Public End Report

Phecam - Project

Project number: TCCU218012
Project title: Preparation pilot reuse CO_2 waste incineration to formic acid
(“voorbereiding Pilot HErgebruik CO_2 Afvalverwerking naar Mierenzuur”)
Coordinator: Twence
Participants: Coval Energy
TU Delft
TNO
Project period: 1 February 2019 – 1 July 2020
Date: 28 September 2020

Het project is uitgevoerd met subsidie van het Ministerie van Economische Zaken, Nationale regelingen EZ-subsidies, Topsector Energie uitgevoerd door Rijksdienst voor Ondernemend Nederland.

Nederlandse samenvatting
Vermindering van CO_2 emissies door het om te zetten naar mierenzuur of formiaat is een heel interessante methode om CO_2 te hergebruiken, omdat het fossiele brandstoffen kan vervangen als grondstof om chemicaliën en plastics te maken. De omzetting gebeurt in een electrolyser, waarin CO_2 en water op een directe wijze worden omgezet naar mierenzuur/formiaat en zuurstof, met als voordeel dat het selectief en energie-efficiënt kan worden gemaakt.
Het doel van het Phecam project is het uitvoeren van het benodigde onderzoek om een ontwerpbestek te maken voor een proefinstallatie voor het omzetten van CO_2 naar mierenzuur/formiaat op het bedrijfsterrein van Twence in Hengelo.

Het project is met een positief resultaat afgesloten, wat inhoudt dat er een proces is gedefinieerd hoe mierenzuur kan worden geproduceerd en opgezuiverd naar de marktkwaliteit. En hiervoor is een ontwerpbestek gemaakt, dat de basis kan zijn voor een daadwerkelijke proefinstallatie in een vervolgproject. Hiervoor is een zogenaamd 'basic engineering' pakket gemaakt. Hierbij is de focus gelegd op het meest nieuwe en onbekende onderdeel, wat de productie van mierenzuur/formiaat is. Een toekomstige proefinstallatie kan gemakkelijk worden gedefinieerd door dit ontwerpbestek te gebruiken voor de elektrochemische processtap. De andere processtappen zijn commercieel verkrijgbaar, maar moeten nog wel gespecificeerd worden, maar betreffen voornamelijk de parameters aan de interfaces van de elke processtap.

Omdat de wereldmarkt voor mierenzuur momenteel relatief beperkt is, goed voor ongeveer 1 megaton CO_2 hergebruik, is Coval Energy voortdurend op zoek naar toepassingen voor mierenzuur en formiaat voor gigatonnen aan CO_2 hergebruik. Zo'n grotere markt voor hergebruikt CO_2 toepassingen kan alleen maar ontwikkeld worden met ondersteuning van regelgeving, omdat huidige toepassingen gebaseerd zijn op fossiele brandstoffen. En omdat fossiele brandstoffen erg goedkoop zijn, is het erg lastig om een positieve business case te maken voor hergebruikt CO_2.
Twee benaderingen zouden kunnen helpen om zo'n positieve business case te maken. De eerste is om mierenzuur of formiaat te gebruiken als halffabricaat in plaats van een eindproduct. De tweede is het gebruik van 'off-spec' mierenzuur of formiaat, dat afwijkt van de marktstandaard, waarbij het product wordt gebruikt zoals het uit de reactor komt, zonder opzuivering.

De mogelijke spin-off van dit project is het inzicht dat deze technologie een grootschalige toepassing van CO_2 hergebruik mogelijk kan maken als deze wordt ingebed in een productieproces, waarbij mierenzuur/formiaat een grondstof is in plaats van een eindproduct.

Het typische vervolgproject voor dit proces is een proefinstallatie in een industriële omgeving, waar een beperkte installatie kan worden getest met langere bedrijfsduur een grotere capaciteit.
Andere vervolgprojecten kunnen de ontwikkeling zijn van productieketens waar de efficiënte omzetting van CO_2 naar mierenzuur/formiaat gecombineerd kan worden met aansluitende omzettingsstappen. Interessante projecten zijn bijvoorbeeld de combinatie met fermentatieprocessen, waarbij bijvoorbeeld ethanol of biokerosine kan worden geproduceerd, en waarbij ongewenst landgebruik voor energiegewassen zoals suikers kan worden voorkomen.

Maatschappelijke acceptatie voor dit soort projecten is haalbaar, maar moet wel worden ondersteund met een voortdurende dialoog met de omgeving.

