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BIO-CEL

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Contents

1.	Samenvatting	3
2.	Summary	5
3.	Introduction	7
4.	Project objectives	9
5.	Approach and activities	11
5	.1. Approach	11
5	.2. Description of work, Workpackages and deliverables	12
	WP 1 Design of integrated reaction-separation process	12
	WP 2 Construction of prototype unit	13
	WP 3 Valorisation	14
	WP 4 Project management	14
6.	Results	16
6	.1. WP1 Design of integrated reaction-separation process (TUD)	16
	Task 1.1 Solvent properties for CO ₂ capture (TUD)	17
	Task 1.2 Electrolyte properties for CO2 conversion to oxalic acid (TUD)	18
	Task 1.3 Electrolyte-capture solvent optimization (TNO / TUD)	23
	Task 1.4 Product recovery (TUD)	27
	Task 1.5 Process design and optimization of integrated process (TT/DMT)	29
	Task 1.6 Life-cycle analysis and multi-criteria analysis (DMT/RUG)	30
6	.2. WP2 Construction of prototype unit (TNO)	33
	Task 2.1 Construction of lab-scale unit (TNO)	33
	Task 2.2 Testing of prototype unit (TNO)	35
	Task 2.3 Integration with renewable energy source (TNO)	37
6	.3. WP3 Valorisation: System integration and Techno-economic evaluation (TT)	38
	Task 3.1 System integration based on P2C, CCU, and source-sink matching (MvF/DMT)	38
	Task 3.2 Techno-economic analysis and business case (DMT, TT, TNO, TUD)	39
7.	Conclusions	43
	Solvent properties for CO2 capture and conversion (TUD)	43
	Electrolyte-capture solvent optimisation (TNO)	43
	Product recovery (TUD)	43
	Process design of integrated process (TT/DMT)	44
	Life-cycle analysis and multi-criteria analysis (DMT/RUG)	44
	Techno-economic analysis and business case (DMT, TT, TNO, TUD)	44
8.	Dissemination & communication	46

1. Samenvatting

Een van de opkomende manieren om CO2 te gebruiken is gebaseerd op de omzetting van CO2 in hoogwaardige chemicaliën die via een elektrochemische reactie worden geproduceerd. CO2 afvang en -utilisatie (CCU) vereist de integratie van een reeks verschillende processtappen. De ontwikkeling van een economisch levensvatbare CO2-conversieroute ondersteunt de belangrijkste doelstellingen van TKI Nieuw Gas/CCUS en het programma Systeemintegratie. Elektrochemische conversie van CO2 wordt nog voornamelijk op labschaal gedemonstreerd, waarbij de ontwikkeling van stabiele en selectieve elektroden centraal staat. Er is minder aandacht besteed aan de essentiële stappen van de integratie van de verschillende processen, zoals afvang, omzetting en productterugwinning, en in het bijzonder is de opschaling van een elektrochemische stack nog niet in overweging genomen. De motivatie van dit project is dus te werken aan de commercialisering van elektrochemische omzetting van CO2 in een hoogwaardig product.

De belangrijkste bijdrage van het voorgestelde project aan het CCUS-programma is de ontwikkeling van nieuwe elektrochemische reactorconcepten, die verschillende scenario's voor zowel elektrificatie als CO2-utilisatie zullen ondersteunen en vergemakkelijken. De nadruk ligt op het procesontwerp voor een geïntegreerd afvang- en omzettingsproces, met efficiënte terugwinning van het product (oxaalzuur). Daarnaast is de opschaling van de elektrochemische flowreactor in termen van stroomdichtheid en opbrengsten een van de belangrijkste realisaties. De CO2-vermindering die wordt bereikt door het voorbeeldproduct waarop we ons in dit project richten (oxaalzuur) is een andere belangrijke bijdrage aan de doelstellingen van CCUS. Per kg oxaalzuur wordt ongeveer 2 kg CO2 verbruikt, en dit zal bijdragen tot de vermindering van de CO2-uitstoot die normaal zou gepaard gaan met de traditionele productieroute op basis van fossiele brandstoffen. Op lange termijn zullen de voorgestelde werkzaamheden bijdragen tot volledig duurzame chemische syntheseketens op basis van CO2-conversieproducten.

Er zijn drie hoofdactiviteiten in dit project: moleculaire simulaties voor het screenen van combinaties van oplosmiddel en elektrolyt, experimentele optimalisatie van de gecombineerde CO2-afvangst- en - conversiestap, en procesontwerp. De verschillende activiteiten zullen een beter inzicht verschaffen in het ontwerp en de werking van CO2 elektrolyzers. In het bijzonder zijn twee verschillende integratieconcepten onderzocht. Het eerste concept is gebaseerd op de integratie van het afvangen van CO2 uit rookgassen, het tweede concept op de integratie met bronnen van CO2 onder hoge partiële druk (b.v. biogas en waterstofproductie). Experimentele resultaten voor een gecombineerd afvangsolvent-elektrolytvloeistof werden gevalideerd met behulp van een numeriek engineeringmodel. Er is een procesontwerp gemaakt met behulp van een flow-sheeting programma om het totale proces van een CO2 afvangststap, een CO2 omzettingsstap en een productterugwinningsstap te integreren en te optimaliseren. Tenslotte is de volledige waardeketen van CO2-afvang en CO2-gebruik tot de productie van een commercieel product geanalyseerd, zowel wat de economische aspecten (TEA) als wat de milieu-effecten (LCA) betreft.

In de simulatiestudie werden de dichtheden, viscositeiten, diffusiviteiten en ionengeleidings - coëfficiënten van gemengde oplosmiddelen bestaande uit DES (d.w.z. reline en ethaline), methanol en propyleencarbonaat berekend met behulp van moleculaire simulaties. Om een kwantitatieve beoordeling van de affiniteit en het massatransport van CO2, oxaalzuur en mierenzuur in de gemengde oplosmiddelen mogelijk te maken, zijn ook de oplosbaarheden en de zelfdiffusiviteiten van deze opgeloste stoffen berekend. Uit onze resultaten blijkt dat de toevoeging van DES aan de organische oplosmiddelen de oplosbaarheden van oxaalzuur en mierenzuur verhoogt, terwijl de oplosbaarheid van CO2 in de ethalinehoudende mengsels in dezelfde orde van grootte ligt als die van de respectieve zuivere organische componenten.

Bij de experimentele optimalisatie en opschaling werden de oplosmiddelen getest. De in dit project geteste ionische vloeistoffen zijn helaas geen geschikt medium om als katholiet te fungeren in dit elektrochemische proces. Hoge afbraaksnelheden, lage activiteit bij de reductie van CO2, en lage selectiviteit van oxaalzuur verlagen hun toepassing als haalbare oplosmiddelen voor de productie van oxaalzuur. Op cholinechloride gebaseerde diep-eutectische oplosmiddelen vertonen een hogere

activiteit bij de reductie van CO2 dan de geteste ionische vloeistoffen, maar een lage selectiviteit bij de vorming van oxaalzuur, en worden daarom ook ontraden als katholyt voor dit elektrochemische proces. De aanwezigheid van water heeft een negatieve invloed op de vorming van oxaalzuur en bevordert de productie van mierenzuur. Concluderend kan worden gesteld dat verder onderzoek nodig is om inzicht te krijgen in de uitdagingen van het opschalen van deze technologie om dezelfde KPI's te bereiken die op kleinere schaal werden verkregen.

De terugwinning van oxaalzuur uit niet-waterige oplossingen zoals propyleencarbonaat is een uitdaging. De toestand van het zuur (gedissocieerd of niet-gedissocieerd), die afhangt van de pH en de eis van een watervrij oplosmiddel in de elektrolyser, bemoeilijkt aanzienlijk de downstream verwerking. Wij hebben vloeistof-vloeistof extractie, electrodialyse, koelkristallisatie, en gas antisolvent precipitatie (GAP) overwogen voor oxaalzuurscheiding. Wij tonen aan dat alleen GAP met CO2 als antisolvent kan worden gebruikt voor oxaalzuurscheiding uit propyleencarbonaat.

Er is een haalbaarheidsstudie uitgevoerd om de elektrochemische omzetting van CO2 naar oxaalzuur op te schalen. Een aantal opties voor de downstream verwerking van oxaalzuur zijn geëvalueerd op basis van een vergelijking van een twee- en een drie-compartimenten celconfiguratie. Over het algemeen zijn de kosten voor een elektrolyser met drie compartimenten hoger dan die met twee compartimenten. Bovendien is, aangezien de Zn-anode tijdens de reactie wordt verbruikt, het downstream-gedeelte voor het zinkanodeproces complexer, aangezien hiervoor een gasafscheider, een centrifuge, een kristallisator en een tweede centrifuge nodig zijn.

Het "global warming potential" (GWP) van de natriumformiaat- en de koolhydraatroute voor de productie van oxaalzuur werd berekend op respectievelijk 1,364 kgCO2/kg(COOH)2 en 3,277 kgCO2/kg(COOH)2. Het GWP van het elektrochemische proces (0,467 kgCO2/kg(COOH)2;-0,511 kgCO2/kg(COOH)2) werd ook berekend. Volgens de berekeningen heeft het theoretische elektrochemische proces een lager GWP dan de twee andere hedendaagse, commerciële processen. Op voorwaarde dat het elektrochemische proces economisch levensvatbaar is, biedt het een veelbelovende mogelijkheid om het GWP van de oxaalzuurindustrie te verlagen wanneer het wordt toegepast.

Er is een procesontwerp en een techno-economische evaluatie van de waardeketen voor de elektrochemische omzetting van CO2 in oxaalzuur uitgevoerd. We hebben aangetoond dat het proces een positieve NPV (\$ 16 M) en een PBT van 4 jaar heeft in het basisscenario, met: een stroomdichtheid van 100 mA/ cm2, een Faraday-efficiëntie van oxaalzuur van 80%, een celspanning van 4 (V), een CAPEX van de elektrolyzer van \$ 20000 / m2, een elektriciteitsprijs van \$ 30 /MWh, en een prijs van oxaalzuur van \$ 1000 / ton).

