20)a	DKK (54,796,439)
Payback period	n/a

As it can be seen in Error! Reference source not found., under current conditions the operation of a P2G plant is not profitable because the generation of revenues from gas at natural gas prices are not enough to cover the cost of operating the plant.

Table 3. Example of a 10 MW plant with support for methanation gas without heat or oxyaen sales

Assumptions:

Capex Methanation + Electrolyzer	DKK 93.4 million
Operating hours	8760
Electricity price	DKK 512
Gas price	DKK 1028

8%

9

Results: Discount rate 10.0% IRR (20)a NPV (20)a DKK 13,823,314 Payback period

As seen in Error! Reference source not found., when providing support for biomethane produced with P2G, it is possible to achieve profitability of operations of such a plant in 9 years assuming a discount rate of 10%.

WP-8: Dissemination 1.5.8

The BioCat plant in Avedøre, Denmark has been used effectively for dissemination of technical and economic information about Power-to-gas systems. There has been a great deal of interest in the plant. Since the beginning of the granting period, more than 200 people from 100 different organizations have taken a tour of the plant. Many interested parties also visit the Electrochaea.GmbH headquarters in Planegg, Germany where they have the opportunity to learn about the power-to-gas process. The accomplishments of BioCat Avedøre have been widely presented. During this granting period, more than 40 presentations have been made in 13 countries. The well-received presentations have been made at scientific and business conferences by many different Electrochaea employees. One of the achievements of BioCat 3, the first injection of renewable methane onto the Danish gas grid, has recently been featured in several news articles.

(<u>https://www.energy-supply.dk/article/view/680869/power2gasanlaeg i avedore lev-</u> <u>erer biomethan til gasnettet?ref=newsletter&utm medium=email&utm source=newslet-</u> <u>ter&utm campaign=daily</u>

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https://ctwatch.dk/secure/nyheder/milj_teknik/article11682856.ece?utm_campaign=CleantechWatch&utm_content=2019-10-17&utm_medium=email&utm_source=cleantechwatch)

1.6 Utilization of project results

The Biocat 3 project, which drew from the results of the Biocat 2 project (EUDP P2G project, Forskel Biocat project), resulted in significant improvements of the demonstration plant and eventually demonstrated the capacity of Electrochaea to design and operate a pre-industrial Power-to-Gas plant by bio-methanation able to inject gas on the Danish gas grid. The BioCat 3 project provided valuable learnings in design and operation of a P2G plant. It allowed Electrochaea to de-risk the technology and develop industry standard design and operating documentation, which previously was not possible due to the limited experience.

The experience and results gathered during the project form the backbone of the engineering package used by Electrochaea to develop commercial projects:

functional requirements of each process stage have been refined and technological solutions have been validated allowing the definition a standardized process description ready for scaleup to commercial scale.

High-level and low-level controls definition have been developed and tested to improve process reliability and flexibility, to allow automatic operation and interaction with grid-balancing entity.

Additionally, new improvements have been identified, test results will support further development to keep improving process performance and reducing operation costs. The effort on process modelling and control will support the scale-up, further development of high-level controls and plant optimization efforts.

Many of the learnings from BioCat 3 have been presented across several continents, further developed Electrochaea's process and led to the development of an informed front-end engineering package which was used successfully in a subsequent project where an automated second generation P2G plant was built.

1.7 Project conclusion and perspective

The P2G-BioCat 3 project aimed at lowering the remaining risks to commercialization, at establishing standards for control and integration, and at identifying in the Danish power and gas markets the economic conditions necessary to attract capital investment for implementation of power-to-gas (P2G) at grid scale in Denmark. The one-year project, with reduced scope from the original application, has provided many benefits to furthering the commercial application of P2G in the Danish market and worldwide and provided valuable learnings in design and operation of a P2G plant. It allowed Electrochaea to de-risk the technology and develop industry standard design and operating documentation, which previously was not possible due to the limited experience. Many of the learnings from BioCat 3 have been presented across several continents, further developed Electrochaea's process and led to the development of an informed front-end engineering package which was used successfully in a subsequent project where an automated second generation P2G plant was built.

The successful completion of the Biocat 3 project allows Electrochaea to design a commercialsize plant within the EUDP Biocat Roslev project with a solid base to define expected performance and scale-up and to engage public and private stakeholders with the return of experience of a proven technology ready to support Denmark path toward a radical decarbonization of the energy sector.