De samenvattende conclusie is dat de technologie op het punt staat om de stap te zetten naar TRL 6, zodat het verder kan worden richting markt toepassing vóór 2030. Grootschalig CO_2 hergebruik kan worden bereikt wanneer het product zodanig wordt gebruikt dat het niet hoeft te worden opgezuiverd.

Summary
Reduction of CO_2 by converting it to formic acid/formate is a very interesting method to reuse CO_2, as it can displace fossil fuels as a feedstock to produce chemicals and plastics. The conversion of CO_2 takes place in an electrolyser, where CO_2 and water are directly converted to formic acid/formate and oxygen, with advantage that it can be produced very selective and energy efficient.
The objective of the Phecam project is to conduct the necessary research to make a design specification of a pilot plant for the conversion of CO_2 to formic acid/formate at the premises of Twence.

The project has been concluded with a positive result, meaning that a process has been defined how formic acid/formate can be produced and purified up to market quality. And herefor a design specification has been made, which can be basis of an actual pilot plant for a follow up project.
This process has been used as basis for a basic engineering package. Here the focus has been put on the most new and unknown element, being the electrochemical production of formate.
A future pilot plant can easily be defined using this design specification for the electrochemical process step. The other process steps are commercially available, but do require user defined specifications. Such specifications can relatively easy be defined once such follow-up project has been decided, and merely address the process parameters at the interfaces of every process step.

As the world market for formic acid is relatively limited, covering approximately 1 megaton of CO_2 reuse, Coval is continuously looking for applications of formic acid/formate for CO_2 reuse in the gigaton range. Such bigger market for re-used CO_2 applications can only be developed with regulatory support, as present applications are based on fossil fuel: as fossil fuel is currently very cheap, it makes it almost impossible to build a profitable business case from re-used CO_2.
Two approaches might help to build profitable business cases. The first one is to use formic acid/formate as a feedstock rather than a ready-to-sell product. The second one is the use of 'off-spec' formic acid/formate, in the sense that the concentration deviates from the 'market-standard' as the reactor raw production will be used, and further purification is not required.
The possible spin-off of this project is the insight that this technology for CO_2 re-use towards formic acid/formate might be an enabler for larger scale CO_2 re-use when applied in a production chain, where the (raw) produced formic acid/formate is a feedstock rather than a ready product.

The typical follow-up project for this process is a field test in an industrial environment, where a small scale setup can be operated for a longer time and at a higher capacity.
Other follow-up projects can be the development of production chains where the efficient conversion to formic acid/formate is combined with other consecutive conversion steps. Interesting projects in this respect is the combination with fermentation processes, where for example ethanol of biokerosene can be produced, and unwanted land use for sugar production can be avoided.

Societal acceptance of these kind of projects is feasible, but will be very much helped by an ongoing communication with stakeholders.

Overall conclusion is that the technology is on the verge to make its step to TRL6, where it can be developed further towards market application before 2030. Large scale CO_2 re-use can be achieved when raw reactor product can be used as intermediate towards a consecutive conversion step, like fermentation.

Introduction

The company Twence, active in the Dutch waste sector, is looking for future opportunities to create more value from its anticipated investment in a 100 kton CO_2 capture plant, which will become operational in 2021-2022. Such investment is a direct consequence of a CO_2 reduction target of 2 Mton in 2030 applied by the Dutch government to the Dutch waste sector.
The first application of the captured CO_2 is supply to neighboring greenhouses, but more applications of CO_2 will give Twence more opportunities to sell its CO_2 and to de-risk its business case.
For this purpose, Twence and Coval Energy are cooperating to develop Coval's proprietary technology to convert CO_2 in a high pressure setup to formic acid/formate.

Reduction of CO_2 by converting it to formic acid/formate is a very interesting method to reuse CO_2, as it can displace fossil fuels as a feedstock to produce chemicals and plastics. The conversion of CO_2 takes place in an electrolyser, where CO_2 and water are converted to formic acid/formate and oxygen. Such production principle is comparable to a hydrogen electrolyser, where water is used to produce hydrogen and oxygen.
Coval is using a technology where formic acid/formate is produced via direct conversion. The advantage of making formic acid/formate is that it can be produced very selectively and energy efficient.
The technology is building on an earlier project as mentioned in the project plan, called P2FA (Power to formic acid; RVO project number TEEI116076), where a consortium consisted of Coval Energy, TNO, TU Delft, CE Delft and Mestverwerking Friesland cooperated to prove the selectivity and efficiency of the process.
For this project also TNO and TU Delft are participating, as a continued cooperation from the P2FA-project. The contribution of TNO is the design and construction of a process and measurement setup, in which the Coval reactor can be tested. The contribution of TU Delft is advanced modelling of the reactor including membrane.