Uit een gevoeligheidsanalyse blijkt dat de marktprijs van oxaalzuur een enorme invloed heeft op de rentabiliteit. Een marktprijs van ten minste \$ 550/ton is vereist om een positieve NPV en een PBT van <10 jaar te hebben. In vergelijking met andere CO2-elektroreductieproducten heeft oxaalzuur een uiterst gunstige rentabiliteit door de relatief hoge marktprijs en het lage aantal elektronen dat per eenheid product wordt ingevoerd.

2. Summary

One of the emerging ways of utilizing carbon dioxide is based on the conversion of carbon dioxide into value-added chemicals produced via an electrochemical reaction. Carbon capture and utilization (CCU) requires the integration of range of different process steps. Developing an economically viable CO2 conversion route will support the main objectives of TKI Nieuw Gas/CCUS and the program Systeemintegratie. Electrochemical conversion of CO2 is mainly demonstrated at the lab-scale, with the development of stable and selective electrodes at the heart of the research. Less attention has been paid to the essential steps of integrating the different processes, like capture, conversion, and product recovery, and, in particular, the scale-up of an electrochemical stack has not been considered, yet. The motivation of this project is thus to work towards the commercialization of electrochemical conversion of CO2 into a high-value product.

The main contribution of the proposed project to the CCUS program is the development of new electrochemical reactor concepts, which will support and facilitate different scenarios for both electrification and CO2 utilization. The main focus is on the process design for an integrated capture and conversion process, with efficient recovery of the solid product (oxalic acid). Additionally, scale-up up of the electrochemical flow reactor in terms of current density and production rate, is one of the main realizations. The CO2 mitigation achieved by the example product we focus on in this project (oxalic acid) is another major contribution toward the goals of CCUS. Per kg of oxalic acid around 2 kg of CO2 is consumed, and this will add to the reduction in CO2 emission that would have normally associated with the traditional production route based on fossil fuel. In the long term, the proposed work will contribute toward entirely sustainable chemical synthesis chains based on CO2 conversion products.

There are three key activities in this project: molecular simulations for screening of solvent-electrolyte combinations, experimental optimization of the combined CO2 capture and conversion step, and process design. The various activities will facilitate a better understanding of how to design and operate CO2 electrolysers. In particular, two different integration concepts have been explored. The first concept is based on integration of capturing CO2 from flue gas, the second concept on the integration with a high partial pressure sources of CO2 (e.g. biogas and hydrogen production). Experimental results for a combined capture solvent-electrolyte liquid were validated using a numerical engineering model. A process design was made using a flow-sheeting program to integrate and optimize the overall process of a CO2 capture step, a CO2 conversion step conversion, and a product recovery step. Finally, the entire value chain of CO2 capture and CO2 utilization to producing a commercial product was analyzed, in terms of both the economics (TEA) and the environmental impact (LCA).

In the simulation study the densities, viscosities, diffusivities and ionic conductivities of mixed solvents comprising DES (i.e., reline and ethaline), methanol and propylene carbonate were computed using molecular simulations. To provide a quantitative assessment of the affinity and mass transport of CO_2 , oxalic and formic acid in the mixed solvents, the solubilities and self-diffusivities of these solutes were also computed. Our results show that the addition of DES to the organic solvents enhances the solubilities of oxalic and formic acid, while the solubility of CO_2 in the ethaline–containing mixtures are in the same order of magnitude with the respective pure organic components.

In the experimental optimization and scale-up work, the solvents were tested. The ionic liquids tested in this project are not a suitable media to function as catholyte in this electrochemical process. High decomposition rates, low activity towards CO2 reduction, and low oxalic acid selectivity lower their application as feasible solvents for oxalic acid production. Choline chloride based deep eutectic solvents show higher activity towards CO2 reduction than the ionic liquid tested, but low selectivity towards oxalic acid formation, and therefore are also discouraged as catholytes for this electrochemical process. Presence of water negatively affects the formation of oxalic acid and promotes formic acid production. In conclusion, further research is needed to understand the challenges of scaling-up this technology in order to reach the same KPIs that were obtained in smaller scale.

The recovery of oxalic acid from non-aqueous solutions like propylene carbonate is challenging. The state of the acid (dissociated or undissociated), which depends on the pH and the requirement of water-

free solvent in the electrolyser significantly complicates the downstream processing. We have considered liquid-liquid extraction, electrodialysis, cooling crystallization, and gas antisolvent precipitation (GAP) for oxalic acid separation. We show that only GAP with CO2 as antisolvent can be used for oxalic acid separation from propylene carbonate.

A feasibility study has been performed in order to scale-up the electrochemical conversion of CO2 to oxalic acid. A number of options for the downstream processing of oxalic acid are evaluated based on a comparison of a two-compartment and a three-compartment cell configuration. Generally, the costs for 3-compartment cell electrolyser are higher than the two-compartment cell. Furthermore, as Zn anode is consumed during the reaction the downstream section for the zinc anode process is more complex, as this requires a gas-separator, a centrifuge, a crystallizer and a second centrifuge.

The global warming potentials of the sodium formate and carbohydrate routes for oxalic acid production were calculated to be 1.364 kgCO2/kg(COOH)2 and 3.277 kgCO2/kg_{(COOH)2}, respectively. The global warming potential of the electrochemical process (0.467 kg_{cO2}/kg_{(COOH)2};-0.511 kg_{co2}/kg_{(COOH)2}) was also calculated. The theoretical electrochemical process was calculated to have a lower global warming potential relative to the other two contemporary, commercial processes. Provided the electrochemical process is economically viable, it provides a promising opportunity to lower the global warming potential of the oxalic acid industry when applied.

A process design and techno-economic evaluation of the value chain for electrochemical conversion of CO2 to oxalic acid was carried out. We have shown that the process has a positive NPV (\$ 16 M) and a PBT of 4 years under the base case scenario, with: a current density of 100 mA/ cm², an oxalic acid Faraday efficiency of 80%, a cell voltage of 4 (V), an electrolyser CAPEX of $\$20000 / m^2$, electricity price of \$ 30 /MWh, and an oxalic acid price of \$ 1000 / ton).

A sensitivity analysis shows that the market price of oxalic acid has a huge impact on the economics. A market price of at least \$550/ton is required to have a positive NPV and a PBT of <10 years. Compared with other CO_2 electro-reduction products, oxalic acid has extremely favourable economics due to the relatively high market price and the low number of electrons input per unit of product.

3. Introduction

One of the emerging ways of utilizing carbon dioxide is based on the conversion of carbon dioxide into value-added chemicals produced via an electrochemical reaction. Carbon capture and utilization (CCU) requires the integration of range of different process steps. Developing an economically viable CO2 conversion route will support the main objectives of TKI Nieuw Gas/CCUS and the program Systeemintegratie. Electrochemical conversion of CO2 is mainly demonstrated at the lab-scale, with the development of stable and selective electrodes at the heart of the research. Less attention has been paid to the essential steps of integrating the different processes, like capture, conversion, and product recovery, and, in particular, the scale-up of an electrochemical stack has not been considered, yet. The motivation of this project is thus to work towards the commercialization of electrochemical conversion of CO2 into a high-value product.

Here we propose to produce oxalic acid ($C_2H_2O_4$) electrochemically from CO₂, as this production route has many interesting aspects. From a commercial point of view the conversion of CO₂ to oxalic acid is much more interesting than, for example, the production of formic acid or methanol. First of all, although oxalic acid is a C2 molecule the electrochemical conversion from CO₂ is a 2 electron reaction. This means that for oxalic acid the same relatively low, the lowest, energy input is required, similar to the energy input required to synthesize carbon monoxide or formic acid electrochemically form CO₂. The electrochemical conversion of CO₂ to oxalic acid has a much higher margin than formic acid or methanol, see Figure 1 and also section 6.3 (TEA).





It seems that oxalic acid as a high-value product has been (completely) overlooked. Finally, during previous work (at both TNO and TU Delft) a narrow window for the temperature of 20 to 40 °C has been evaluated to synthesize oxalic acid, where solid oxalic acid has been obtained. The fact the oxalic acid is a solid crystal open up some alternative, solid - liquid product recovery options.

The main research activities will focus on the electrochemical conversion of CO₂ to value-added 2 electron and 4 electron products (generally C1 and C2 in aqueous electrolytes). C1 chemicals are species containing only one carbon atom, like: carbon monoxide, formaldehyde, formic acid/formate, methanol, and methane. Such C1 and C2 products can either be directly used in the existing infrastructure, be conveniently converted into industrially relevant gases (e.g. via syngas using existing infrastructure), or combined with other feedstock to produce a range of so-called derived products.

This project will facilitate the integration of different applications relevant for Carbon Capture and Utilization (CCU). The aim is to convert electrochemically biogenic, captured CO2, and to make use of solar or wind energy to provide renewable electricity. Utilization of electric power in the process industry, electrification, to facilitate efficient chemical reactions (electrocatalysis) is a target topic for different TKI's, including TKI Nieuw Gas and TKI Energy & Industry. Electrochemical conversion holds the promise of such development: mild operating conditions and comparatively good selectivities for a range of potential C1 and C2 products based on CO2. For the bio-based economy (TKI - BBE) many conversion routes of biomass result in CO2 as a by-product gas stream. This project foresees utilization of biogenic CO2, leading to higher added value of bioenergy value chains. For the implementation of large-scale CCU(S) solutions efficient conversion of CO2 to value added products will be required. One of the emerging technologies in this area is the electrochemical conversion of CO2.

4. Project objectives

The main contribution of the proposed project to the CCUS program is the development of new electrochemical reactor concepts, which will support and facilitate different scenarios for both electrification and CO_2 utilization. The main focus is on the process design for an integrated capture and conversion process, with efficient recovery of the solid product (oxalic acid). Additionally, scale-up up of the electrochemical flow reactor in terms of current density and production rate, is one of the main realizations. The CO_2 mitigation achieved by the example product we focus on in this project (oxalic acid) is another major contribution toward the goals of CCUS. Per kg of oxalic acid around 2 kg of CO_2 is consumed, and this will add to the reduction in CO_2 emission that would have normally associated with the traditional production route based on fossil fuel. In the long term, the proposed work will contribute toward entirely sustainable chemical synthesis chains based on CO_2 conversion products.

The main challenge we take up in this project is to design new reactor configurations to convert CO2 in an optimal way based on reactor modelling and by validation on a reasonable lab-scale. One of the starting points is the source of the CO2. The reactor design will need to be adapted to the input CO2 source since the concentration and type of impurities will differ (e.g. if the CO2 is derived from biomass or from industrial flue gases). The second aspect that will be considered is to develop an integrated capture and conversion process, where the liquid phase is used to absorb CO2 and can work as an electrolyte solution as well, see Figure 2.



Figure 2. Schematic layout of integrated reaction and separation process for the production of oxalic acid/oxalate from CO2, coupled to a CO2 capture unit based on absorption.

Oxalic acid (C2H2O4) is a solid at room temperature and, in principle, should be relatively easy to separate from the (liquid) electrolyte solution. In previous work we have studied an ionic liquid and methanol as electrolyte solution for the formation of oxalic acid. It is of importance to note that the use of methanol as physical solvent for the removal of CO2 is well known industrial process (rectisol process). Different types of ionic liquids, ionic liquids (ILs) and deep eutectic solvents (DES), have been studied for reaction and separation purposes at both TNO and the ETh group (TU Delft). These different ionic liquids have a number of features that are relevant for both CO2 capture and electrochemical conversion of the (captured) CO2, like high solubility of CO2, high electrical like high solubility of CO2, high electrical conductivity, high chemical and thermal stability, negligible vapor pressure, and tunable solvent properties.

It should be noted that currently there are no commercial CO2 electrolyzes that operate at industrially relevant conditions. Electrochemical reactors are mostly in the lab-phase with few exceptions, typically TRL 3, and the aim of this project is to bring the TRL to level 5: demonstration in a relevant environment. Furthermore, it is important to develop a full value chain from captured CO2, to the conversion of CO2, to the recovery of the final product.

Moreover, the use of a hybrid solvent (i.e. physical solvent and electrolyte solution) can create significant higher CO2 loadings near the electrode. Significantly eliminating mass transfer issues, which under normal conditions would have led to sustainable lower current densities. An alternative approach would have been to use gas diffusion electrodes where CO2 is supplied at the back side of the electrode. However, these systems have major issues related to industrial applicability (stability of the materials is one of the concerns).

The overall result of the project will deliver a test setup comprising of a capture unit, an integrated pressurized reactor, and a solid - liquid separator. Additional results include the data from a series of experiments evaluating ionic liquids that serve as solvent-electrolyte solution, a computer model of an elevated pressure CO_2 electrolyser, and the results of an environmental and economic analysis of a full CO_2 value chain with oxalic acid as the added-value product. Special interest will be paid to how to design stacks of elevated pressure electrolysers as well as how the source of the CO_2 (purity and pressure and temperature conditions) affects the entire process. The main target in this project is to have a current density of 100 mA/cm² and faradaic efficiency of 80%. Finally, based on a techno-economic assessment, the proposed activities will provide the details of a full CO_2 value chain and a dedicated business case. Moreover, an exploration will be made to identify other products made from CO_2 which can also benefit from this methodology.

The main holistic activities are directed to the design and testing of electrochemical reactors and integrating those reactors into further valorisation chains. The main reaction will be to convert CO2 to oxalic acid. The outcomes of this project will be to refine and disseminate knowledge of both the design and the operation of high pressure CO2 electrolysers to enable the manufacture, and optimal use, in general. More specifically, the main aim of the proposed activities is to work on the valorisation of the unique properties of ionic solvents towards an efficient application in the electrochemical conversion of carbon dioxide to oxalic acid.

The identifiable objectives in meeting this aim are as follows:

Construction of a lab-scale prototype, combining a CO2 conversion step, recovery of the solid product (oxalic acid) and the power input from a (small-scale) solar cell and wind turbine. These activities will involve some performing testing of the prototype (lab-scale pilot) unit.

Develop a detailed **process design** in order to scale-up the concept, specifying the mass, heat, and energy balances, and the requirements for the electrical power input and CO2 feed flow rate. One of the main results should be a flow-sheet specifying the conditions and size for the various units, the overall energy efficiency, and the gas, liquid and solid flow rates, like production rate and CO2 consumption in terms of kg/h.

Valorisation of the basic process design and knowledge transfer activities, related to the general concepts in the field of sustainability and electrification, and around more specific aspects related the electrochemical conversion of CO2 to high value products, like oxalic acid.

Develop a full value chain, based on a **techno-economic assessment** and **life-cycle assessment** of the integrated concept, based on CO2 capture from biogas, an electrochemical reactor (CO2 electrolyser), electrical power from a renewable source (wind or solar), downstream processing of the required product (solid - liquid separation), recycling of the solvent - electrolyte solution, and recycling of the unreacted CO2.

5. Approach and activities

5.1. Approach

The focus of the work will be on the development of the integrated reaction and separation concept for the electrochemical conversion of CO_2 to oxalic acid (Figure 2). We target the design of high pressure reactors which produce industrially relevant products which are easier to separate (such as oxalic acid), but the reactor design will be also suitable for different routes and products. Therefore, the purpose of this project is two-fold: (1) model, design, test and scale-up electrolysers for CO_2 conversion to value added products, and (2) develop an integrated process of an electrochemical reaction with a solid - liquid separation step.

There are three key activities in this project: molecular simulations for screening of solvent-electrolyte combinations, experimental optimization of the combined CO_2 capture and conversion step, and process design. The various activities will facilitate a better understanding of how to design and operate CO_2 electrolysers. In particular, two different integration concepts will be explored. The first concept is based on integration of capturing CO_2 from flue gas, the second concept on the integration with a high partial pressure sources of CO_2 (e.g. biogas and hydrogen production). Experimental results for a combined capture solvent-electrolyte liquid will be validated using a numerical, engineering model. A process design will be made using a flow-sheeting program to integrate and optimize the overall process of a CO_2 capture step, a CO_2 conversion step conversion, and a product recovery step. Additionally, the other area of activity will be an analysis of the entire value chain of CO_2 capture and CO_2 utilization to producing a commercial product, in terms of both the economics (TEA) and the environmental impact (LCA).

The various activities will be carried out based on four work packages (WP) and associated Tasks, further described below.

Party	Contribution to project
TNO	 Coordinator Experimental valorization of integrated capture -reaction - product recovery technology Process design and flow-sheeting Techno-economic and life-cycle analysis and business-case
TU-Delft, Eth, Engineering Thermodynamics Group	 Molecular simulation for screening of integrated solvents -electrolyte solutions Process design and experimental testing of individual process steps (capture, conversion, product recovery, recycles)
DMT IP & Technology	 Provides biogas technology and specifications for the biogenic CO₂ stream (purity, flow rate, pressure, and temperature) Evaluation of commercialization of the concept, best way forward to introduce the process into the market. Asses and calculate the business case
Mestverwerking Fryslan	 Process design aspects related to integration of renewable power and CO₂ utilization. Valorization of manure and CO₂ value chain. Provide input for the business case.
Tielo-Tech	 Technology screening and optimization for reactor design and solid - liquid separation System integration and techno-economic analysis Experimental study of electrochemical flow reactor properties Optimization of capture and conversion step

Table 1. Contribution of parties to the project

5.2. Description of work, Workpackages and deliverables

The various activities are carried out based on four work packages (WP) and associated Tasks. The contribution of each party over the project as a whole is summarized in Table 1. In this section the plan of work is described, on WP task level.

WP1 Design of integrated reaction-separation process

In this work we start with optimizing the conditions for the individual process steps. A number of conditions and non-aqueous liquids will be computational screened to assess the performance for each step. After the promising liquids have been identified with molecular simulation, experimental tests on the performance of these liquids will be performed for the CO2 capture step, the CO2 conversion step, and the product recovery. Main parameters that will be considered are the pressure, temperature, pH and water fraction.

Task 1.1 Solvent properties for CO2 capture

Molecular simulation will be used to screen solvents and electrolyte proprieties of potentially interest non-aqueous solutions. Part of this study will focus on identifying promising ionic liquids (ILs) and deep eutectic solvents (DES) based on their CO2 capture capacity and conversion capability. The intrinsic advantage of ILs and DES is that they can be fine-tuned for specific applications by choosing different combinations of anions, cations, and hydrogen bond donors and acceptors. Except from the ILs and DES, aqueous solutions with commonly used electrolytes will be studied (e.g., sodium, bicarbonate, calcium, chloride, phosphate) and will be compared to the findings for the ILs and DES. The ability of the various solvents for capturing CO2 is mainly determined by the exact solute -solvent interactions.

In this project we will use state-of-the-art molecular dynamics (MD) and Monte Carlo simulation methods to scrutinize the complex interplay between van der Waals and electrostatic interactions, and hydrogen bonding. The structure of the solvents, analysed by the radial distribution function, and the structure factor will be correlated to the CO2 capture capacity. The screening study will be performed at a wide variety of temperatures, pressures and compositions (for the ILs and DES) as these properties drastically affect the thermodynamic behaviour of the CO2 - solvent system and thus the capturing ability of the various solvents. The ETh group at TU Delft is one of the leading groups in the field of molecular simulation and has a wide expertise in computing thermodynamic, transport and structural properties of complex fluids. Moreover, the ETh group has worked extensively in modelling the CO2 capture by different solvents.