Objective

The objective of the Phecam project is to conduct the necessary research to make a design specification of a pilot plant for the conversion of CO_2 to formic acid/formate, as a preparation on a real pilot plant or field test. Such specification contains all design parameters needed to actually build such pilot plant at the premises of Twence. The pilot will use CO_2 from an existing (small) CO_2 capture plant which Twence is already deploying for making sodium bicarbonate.
The research questions are addressing practical design questions determining the conditions for an optimal operation of the technology with the present knowledge.
Such questions address amongst others the choice of electrolytes and concentration, overpotential, cell geometry, cell stacking design, operational pressure, electrode composition, purification process, and optimization of the interface conditions between the different process steps.
The outcome should lead to the lowest electricity consumption per unit of product produced, which will be addressed in a business case.
As the anticipated pilot plant will be located at Twence, the company will use its regular communication channels with local representatives and neighbors to gauge the attitude towards the production of formic acid/formate.

Working method

The project is subdivided in 5 blocks:

1. Reactor research: research of several variables in the electrochemical process to determine the most optimal process conditions. Here several smaller electrochemical cells for selection purposes will be used, as well as a new developed high pressure electrochemical reactor, and

a measurement setup where the whole process can be tested and measured under the anticipated process conditions.
2. Purification: determining of the most effective method to purify the mixture formed in the electrochemical reactor to formic acid with a market quality of 85%, with the help of a dedicated test setup based on electrodialysis.
3. Design spec: conception of a design package containing all process conditions and basic engineering documents, as a basis for the design and construction of a pilot plant.
4. Business case: determining a business case for the reuse of CO2 to formic acid/formate based on the experimental results.
5. Societal acceptance: determining of potential issues regarding the reuse of CO_2 to formic acid/formate, based on existing communication structures of Twence.

<u>Measurement setup</u>
Hereunder an impression of the applied measurement setup, called HiPE2, as developed by TNO;

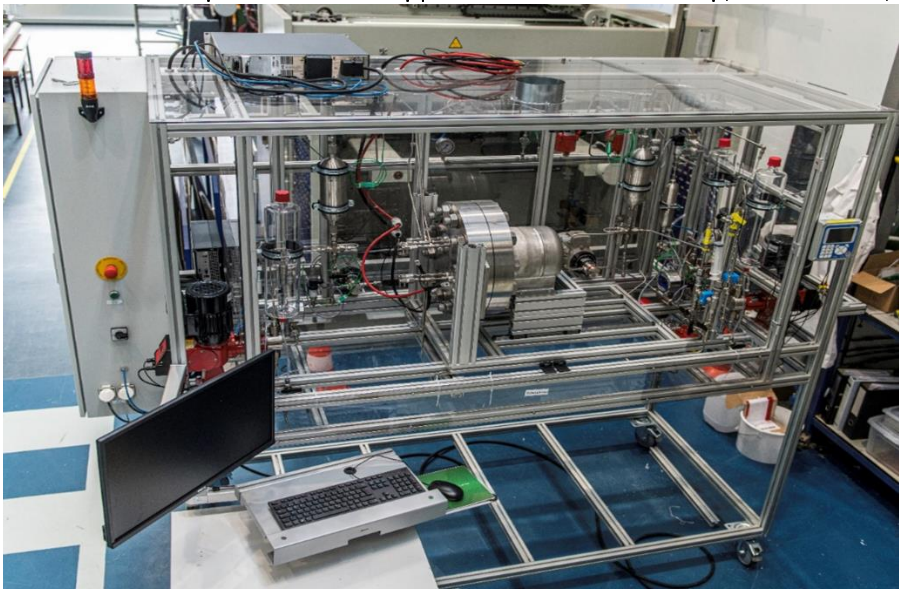

Figure 1: HiPE2

<u>Results of the project</u>
The project has been concluded with a positive result, meaning that a process has been defined how formic acid/formate can be produced and purified up to market quality. And herefor a design specification has been made, which can be basis of an actual pilot plant for a follow up project.