Task 1.2Electrolyte properties for CO2 conversion to oxalic acid

Molecular simulations in various statistical ensembles will be utilized to screen solvents also for optimal electrolyte properties, e.g., the pH and the 'salt' concentration in the electrolyte solution as function of pressure and temperature. Besides the temperature and pressure, one of the main parameters that will affect the product selectivity towards oxalic acid is the water fraction in the system. Thus, the accurate knowledge of phase behaviour of the system is essential.

To that purpose Monte Carlo simulation in the Gibbs and extended ensembles will be performed to predict the solubility of CO2 and water in the various solvents. A key electrolyte property is the electric conductivity. The accurate prediction of electric conductivity is needed in order to optimize the current density that can be applied on the electrodes. Such predictions will be performed with MD simulation using the recent open source computational tools designed by the ETh group. Moreover, MD simulations will be utilized for the accurate prediction of other transport properties of the mixture, including the shear viscosity and diffusion coefficients (of all species), as these properties are crucial for the optimization of the system. In parallel to the simulation work, experimental verification of the properties of the solvent - electrolyte system will be performed. Accurate experiments will be performed for the CO2 capture and the CO2 conversion step.

Task 1.3 Electrolyte-capture solvent optimization

In this task, the identified electrolyte solvent will be tested and experimentally evaluated, regarding CO2 capture efficiency and the use as solvent-electrolyte for the electrochemical conversions. Regarding

the first step, amongst others detailed vapor liquid determination experiments will be conducted. Regarding the second step, the solvent will be characterized from an electrochemical point of view. The results will be brought as a feedback loop in the Tasks mentioned above. In an iterative manner, the hybrid solvent will be optimized. The basic knowledge will be used for the design and operation of the TRL5 demonstration.

Task 1.4 Product recovery

The main aspect related to the product recovery is the solubility of oxalic acid in the solvent - electrolyte system. This is determined by the water fraction, the pH, the temperature, and pressure. This work will involve both modelling activities and experiments. There are clear engineering heuristics that provide guidelines for the design of a solid - liquid separator. For the product recovery step, the focus will be on a combination of a filter step and a precipitation step. This will provide flexibility in terms of operating the integrated unit over a wide range of experimental conditions. Evaluating a number of recovery options will provide guidelines for the recovery and flow rates for the product and the recycles.

Task 1.5 Process design and optimization of integrated process

This work will build on the previous tasks, Task 1.1 to Task 1.4, and will combine the various results to simultaneously optimize for three important aspects, i.e., capture, conversion, and recovery. T, the most efficient conversion routes of CO2 to oxalic acid will be analysed based on the exact electrolytes (e.g., ILs, DES, and NaCI). In particular, two key aspects will be addresses: optimization of the solvent-electrolyte solution and optimization of the recovery of the product and the liquid solution in the solid - liquid step. A numerical model recently developed by the ETh group will be used to describe and optimize the reactor properties at elevated pressures.

Task 1.6 Life-cycle analysis and multi-criteria analysis

The information obtained from the screening of the solvent - electrolyte solution for CO2 capture and electrochemical conversion (Task 1.1 and Task 1.2) will lead to a pool of potential components, for which life-cycle analyses (LCA) will be performed. This is essential in order to further narrow down the number of potential solvents for CO2 capture and electrochemical conversion, based on techno-economic criteria. Furthermore, a multi-criteria

WP 2 Construction of prototype unit

Task 2.1 Construction of lab-scale unit

A basic reactor will be designed taking into consideration various features, such as stacking of a number of electrolyser cells, the solid - liquid separation, and the recycling of the solvent - electrolyte solution into a single setup. Most of the infrastructure is already available at TNO and the ETh group. A dedicated high-pressure set-up is available for the testing of the integrated capture, electrochemical conversion, and separation process. Additionally, all the materials are also available, such as the solvent - electrolyte solutions, including the various ionic liquids, and the membranes and the metal electrodes for the construction of the electrochemical reactor.

Task 2.2 Testing of prototype unit

The working of the unit will be tested for a relatively short duration, in order to perform the so-called site-acceptance test (SAT). Further optimization will be directed towards continuous operation for a prolonged time, i.e., several days to a week, to evaluate the performance in terms of conversion and selectivity towards oxalic acid. The main objectives are to assess the current densities and the stability of the solvent - electrolyte solution and the electrodes. Additionally, a procedure to establish the product quality of the solid oxalic acid will be developed.

Task 2.3 Integration with renewable energy source

In this work a the lab-scale unit will be coupled to a lab-scale wind turbine and solar panel. This will be used to simulated and study the basic of how to supply renewable power to the CO2 electrolyser. A number of contacts exist at both TNO and ETh group that have expressed their interest to provide a solar panel and auxiliary equipment to see power a CO2 electrolyser by renewable energy.

WP 3 Valorisation

Task 3.1 System integration based on P2C, CCU, and source-sink matching

To support the energy transition, a number of concepts, like power-to-chemical (P2C) and recycling of carbon dioxide through CCU (carbon capture and utilization) are paramount to facilitate the electrification of society, in general, and the chemical process industry, in particular.

Eventually, the full value chain needs to be addressed, ranging from the CO2 source, like for example, the removal of (biogenic) CO2 from biogas, coupling with a renewable energy source (solar, wind) to provide the electric power, to different end-user applications for electrochemically produces chemicals.

One of the key aspects of every CCU chain is to match the supply and demand of the CO2, this is known as source -sink matching. There are basically two options: (1) collection and transport of CO2 over a long distance and central production of the desired product, or decentralized production of oxalic acid with local collection of the CO2 from a number of adjacent sites.

This will involve an evaluation of the long distance cost for the transport of the CO2 against the cost for the transport of a solid product.

Based on the first CCU cases (Covestro and Carbon Recycling International), a relevant scale where local production a chemical will be feasible is in the order 5 to 10 kton CO2 per year [,]. This amount of around 10 kton CO2 per year can be achieved by combining two to three smaller digesters, and it should be noted that more and more large-scale digester are being installed, especially in Germany and the USA, see also Section 6 and reference []. A typical digester in the Netherlands and the USA produces:

- NL 500 to 1000 Nm3 biogas per hour, which gives 3.5 to 7.0 kton CO2 per year
- USA 2500 Nm3 biogas per hour, which gives around 17.5 kton CO2 year.

Task 3.2 Techno-economic analysis and business case

This task, the techno-economic evaluation will be performed by TNO and DMT. TNO has extensive experience in assessing the full value chain associated with so-called carbon capture and utilization (CCU) routes. The electrochemical system will be integrated with a methane reforming unit (hydrogen production), with the possibility of capturing CO2 in the hybrid solvent. Outcomes from the other WP will serve as input, in particular the process design prepared in Task 1.5.

The techno-economic evaluation will be based on a detailed process flow diagram and flow-sheeting of the process in order to establish the sizing of the main unit (absorption column, electrochemical reactor integrated with the separation step), the gaseous and liquid flow rates, the production capacity for oxalic acid, and the optimal operating conditions (mainly temperature, pressure, and pH). The outcomes of the pervious WPs will be used to calculate and optimize the business case.

WP 4 Project management

Task 4.1 Knowledge transfer, progress meetings, and final report

Regular project meetings will be held on a monthly basis. In addition, there will be weekly more informal progress meeting with all the people involved, either by attending the face-to-face meeting or by participating by phone. The main findings will be documented in the final report.

All the appropriate ways to disseminate the (scientific) outcome of the project will be used, including an (oral or poster) presentation at a conference and through publication of the results on the web pages of the different partners.

The different partners will also use the business-oriented results, in particular the economic evaluation and the system integration work for marketing and acquisition purposes.

Planning

The original envisioned planning is shown in the following schematic:

	Bio-cel - CO2 to oxalic acid					2020 202			021		
	u						04	01	02	03	04
Legend	WP 1 Design of integrated reaction-separation process	TUD	Partner	-	-			-		4.5	
WP	1.1 Solvent properties for CO2 capture	TUD									
individual tasks	1.2 Electrolyte properties for CO2 conversion to oxalic acid	TUD									
Deliverables/milestones	1.3 Electrolyte-capture solvent optimization	TNO	TUD					D11			
Students	1.4 Product recovery	TT									
	1.5 Process design and optimization of integrated process	TT	DMT								
	1.6 LCA and multi-criteria analysis	DMT									
	WP 2 Construction of prototype unit	TNO									
	2.1 Construction of lab-scale unit	TNO	TUD				M2.1			_	
	2.2 Testing of prototype unit	TNO							D2.1		
	2.3 Integration with renewable energy source	TT									
	Π										
	3.1 System integration based on P2C, CCU, and source- sink matching	TT	DMT								
	3.2 Techno-economic analysis and business case	TT	DMT/MF								
	WP 4 Project management	TNO									
	4.1 Knowledge transfer, progress meetings, and final report	TNO									

Note that due to the COVID pandemic, the partners had to change the original planning and tasks according to what was possible in their laboratories. Furthermore, the project timeline has been extended to 1st of May 2022.

The work is subdivided into the following work packages with deliverables as shown in Table 2. The results are compiled into this final report.

Table 2. Contribution to workpackage	e per party and workpackage results
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WP	Korte beschrijving	Uitvoerders	Resultaat
WP 1	Design of integrated reaction-	TUD, TNO, TT,	- Molecular modelling of high-pressure solubility and
	separation process	DMT, MF	electrochemical conversion
			- Process design and optimization
			- Hybrid solvent optimization
			- Software code and report with main results of modelling
			work and experimental work
			- Report with flow-sheet of integrated process
WP 2	Construction of prototype unit	TNO, TUD, TT,	- Construction and testing of integrated process
		DMT	- Product specifications
			- Integration with CO ₂ source and renewable power
WP 3	Valorisation: System	TNO, DMT, MF, TT,	- Techno-economic analysis of full CO ₂ value chain
	integration and Techno-	TUD	- Business case
	economic evaluation		
WP 4	Project management and	TNO	- Monthly progress meetings, planning, reporting, and
	dissemination		budgeting
			- Various dissemination activities

6. Results

In this section all the project results are reported, per workpackage.

6.1. WP1 Design of integrated reaction-separation process (TUD)

The integrated process that we consider here is shown in Figure 3. The overall process can be divided in three sub-processes; a CO_2 capture step, the electrochemical conversion of the CO_2 to the desired product (oxalic acid), and the downstream separation. The third step, the downstream separation, includes the separation of the main product from the by-products as well as solvent recycling.

The starting point is a biogas stream consisting of gas mixture of CO2 and CH4. The CO2 is captured by a non-aqueous solvent, where the solvent has properties that are optimizing for capturing the CO2 as well as for being used as an electrolyte. In this case the CO2 is removed from the biogas by propylene carbonate.



Figure 3. Integrated capture and conversion process, for the electrochemical reduction of CO2 to oxalic acid.

Normally, the CO2-rich propylene carbonate is regenerated in a desorbed unit, using heat, a flash or both. In the integrated process proposed here the CO₂-rich solvent is sent directly to the CO₂ electrolyser. This means that we basically remove the dedicated desorber unit from the process. In the electrolyser, the CO₂ is converted to oxalic acid and some by-products like glycolic acid and glyoxylic acid. The solvent stream leaving the electrolyser containing the main products and by-products are then directed to the separation section, with the man purpose to recover the oxalic acid.

Recovering the oxalic acid/oxalate mixture from a non-aqueous solution is not an easy task. The configuration and conditions for the downstream section depends on a range of parameters. In this case, one of the key parameters is the pH of the oxalic acid/oxalate mixture, however the pH for non-aqueous solution is not well-defined. This essentially means that depending on the pH, the main product is either oxalate or oxalic acid

For the separation step, it is important whether oxalate or oxalic acid is present in the cathode compartment of the electrolyser, as the state of the product, dissociated or un-dissociated form of the base/acid component depends in the case of oxalate/oxalic acid on a number of parameters, most importantly the anode. When using an undivided cell that used zinc this will produce zinc oxalate as product and protons from the water oxidation in acidic media (i.e., H₂SO₄) diffuse through the membrane and a more acid catholyte solution is obtained, and as consequence oxalic acid is produced). We have extracted the main product, oxalic acid/oxalate complex, from the organic, poly-carbonate phase into an aqueous phase by mixing the catholyte solution with water and measuring the pH of the resulting phase. In this case, a pH was obtained between 1.4 and 1.7, which corresponds well with the expected pH based on the oxalic acid concentration, and this confirms that mostly oxalic acid was produced in at the cathode side.

Task 1.1 Solvent properties for CO₂ capture (TUD)

MC simulations were performed to compute the excess chemical potentials (μ^{ex}) and Henry coefficients (H), which are used to quantify the solubilities of solutes (i.e., CO2, oxalic acid and formic acid) in different mixed solvents. For a component *i*, the excess chemical potential μ^{ex} follows from:

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$$\mu^{\rm ex} = \mu_{\rm i} - \mu^{\rm IG}$$

where μ_i and μ^{IG} are the chemical potentials of the component and the ideal gas at the same conditions, respectively. For a specific solute–solvent combination, μ^{ex} indicates the affinity of the solute towards the solvent as it is related to the activity coefficient γ_i of component *i*:

$$\gamma_i = \frac{\langle \rho_i \rangle}{x_i \langle \rho_{0i} \rangle} \exp\left[\frac{\mu_i^{\text{ex}} - \mu_{0i}^{\text{ex}}}{k_{\text{B}}T}\right]$$

where $\langle \rho_{0i} \rangle$ is the ensemble average number density of pure component *i*, $\langle \rho_i \rangle$ is the ensemble average number density of i, x_i is the mole fraction of i, μ^{ex} is the excess chemical potential of pure i with respect to the ideal gas, k_B is the Boltzmann constant, and *T* is the temperature in units of K. The Henry coefficient of the solute, H_i is defined as:

$$H_i = \lim_{x_i \to 0} \frac{P_i}{x_i} = \lim_{x_i \to 0} \frac{f_i}{x_i}$$

where P_i and f_i are the partial pressure and fugacity of the solute, respectively. H_i is directly related to μ^{ex} as follows:

$$H_i = \lim_{x_i \to 0} k_{\rm B} T \rho \exp\left[rac{\mu_i^{
m ex}}{k_{\rm B} T}
ight]$$

where ρ is the number density of the solvent, and T is the temperature in units of K.

All MC simulations were carried out with the open–source software package Brick–CFCMC, which utilizes the Continuous Fractional Component (CFC) method (i.e., gradual insertion/deletion of fractional molecules during the simulations). The degree of interaction between a fractional with the surrounding molecules is varied using a scaling parameter λ ($0 \le \lambda \le 1$), which is a degree of freedom in an expanded ensemble formulation. During CFCMC simulations, separate scaling parameters are used for intermolecular Lennard-Jones and electrostatic interactions. The scaling parameters are continuous functions of λ and are implemented such that electrostatic interactions are not switched on before fully scaling down the Lennard-Jones interactions. To compute μ^{ex} of CO2, oxalic acid and formic acid in different solvents using:

$$\mu^{ex} = \int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle d\lambda$$

The λ space was discretized into 50 bins. Separate simulations in the NPT ensemble were performed for each solute with a fixed value of λ to compute $\langle \partial U/\partial \lambda \rangle$. Subsequently, numerical integration of the above equation was performed. μ ex and H were computed for mixtures with $0 \le xDES \le 0.4$ at 298.15 K and 1 atm, and for pure reline and ethaline at 350.15 K and 1 atm.

A cut-off radius of 12 Å was used for both the Lennard-Jones and the Coulombic potential in all MC simulations except for the ones of pure DES in which a cut-off radius of 10 Å was used. Electrostatic interactions were handled with the Ewald summation method with a relative precision of 10⁻⁶. During the MC simulations, trial moves were selected with the following probabilities: 35% translations, 35% rotations, 29% changes in the internal configuration of molecules (i.e., angles and dihedrals), and 1% volume changes. A minimum of 8x10⁵ cycles were carried out for equilibration, and 8x10⁵ cycles for production. At each MC cycle, the number of the trial moves performed equals the number of molecules of the system.

The computed values for μ^{ex} and Henry coefficient of CO2, oxalic acid and formic acid in the different solvents are listed in Table 3. As can be seen, the solubility of CO2 in pure methanol and pure propylene carbonate is almost equal (absolute deviation of ca. 5%). Clearly, the addition of DES in these organic solvents reduces the CO2 solubilities. For xDES = 0.4, the solubilities of CO2 are reduced by ca. 50% and 30% for reline–methanol and ethaline–methanol mixed solvents, respectively. For the same xDES in ethaline–propylene carbonate mixture, the solubility of CO2 is reduced by ca. 20%. The Henry coefficients listed in Table 1.1 indicate that solvents containing ethaline are slightly better adsorbents of CO2 than reline–containing mixtures.

Table 3. Computed excess chemical potentials μ^{ex} (relative to an ideal gas, in units of kJ/mol) and Henry coefficients H (in units of MPa) of CO2, oxalic acid (OA), and formic acid (FA) in different solvents. The temperature T is 298.15 K for all solvents except for pure reline and pure ethaline for which T = 350.15 K. Pressure is equal to 1 atm for all systems.

Solvent	$x_{\rm DES}$	$\mu_{\mathrm{CO}_2}^{\mathrm{ex}}$	H_{CO_2}	$\mu_{\mathrm{OA}}^{\mathrm{ex}}$	$H_{\rm OA}$	$\mu_{ m FA}^{ m ex}$	H_{FA}
Reline-MeOH	0	-3.2	0.5	-50.5	$2.7 \ 10^{-9}$	-47.1	$1.1 \ 10^{-8}$
Reline-MeOH	0.1	-3.0	0.6	-63.0	$1.9 \ 10^{-11}$	-43.1	$6.1 \ 10^{-8}$
Reline-MeOH	0.2	-2.2	0.9	-61.3	$4.1 \ 10^{-11}$	-43.9	$4.6 \ 10^{-8}$
Reline-MeOH	0.4	-1.6	1.3	- <mark>68.0</mark>	$3.1 \ 10^{-12}$	-42.2	$1.0 \ 10^{-7}$
Reline-MeOH	1	2.4	7.9	-62.1	$1.9 \ 10^{-9}$	-45.7	$5.2 \ 10^{-7}$
Ethaline-MeOH	0.1	-3.6	0.5	- <u>62.6</u>	$2.2 \ 10^{-11}$	-43.0	$6.0\ 10^{-8}$
Ethaline-MeOH	0.2	-2.8	0.7	-62.0	$3.0 10^{-11}$	-42.8	$6.9\ 10^{-8}$
Ethaline–MeOH	0.4	-2.3	1.0	-66.0	$6.5 \ 10^{-12}$	-49.8	$4.5 \ 10^{-9}$
Ethaline–MeOH	1	1.4	5.0	- 64.1	$8.3 \ 10^{-10}$	-44.3	$7.5 \ 10^{-7}$
Ethaline–PC	0	-3.5	0.7	-62.1	$3.9 \ 10^{-11}$	-38.8	$4.7 \ 10^{-7}$
Ethaline-PC	0.1	-3.2	0.8	- <mark>66</mark> .5	$6.5 \ 10^{-12}$	-42.2	$1.2 \ 10^{-7}$
Ethaline-PC	0.2	-3.5	0.7	-65.7	$9.0 \ 10^{-12}$	-42.4	$1.1 \ 10^{-7}$
Ethaline-PC	0.4	-2.5	1.1	-70.0	$1.6 \ 10^{-12}$	-47.6	$1.3 \ 10^{-8}$
Ethaline–PC	1	1.4	5.0	-64.1	$8.3 \ 10^{-10}$	-44.3	$7.5 \ 10^{-7}$

Interestingly, the Henry coefficient of oxalic acid in DES-methanol mixtures is much lower compared to the one in the pure solvents (i.e., xDES = 0 and 1). We speculate that this could be due to an interplay between hydrogen bonding interactions and a commensurate fit of the oxalic acid molecule in the liquid structure. Overall, the computed Henry coefficients show that adding a choline–based DES to the organic solvent increases the solubilities of oxalic acid and formic acid. While the solubility of CO2 is reduced as a result of adding a DES to methanol or propylene carbonate, it is important to note that the reduction is not very large and the Henry coefficients are still relatively high. The mixed solvents investigated here have higher CO2 Henry coefficients compared to aqueous solutions at the same conditions, which are typically used in electrochemical processes. This is an important finding since the design of an electrolyte with high CO2 solubility could potentially improve conversion rates by increasing the concentration of CO2 at the surface of the electrode.