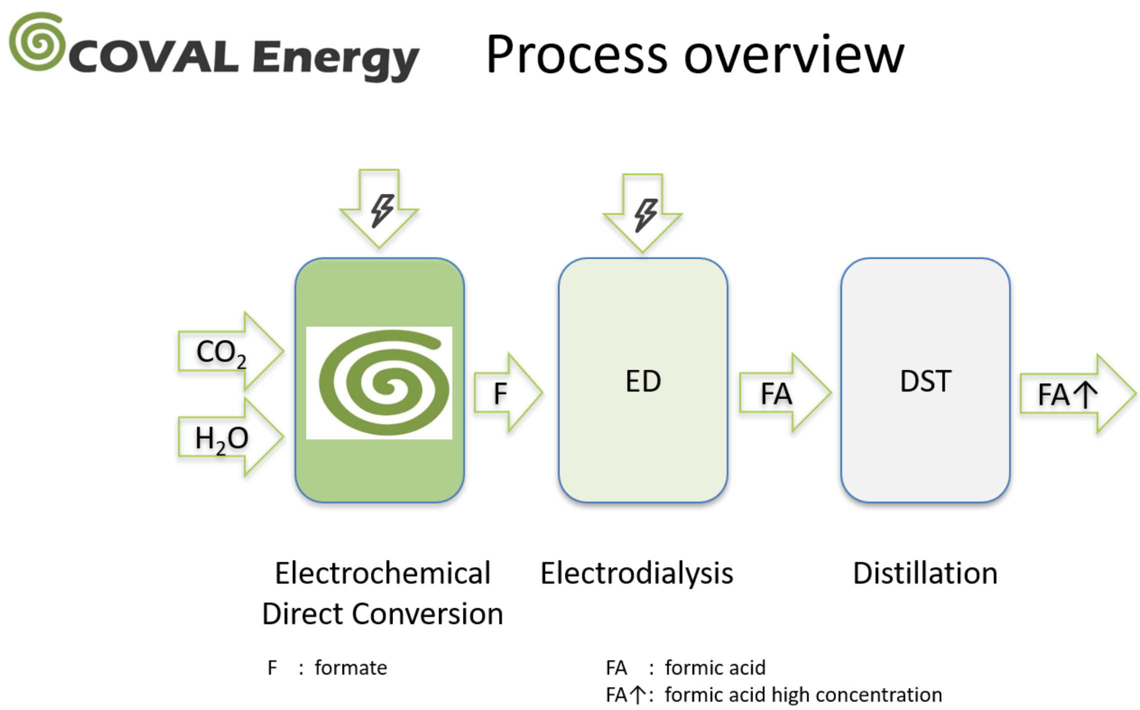

Figure 2: Coval process from CO_2 to formic acid

The full process up to market quality formic acid consists of 3 process steps:

1. Direct CO_2 conversion to formate using high pressure technology (proprietary technology of Coval).
    - The reactor contains a stack of cells producing formate;
    - The reactor will be operated at its highest Faraday efficiency, whereby 90% is feasible;
    - Multiple identical reactors can be combined in such way (serial and/or parallel) that the formate concentration at the reactor outflow will be 1 Molar (9%);
    - Capacity can be increased by repeating the above mentioned configuration by adding more identical reactors;
    - For the anticipated filed test an initial stack of 20 cells per reactor is assumed, but an extension towards 100-200 cells per reactor seems feasible;
2. Conversion of formate to formic acid by electrodialysis (commercial available technology with Coval specifications).
    - The formate reactor outflow can be converted to formic acid using electrodialysis (ED);
    - ED can convert 1 Molar formate to approximately 3-6 Molar formic acid, or approximately 9% formate concentration to 25-50% formic acid concentration;
    - The achievable concentrations of formic acid have the right specs for application in bioreactors as feedstock for fermentation processes;
    - ED units are commercial available to be built on specification, but Coval needs to determine the spec depending on the anticipated application;
3. Distillation of formic acid to market quality specification of 85% (commercial available technology with Coval specifications).
    - For concentration of formic acid of 25-50% up to 85% a distillation step is required;
    - Such technology is commercial available, and can potentially be optimized and improved applying for example 2-pressure-distillation, or the use of mechanical vapor recompression.

This process has been used as basis for a basic engineering package. Here the focus has been put on the most new and unknown element, being the electrochemical production of formate.
A future pilot plant can easily be defined using this design specification for the electrochemical process step. The other process steps are commercially available, but do require user defined specifications. Such specifications can relatively easy be defined once such follow-up project has been decided, and merely address the process parameters at the interfaces of every process step.

The design package has been composed in cooperation with Twence, Coval Energy and the engineering company Emmtec. The latter has made all engineering documents needed for the pilot plant.
The design is described in a 'Basis of Design' for the Phecam project. The full engineering documentation consists of the following documents:

Document number	Title	revision
12275.1000	Equipment list	[-]
12275.1001	Cross index	[-]
12275.1002	PFD's	1
12275.1003	P&ID's	1
12275.1004	Line list	[-]
12275.1005	Valve list	[-]
12275.1006	Mass Balance	[-]
12275.1019	Functional description	[-]
12275.1029	Safety valve list	[-]
12275.1030	Hazop Twence PHECAM	[-]
12275.1038	Lay-out Container	[-]

Hereunder a short impression of the design work.

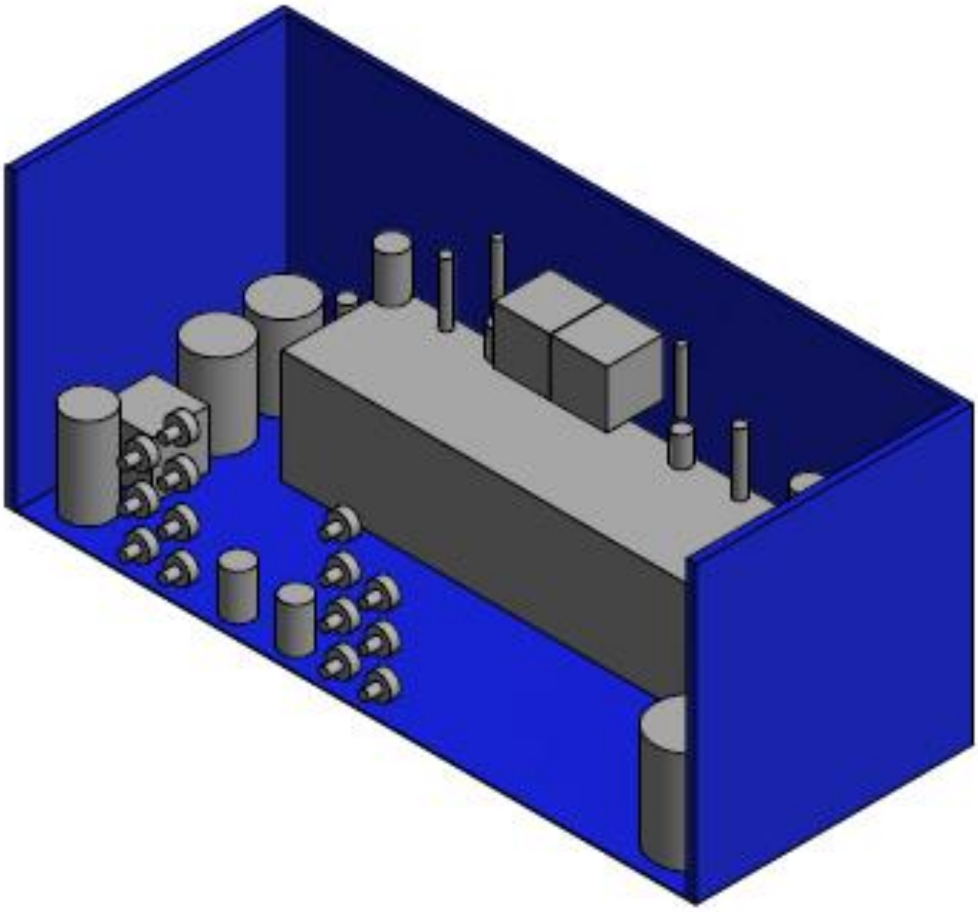

Figure 3: Layout of pilot plant

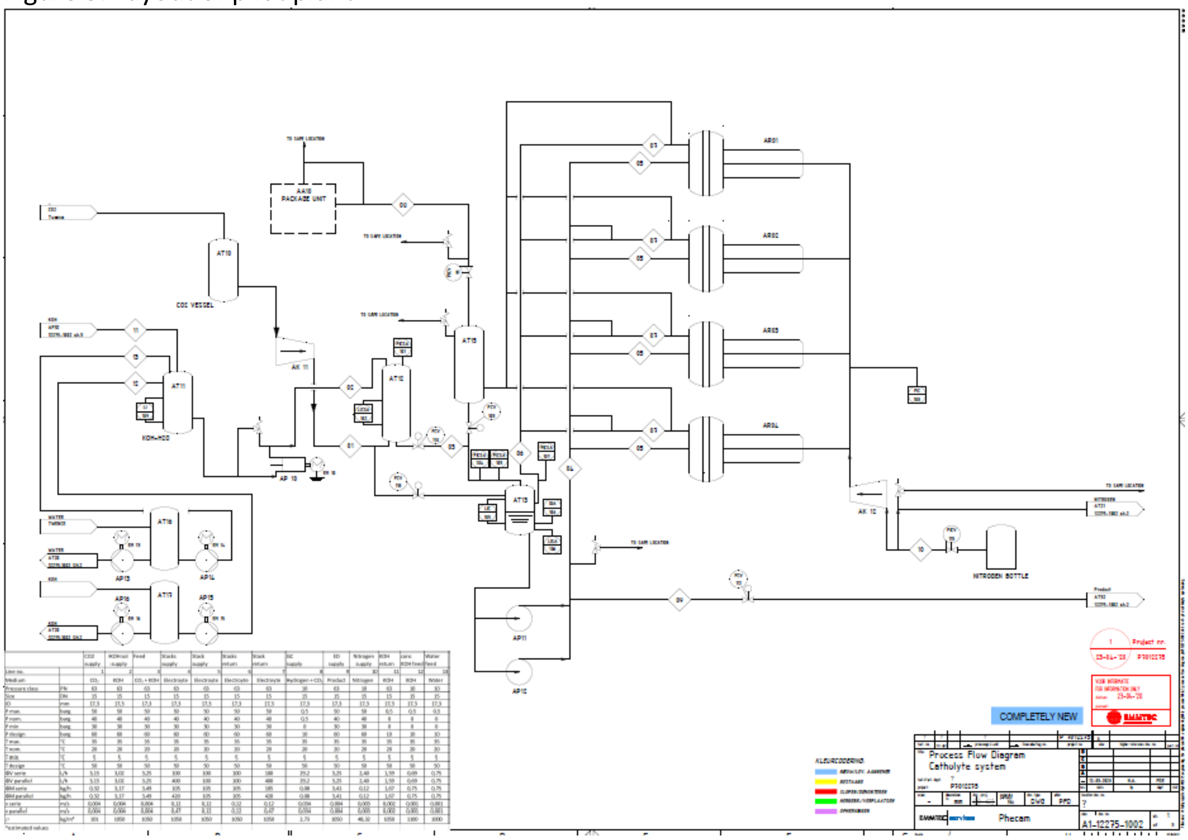

Figure 4: Process Flow Diagram of the catholyte system

Another achievement of this project is the modeling of the electrochemical cell, where the whole cell has been modeled including all relevant reactions. As a novelty, the bipolar membrane has been modeled, gaining a better insight in reactions at the interface between membrane and fluid, and consequently between fluid and electrodes. On this work an article is in the process of being published.
For this project, the most important results of this modeling so far is the insight that the diffusion of CO_2 through the liquid is the most limiting factor to achieve higher current densities.