Task 1.2 Electrolyte properties for CO2 conversion to oxalic acid (TUD)

MD simulations were performed for the computation of the densities, number of hydrogen bonds (HBs), shear viscosities and self-diffusion coefficients. All MD simulations were carried out using the Large– Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). The initial configurations were generated with the PACKMOL package. Long–range electrostatic interactions were handled using the particle–particle particle–mesh (PPPM) method with a relative error of 10⁻⁶. The cut-off radius was set to 12 Å for both Lennard-Jones and the short-range part of the Coulombic interactions. Periodic boundary conditions were imposed in all directions. The Verlet algorithm with a time step of 1 fs was used to integrate Newton's equations of motion. Temperature and pressure were maintained constant using the Nose–Hoover thermostat and barostat with coupling constants of 100 fs and 1000 fs, respectively. Transport properties were computed with the OCTP (On-the-fly Computation of Transport Properties) plugin in LAMMPS which yields the mean-squared displacements (MSDs) of dynamical properties as a function of time. The transport coefficients can be then obtained by linear regression to the long-time MSDs at time-scales where the slopes as a function of time are equal to 1 in a log-log plot. Diffusion coefficients are computed from:

$$D_{i}^{\text{MD}} = \lim_{t \to \infty} \frac{1}{6N_{i}t} \left\langle \sum_{j=1}^{N_{i}} \left(\boldsymbol{r}_{j,i} \left(t \right) - \boldsymbol{r}_{j,i} \left(0 \right) \right)^{2} \right\rangle$$

where DMD is the self-diffusivity of species *i*, $r_{j,i}(t)$ is the position vector of the *jt*h molecule of species *i* at time *t*, and *Ni* is the number of molecules of species *i* in the system. The shear viscosity η follows from:

$$\eta = \lim_{t \to \infty} \frac{1}{10 \cdot 2t} \frac{V}{k_{\rm B}T} \left\langle \sum_{\alpha\beta} \left(\int_0^t P'_{\alpha\beta}\left(t'\right) \mathrm{d}t' \right)^2 \right\rangle$$

where

$$P_{\alpha\beta}' = \frac{P_{\alpha\beta} + P_{\beta\alpha}}{2} - \delta_{\alpha\beta} \left(\frac{1}{3}\sum_{k} P_{kk}\right)$$

where *V* is the volume of the system, $P'_{\alpha\beta}$ are the components of the traceless pressure tensor, $P_{\alpha\beta}$ are the off-diagonal components of the pressure tensor, and $\delta_{\alpha\beta}$ is the Kronecker delta. All self-diffusion coefficients were corrected for finite–size effects using the Yeh-Hummer (YH) equation:

$$D_i = D_i^{\rm MD} + \frac{k_{\rm B}T\xi}{6\pi\eta L}$$

where *Di* is the corrected self-diffusion coefficient corresponding to the thermodynamic limit, η is computed from MD simulations and does not depend on the system size, and ξ is a dimensionless constant equal to 2.837298 for a periodic cubic simulation box. To compute the ionic conductivities, the Nernst–Einstein (NE) equation was used:

$$\kappa = \frac{e^2}{k_{\rm B}TV} \sum_i N_i q_i^2 D_i$$

where e is the elementary charge, qi is the charge of the molecules of species i.

Viscosities

The computed viscosities of the ethaline–propylene carbonate, ethaline–methanol and reline– methanol mixtures are shown in Figure 4 as a function of the DES content. Available experimental data is also shown in this figure along with the available experiments. Clearly, the viscosity increases with the DES content. Interestingly, for the ethaline–propylene carbonate mixture this is the opposite behavior compared to the densities discussed earlier. The reason is that the density of pure propylene carbonate is slightly higher compared to pure ethaline, while the viscosity of propylene carbonate is much smaller than that of ethaline. This can be mainly attributed to the fact that, unlike pure propylene carbonate, pure ethaline has a strong hydrogen bonding network (this is discussed in detail in the following section). The viscosities of the pure organic solvents are predicted with deviations from experiments of ca. 7% and 20% for methanol and propylene carbonate, respectively. For all mixed solvents, the deviation between the computed and the experimentally measured viscosities increases with the addition of DES in the mixtures (absolute standard deviations range from ca. 7% to 44% and ca. 20% to 50% for

ethaline–methanol and ethaline–propylene carbonate, respectively). Although these deviations seem rather high, the available experimental data are limited (e.g., no experimental data exist for the reline–methanol mixture) and the uncertainties in the computed values are quite large, ranging from 7 to 25% (due to the difficulty in sampling the slow dynamics caused by the relatively low temperature). It is also important to note that large deviations are reported between different experimental measurements of viscosities of DES. For example, different sources report viscosity values of pure reline in the range 630–840 mPa s. In absolute values, the predicted viscosities from MD simulations are satisfactory, while the qualitative behavior of the systems is captured accurately. Given the scarcity of experimentally measured viscosities for most of the mixtures considered here, our MD data can serve as a first set of predictions to aid the design of industrial processes and further motivate experimental efforts. To improve the accuracy of the computations, further modifications to the force fields, combining rules, and/or charge scaling should be considered. Such an investigation is beyond the scope of the present study.

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Figure 4. Viscosities of the ethaline–propylene carbonate, ethaline–methanol and reline– methanol mixtures as a function of the mole fraction of DES at 298 K and 1 atm. The red and green lines represent experimental measurements by Wang et al. (ethaline–methanol) and by Zafarani–Moattar et al. (ethaline–propylene carbonate), respectively. The experimentally measured viscosity of pure reline is equal to 750 mPa s.

As can be seen in Figure 5, reline–methanol mixtures are significantly more viscous than ethaline– methanol for the whole DES composition range. For $x_{DES} = 0.8$, the viscosity of reline–methanol is higher than the viscosity of ethaline–methanol by almost a factor of 3. This is not surprising since pure reline is significantly more viscous than ethaline (i.e., $\eta_{reline} = 455$ mPa s and $\eta_{ethaline} = 62$ mPa s at 298 K). For $x_{DES} < 0.2$, the viscosities of both mixtures are within the same order of magnitude. In the range ($x_{DES} \le 0.6$), ethaline–propylene carbonate mixtures exhibit the largest viscosity. For $x_{DES} > 0.8$, reline– methanol viscosities are the highest, and ethaline–propylene carbonate viscosities become comparable to the viscosities of ethaline–methanol.

Overall, our results reveal that the addition of DES to the organic solvents have a very strong effect on the viscosities. From a practical point of view for electrochemical processes, this finding dictates the careful selection of the composition of the mixtures since large viscosities can limit mass transport, and thus, reduce the current density of the electrolytes. To this end, DES with relatively low viscosities such as reline or ethaline (or other) can be promising.

Self-diffusivities

As slow diffusion rates can be a limiting factor in electrochemical processes, it is essential to integrate an electrolyte that yields sufficient mass transfer of the reactants and products to and from the catalyst. Since no experimental diffusivity data are available for the mixtures studied here, our results are the first step towards the screening of solvents for an optimum electrolyte containing DES, methanol, and propylene carbonate. In this section, we present the computed self–diffusivities of all the species in the DES–organic solvent mixtures, and the self–diffusivities of infinitely diluted solutes (CO₂, oxalic acid and formic acid) in these mixtures.

The computed self-diffusion coefficients of the different molecular species in the reline- methanol, ethaline-methanol, and ethaline-propylene carbonate mixed solvents are shown in Figure 4. All reported diffusivities were corrected for finite-size effects. As can be clearly seen, the self-diffusivities of all components monotonically decrease as the DES composition increases. This is mainly due to the increasing viscosities of the mixtures upon the addition of DES (see Figure 3), resulting in reduced mobilities of the different species. Due to the very high viscosity of propylene carbonate, the ethalinepropylene carbonate mixtures are the most viscous for $x_{DES} < 0.8$. This is clearly reflected to the selfdiffusivities of all species in this mixture for the same range of DES compositions, which have lower values compared to the methanol-containing solvents. The difference of all diffusivities in the ethalinepropylene carbonate and methanol-based mixtures becomes very pronounced at low DES concentrations. For example, at $x_{\text{DES}} = 0.1$, the diffusivity of ethylene glycol (i.e., the HBD) is ca. 4.5 times faster in ethaline-methanol than in ethaline-propylene carbonate. For high DES contents (i.e., $x_{\text{DES}} \ge 0.6$), the differences between the self-diffusivities of the individual components in the different solvents becomes rather low. For such xDES, the diffusivities of both HBD, HBA, and organic components are very similar for the mixtures of reline-methanol and ethaline-propylene carbonate. The respective diffusivities in the ethaline-methanol solvent are the highest (but of similar magnitude), following the (opposite) viscosity trend.