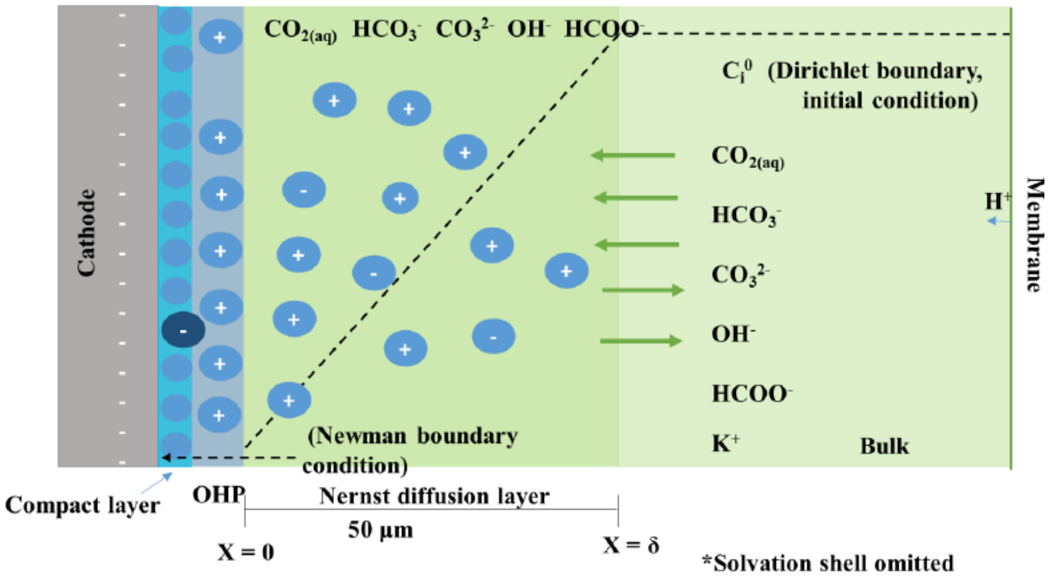

Figure 5: Impression of model for cathode chamber

The goal of Phecam is to make a design specification for a pilot plant to produce market quality formic acid/formate.
But seen the current relatively limited world market for such product, covering approximately 1 megaton of CO_2 reuse, Coval is continuously looking for applications of formic acid/formate for CO_2 reuse in the gigaton range, as such products can be produced very selective and efficient from CO_2.

For potential markets for formic acid and formate from reused CO_2 the following pathways can be considered, as is depicted in the figure hereunder:

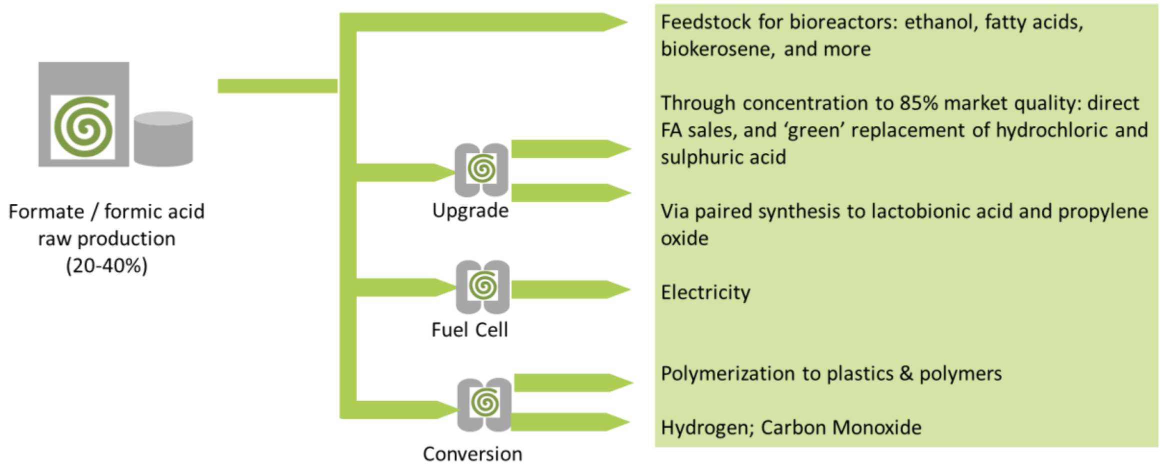

Figure 6: Potential larger market applications for formic acid/formate

Important aspect is that formic acid/formate might be used as a feedstock rather than a ready-to-sell product.
Another important aspect herewith is the use of 'off-spec' formic acid/formate, in the sense that the concentration deviates from the 'market-standard' as the reactor raw production will be used, and further purification is not required.
In line herewith 3 products have been defined in the business case in Annex 8.
These product are (in line with the process as depicted in Figure 5):

- Product 1: Formate at 30% concentration;
- Product 2: Formic acid at 30% concentration;
- Product 3: Formic acid at 85% market quality.

For these products profit and cost have been estimated, assuming a parallel development like hydrogen electrolysis.

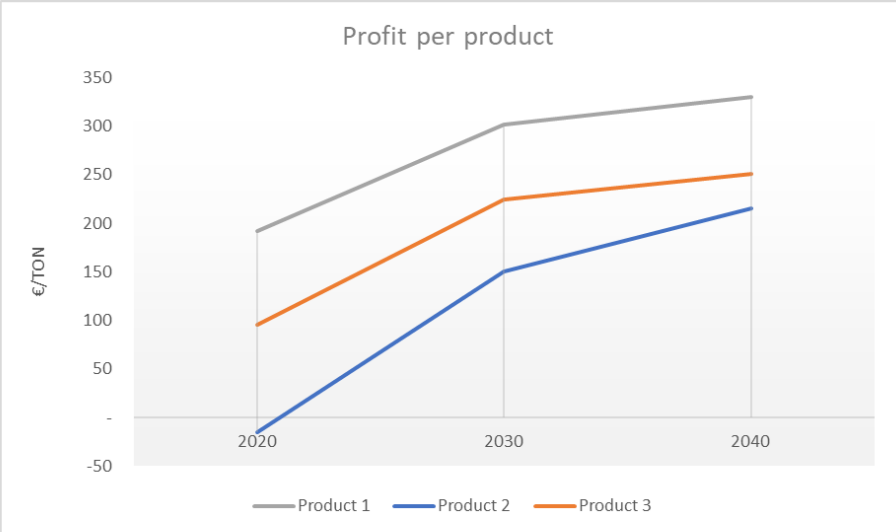

Figure 7: Estimated profit per defined product

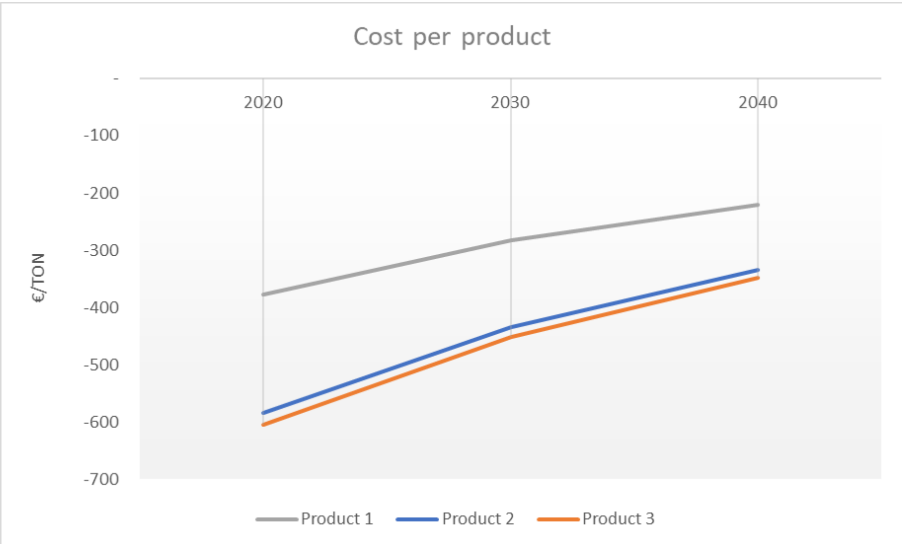

Figure 8: Estimated costs per defined product

<u>Social Acceptance</u>
The anticipated location of a pilot plant is at the premises of the company Twence. That's why the project has made use of existing communication channels of this company with its stakeholders.

The main communication of Twence was addressing its efforts to get permits for the envisaged large 100 kton CO_2 capture plant, in which they succeeded. To motivate the circular use of carbon, Twence has not only addressed the application of CO_2 to surrounding greenhouses, but also the further valorization of CO_2 to formic acid or green fuels. These efforts are appreciated by Twence's stakeholders, but for Twence it is clear that an ongoing communication is vital in every further step in the development.

Possible spin-off and follow-up projects

The possible spin-off of this project is the insight that this technology for CO_2 re-use towards formic acid/formate might be an enabler for larger scale CO_2 re-use when applied in a production chain, where the (raw) produced formic acid/formate is a feedstock rather than a ready product.
This would be the development of a production chain where the combination of 2 production steps would result in a better process than an existing production process.
The typical follow-up project for this process is a field test in an industrial environment, where a small scale setup can be operated for a longer time and at a higher capacity.

Other follow-up projects can be the development of production chains where the efficient conversion to formic acid/formate is combined with other consecutive conversion steps. Interesting projects in this respect is the combination with fermentation processes, where for example ethanol of biokerosene can be produced, and unwanted land use for sugar production can be avoided.

Conclusions and recommendations

Overall conclusion is that the technology is on the verge to make its step to TRL6, where it can be developed further towards market application before 2030.
Large scale CO_2 re-use can be achieved when raw reactor product can be used as intermediate towards a consecutive conversion step, like fermentation.
Product prices of (raw) formic acid/formate will decline as technology and its scale will develop over the coming years.

Information of this report

Publications on Phecam:

- This public report;
- Article on modelling (to be published);

Extra copies of this report:

- Only digital distribution;

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