Figure 5. Self-diffusivities of all molecular species in the reline-methanol, ethaline-methanol, and ethalinepropylene carbonate mixtures as a function of the mole fraction of the DES at 298 K and 1 atm. (a) Choline (Ch+), (b) Chloride (Cl-), (c) HBDs: Urea and ethylene glycol (EG), and (d) organic solvents: methanol (MeOH) and propylene carbonate (PC). All computed diffusivities were corrected for finite-size effects. The lines connecting the symbols are shown to guide the eye

Ionic conductivities

Another important property to optimize when designing electrolytes for electrochemical applications is ionic conductivity since electrolytes ensuring fast electron transfer are essential for high-performance electrochemical conversions. Recently, ionic liquid-based electrolyte solutions have been studied for the electroreduction of CO₂ to valued added products. To the best of our knowledge, no experimental data are available for the ionic conductivities of the DES–organic solvent mixtures considered here. The

ionic conductivity of pure reline has been measured experimentally by various groups to be in the range $0.024 - 0.764 \text{ Sm}^{-1}$ for T = 293-353 K, respectively. It is important to note that the actual values reported in literature significantly vary depending on the experimental technique used and the purity of the DES. For example, Agieienko and Buchner reported an electric conductivity of 0.024 Sm^{-1} for pure reline at 298 K, while at the same conditions, Mjalli and Ahmed report a value of 0.18 Sm^{-1} , which is an order of magnitude higher. Celebi et al. reported a value of 0.09 Sm^{-1} computed in MD simulations at 303 K. Here, a value of 0.11 Sm^{-1} has been computed for T = 298 K. The measured ionic conductivity of ethaline ranges from ca. $0.62 \text{ to } 2.08 \text{ Sm}^{-1}$ in the temperature range 293–353 K. At room temperature it is equal to ca. 0.70 Sm^{-1} (the exact value depends on the experimental study). Here, we computed a value of 0.63 Sm^{-1} , which is in reasonable agreement with the experiments. Since a thorough validation of the computed conductivities for the mixtures of DES with methanol and propylene carbonate is not possible due to the absence of experimental measurements and due to the fact that NE equation has been shown to slightly overpredict conductivities, our results should be interpreted mostly qualitatively.

The computed ionic conductivities of all mixed solvents studied in this work are shown in Figure 6 as a function of x_{DES} . For all solvents, the ionic conductivities exhibit a non-monotonic behavior. As x_{DES} increases, the ionic conductivities initially increase until a maximum value after which a sharp decline is observed. This can be explained by the fact that as ionic content (i.e., DES) is added to the mixture, the ionic conductivity initially increases up to the maximum value. However, the sharp increase of the viscosity due to the formation of the strong HB network within the DES restricts the mobility of the ions, causing the decline of κ after a certain x_{DES} . This non-monotonic behavior is fully consistent with the MD data by Celebi et al. and the experiments by Agieienko et al. for aqueous reline and ethaline solutions. Mjalli and Ahmed also observed this behavior for reline–ethaline mixtures.



Figure 6. Ionic conductivities of the reline–methanol, ethaline–methanol, and ethaline– propylene carbonate mixtures as a function of the mole fraction of DES at 298 K and 1 atm. The dotted lines connecting the symbols are to guide the eye.

Methanol-containing solvents have higher ionic conductivities compared to ethaline– propylene carbonate. For $x_{DES} \le 0.6$, this difference is significant, i.e., a factor of 2 to 6. The only exception is for $x_{DES} = 0.8$, for which the ethaline–propylene carbonate solvent exhibits slightly higher ionic conductivity than the reline–methanol one. This is in-line with the viscosity of these mixtures, which follows the exact same trend. The maximum electric conductivities are at $x_{DES} = 0.2$ for both the methanol-containing mixtures, and at $0.4 \le x_{DES} \le 0.6$ for ethaline–propylene carbonate. Since the increase in mobility by diluting ethaline with propylene carbonate is much lower compared to methanol, the peak of ionic conductivity for ethaline–propylene carbonate is shifted towards higher x_{DES} . As x_{DES} approaches 1, the hydrogen bonding network in the DES becomes extensive, causing the viscosity to significantly

increase, and thus, the ionic conductivities of all solvents to reach their minimum. The only exception is ethaline–propylene carbonate, due to the very high viscosity of the pure organic component.

Task 1.3 Electrolyte-capture solvent optimization (TNO / TUD)

Electrolyte selection

lonic liquids (ILs) and Deep Eutectic solvents (DES) have been a subject of interest for their potential application as electrolytes due to their intrinsic conductivity, compositional flexibility and thermal stability among other properties. In this project, different types of electrolytes were tested to verify properties such as activity towards CO₂ reduction reaction, stability under reductive conditions, selectivity towards oxalic acid production, and suitability as CO₂ capture liquid and electrolyte.

Experimental methodology

To select a suitable catholyte, several cyclic voltammetry (CV) measurements were performed in a undivided electrochemical by applying dynamic potential between -0.5 and -2.3V (max range 1A, scan rate: 50mV/s; 3 scans). The potentials were controlled using an Autolab PGSTAT204 potentiostat and a 10A booster supplied by Metrohm Nederland[©].

Several different catholytes were tested using a Pb working electrode (1 cm2, Alfa Aesar, 99.9%). As counter electrode (CE) Pt coil (15 cm2, Alfa Aesar, 99.9%) was used. Prior, Pb was treated electrochemically in a 0.5 M H2SO4 by applying -1.8V vs Ag/AgCl with Pt as counter electrode for 500 s. Pb was rinsed with acetone after treatment to avoid oxidation by air. The Pt coil was flame annealed followed by quenching in Milli-Q water. CV measurements were performed on a blank electrolyte, then after CO₂ was bubbled through it for 15 minutes, and finally. the CO₂ was flushed out with a 15 minutes N₂ flush.

After selecting a suitable electrolyte, small scale (~130mL) electrolysis experiments were carried out in a divided electrochemistry cell, H-cell. Anode and cathode compartments divided by pre-treated cation exchange membrane (Nafion 117). With a Pb coil working electrode (10 cm², Alfa Aesar, 99.9%), a Pt coil counter electrode (14 cm², Alfa Aesar, 99.9%) and a leak free Ag/AgCl reference electrode (Innovative Instruments LF-1-100). Prior every experiment the working and counter electrode were treated. Pb was treated electrochemically in a 0.5 M $_{H2}SO_4$ by applying -1.8V vs Pt as counter electrode for 500s. Pb was rinsed with acetone after treatment to avoid oxidation by air. The Pt coil was flame annealed, followed by quenching in Milli-Q water.

Electrolysis were performed in potentiostatic mode with the selected potentials particular to each experiment controlled by AutoLab potentiostat (PGSTAT20). Liquid product distribution was measured by UPLC measurements. Catholyte and anolyte samples were analyzed on a ACQUITY UPLC, running on an Aminex HPX- 87H Ion exclusion Column (300 x 7.8mm), 0.05M H₂SO₄/water eluent, measured with RID (35°C) and UV (210 nm) detector – the RID values were processed. In the case where gas products where measured, this was achieved with a Trace 1300 GC with TCD detector, supplied by Interscience B.V.

Ionic Liquids as catholytes.

The following ILs were used as catholytes during CO₂ electrolysis:

- [EMIM] [BF4] 1-Ethyl-3-methylimidazolium tetrafluoroborate
- [EMIM] [BTI] 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
- [EMIM] [Otf] 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate
- [BMIM] [BF4] 1-Butyl-3-methylimidazolium tetrafluoroborate
- [BMIM] [PF6] 1-Butyl-3-methylimidazolium hexafluorophosphate

To evaluate the feasibility of ILs as catholyte during CO_2 electrolysis, Cyclic voltammetry (CV) was performed on Lead (Pb) and Nickel (Ni) electrodes using Platinum (Pt) as counter electrode. Cyclic voltammetry was performed in the absence and in the presence of CO_2 in order to evaluate if there is a current associated to the reduction of CO_2 .

Table 4. Overview of results obtained after running CVs of the different lonic Liquids/Cathodes systems, before and after CO_2 is present in the system

	[EMIM][BF4]	[EMIM][Otf]	[BMIM][BF4]	[BMIM][PF6]	[EMIM][BTI]
WE: Pb	Peak associated to CO ₂ at -2,2 V: ~-10 mA/cm ²	No peak associated to CO2No peak associated to CO2		No peak associated to CO ₂	No peak associated to CO ₂
WE: Ni	No peak associated to CO ₂	No peak associated to CO ₂	-	-	-

Of the systems tested, the only one that showed activity towards CO₂ reduction was when [EMIM] [BF4] was used as electrolyte. (See Figure 7, left). Chronoamperometry test was then performed in an H-Cell on a Pb electrode in a [EMIM] [BF4] solution and applying a cathode potential of -2.1V vs Ag/AgCl. (See Figure 7, middle and right).



Figure 7. left) Cyclic voltammetry in the presence and absence of CO_2 on a Pb electrode in a [EMIM] [BF4] solution. Middle) Current density and right) Concentration of the products detected and measured during chronoamperometry on Pb electrode at -2.5 V vs Ag/AgCL in a CO_2 saturated [EMIM] [BF4] solution.

During CO₂ electrolysis on Pb electrodes in a [EMIM] [BF4] solution, only formic acid was detected. Given the lack of oxalic acid formation, and the high degree of decomposition of the ionic liquid during electrolysis, ILs were no longer used as electrolyte for the production of oxalic acid from CO₂.

Deep Eutectic solvent as catholytes

Considered by some researchers a subset of lonic Liquids, Deep Eutectic Solvents (DES) are also an interesting possibility as electrolyte material, with similar advantages to ILs, with the added benefit of lower cost, lower environmental impact, and normally a wider electrochemical stability window. The next series of experiments was performed using different combinations of deep eutectic solvents as catholytes. As one of the most studied DES base compounds, Choline Chloride (ChCI) was mixed with different other compounds to produce an assortment of DES to be studied. The DES tested and their molar ratios are listed in Table 5.

Table 5. Deep Eutectio	solvents and their	molar ratios used	as electrolytes for	CO ₂ electrolysis.
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Key	Components	Molar ratio
Α	Choline Chloride : Ethylene Glycol	1:2
В	Choline Chloride : Ethylene Glycol : Propylene Carbonate	1 : 2 : 2.58
С	Choline Chloride : Ethylene Glycol : Isopropanol	1 : 2 : 0.22

D	Choline Chloride : Urea : Isopropanol	1 : 2 : 0.22
E	Choline Chloride : Urea : Methanol	1 : 2 : 8.16
F	Choline Chloride : Ethylene Glycol : Methanol	1 : 2 : 8.16
G	Choline Chloride : Urea : Ethylene Glycol	1 : 2 : 4.18
H	Choline Chloride : Urea : Propylene Carbonate : Ethylene Glycol	1 : 2 : 2.52 : 4.18
I	Choline Chloride : Propylene Carbonate	1:2
J	Choline Chloride : Urea : Propylene Carbonate	1 : 2 : 2.52

All of the mixtures except solvents I and J resulted in a homogeneous on phase liquid solvent. Solvents I and J were therefore not used in further experiments.

Cyclic voltammetry using Pb electrode and the one-phase DES were performed in the presence and in the absence of CO₂. (See Figure 8a).

In the presence of CO₂, all solvents tested showed a reductive current associated to CO₂ reduction with a maximum current at ca. -1.9 V vs Ag/AgCl. This potential was chosen for electrolysis which was performed for on a Pb electrode in a CO2-saturated electrolyte consisting of different DES mixture. The results are shown in See Figure 8 b, c and d.

The highest current measured during chronoamperometric studies was measured when ChCl/Urea/EG/PC mixture was used as electrolyte. This system also showed the highest faradaic efficiency toward oxalic acid after 3 h of electrolysis. However, the FE towards oxalic acid was only of ca. 2 %. The main product observed in all the chronoamperometries with different DES was formic acid. The highest faradaic efficiency and stability towards formic acid was achieved when ChCl/Urea/MeOH was used as electrolyte, reaching ca. 95% faradaic efficiency. However the efficiency slightly decreased over time. A more stable system was achieved when ChCL/EG/PC mixtures was employed as catholyte. The faradaic efficiency towards formic acid remained stable at ca. 85% for the 3h of electrolysis.



Figure 8. A) CVs on 10 cm² Pb electrode with different CO₂-saturated Deep Eutectic Solvents as electrolyte. B) Current density measured during CO₂ electrolysis on different DES at a working potential of -1.9V vs Ag/AgCl C) Faradaic efficiency towards formic acid and D) Faradaic efficiency towards oxalic acid measured during CO₂ electrolysis at -1.9 v VS Ag/AgCl.

Nevertheless, in all the solvents tested, extremely low faradaic efficiency towards oxalic acid was observed. Therefore, alternative solvent was considered as electrolyte. This solvent consisted on a physical CO₂ absorption solvent, namely, propylene carbonate (PC) and a tetraethylammonium chlorate salt (TEACI) as supporting electrolyte to ensure enough conductivity for electrolysis.

TEACL in PC as catholyte

Boor ¹ have shown that using TEACL in PC as catholyte and a Pb electrode, oxalic acid can be produced with a faradaic efficiency above 90%.

Chronoamperometric studies at -2.5 V vs Ag/AgCl were performed on a Pb electrode in a 0.7 M TEACL in PC. The results are shown in Figure 9.

Although relatively low current densities were measured during CO_2 electrolysis at -2.5 V vs Ag/AgCL, high faradaic efficiencies towards oxalic acid were obtained, being close to 100% during the 3 h of electrolysis. Contrary to the other ILs and DES tested, PC showed oxalic acid as major product during CO_2 reduction and only traces of formic acid were produced.

¹ V.S. Boor, 2020, *Electrochemical reduction of CO2 to oxalic acid: electrochemical conversion, downstream processing and techno-economic analysis.*

The system consisting on Pb as cathode, 0.7 M TEACL in PC solution as catholyte, Pt as anode and 0.5 M H_2SO_4 solution as anolyte were selected as the optimal system for the production of oxalic acid and was used for the scaled-up phase. (See section 5.2)



Figure 9. Current density and Faradaic efficiency towards oxalic acid and formic acid measured during chronoamperometry on Pb electrode at -2.5 V vs Ag/AgCL using 0.7 M TEACL in PC as catholyte. Pt wire was employed as counter electrode in a 0.5 M H_2SO_4 solution.

Task 1.4 Product recovery (TUD)

CO₂ absorption in propylene carbonate

The removal of the CO2 by absorption from biogas with poly-carbonate as a solvent was modeled in Aspen Plus. We assumed that the feed with a composition of 40 mol% CO2 and 60 mol% CH4 enters the absorber at 25 \circ C and 10 bar. The absorber is designed to process 1 ton/h of biogas with a methane purity of at least 94 mol% to comply with the standards for bio-methane injection into the natural gas grid of the Netherlands (<6 mol% of CO2 is allowed). This means that roughly 90% of the CO2 should be removed from the biogas. The solvent flow and the number of stages were varied to meet the design specifications. For the property calculations, the Peng-Robinson (PR) equation of state (EOS) was used. The binary interaction parameters of the PR-EOS were fitted to available experimental solubility data of CO₂ and CH₄ in poly-carbonate, see the Supporting Information. Some of the methane is co-absorbed, which will be carried along with the poly-carbonate stream to the cathode compartment of the electrolyser.

Electrochemical conversion of CO2

To evaluate the economics in detail we start with a base case where it is assumed that CO2 is converted to oxalic acid with a Faraday Efficiency of 80% at a current density of 100 mA / cm^2 and with cell voltage of 4.0 V. We considered hydrogen as the only by-product, which is obtained with an Faraday Efficiency of 20%. It is assumed that 60% of all the dissolved CO₂ in poly-carbonate is converted to oxalic acid. This means that a conversion of 60% is assumed.

The electrolyser is operated at the same pressure as the absorber (10 bar). We assume that the coabsorbed methane is not reduced in the electrolyser and remains in the liquid phase. The by-product hydrogen will mostly escape to the gas phase, since the solubility of H₂ in poly-carbonate is very low. The mixture from the electrolyser is flashed to obtain a gas stream that contains mostly CH₄ and hydrogen, and a liquid stream containing poly-carbonate, oxalic acid, and unconverted CO₂. The gas stream can be separated into CH₄ and H₂ using available technologies, like a membranes or adsorption, but in our process design we have decided to blend this H₂/CH₄ mixture with the methane stream from the absorber and inject into the natural gas grid. The liquid stream containing poly-carbonate and oxalic acid is subjected to further downstream processing.

Separation of oxalic acid from non-aqueous solutions

Different technologies are available for the separation of oxalic acid, but this applies mostly to aqueous systems. From the different separation technologies we select the most promising one based on a process of elimination. The state of the acid, dissociated or un-dissociated) and the requirement of a dry water-free solvent in the electrolyser have a major influence on the downstream processing.

Liquid-liquid extraction (LLE) is a well-established separation technique that is used on an industrial scale, for example for formic acid and acetic acid extraction. In LLE, the solute, oxalic acid, is transferred from one liquid phase, the feed, to a second liquid phase, the extraction solvent, which has a higher affinity for binding the solute.

Typically, a water-immiscible solvent is used to extract the solute from an aqueous solution. In our process, the oxalic acid, the solute is present in a water-immiscible solvent (poly-carbonate) and the oxalic acid needs to be transferred to another solvent. We have used water as the solvent to extract the oxalic axid from the poly-carbonate phase. Some the LLE experiments with, different amounts of water were added to a solution containing 10 mM oxalic acid and 0.7M TEACI in poly-carbonate. The system was mixed for 48 hours. After settling, the concentration of oxalic acid and TEACI in both phases, the water-rich phase and the poly-carbonate-rich phase were measured with HPLC.

The distribution coefficient of oxalic acid and water at 25 C were 9.6 and 8.6, respectively. In principle, water is a good solvent to extract oxalic acid from poly-carbonate, but a significant amount of TEACI is co-extracted as well. The consequence of this is that a second step will be required to separate the oxalic acid from TEACI, which should be recycled to the electrolyser. The main problem of the LLE process is that at 25 C around 7 wt% of water is dissolved in the poly-carbonate-phase, while 17.5 wt% of poly-carbonate is dissolved in the water- phase. Therefore, the poly-carbonate phase cannot directly be recycled to the electrolyser, because the presence of this amount of water would lead to the production of formic acid and other by-products. The poly-carbonate-water mixture cannot simply be distilled due to the presence of a heterogeneous azeotrope. Therefore, a costly dehydration step will be required to dry poly-carbonate before it can be recycled to the electrolyser. For this reason, we exclude liquid-liquid extraction with water as a feasible option for oxalic acid separation from the poly-carbonate stream.

Electro-dialysis can be used to purify different types of acids, like formic acid, acetic acid, propionic acid, lactic acid, citric acid, and oxalic acid. Here we use a bipolar membrane based electrodialysis (BMED) to convert oxalate from an aqueous solution to oxalic acid, which requires an energy consumption of 6 kWh/kg for an oxalate concentration of 0.25 mol/L and a current density of 30 mA/cm² at 80% current efficiency, but the obtained oxalic acid concentration was relatively low. In our process, we cannot use electro-dialysis, because the feed contains oxalic acid instead of oxalate salt.

Crystallization is commonly used in fermentation processes to separate poorly soluble solutes from a solution. In crystallization, the solution is cooled or evaporated beyond the solubility limit of the solute, which then precipitate/crystallize out. It is clear that solubility data is required to assess the suitability of crystallization for oxalic acid crystallization from non-aqueous solvents.

We performed Crystal16 (Technobis) experiments to study the crystallization behavior of oxalic acid in poly-carbonate. In these experiments, the transmission coefficients of 1 M oxalic acid samples were measured, while the system was cooled from 60 C to -10 C at different cooling rates. The transmission coefficient was close to 100%, which means that no precipitation occurred during the cooling process. For this reason, we exclude cooling crystallization as a potential method for oxalic acid separation from poly-carbonate.

Gas Anti-solvent Precipitation (GAP) is a popular method to crystallize pharmaceutical compounds. In GAP, the solution of an organic solvent containing the product is gradually pressurized with a gas, like supercritical CO₂, which expands the solution and decreases the solvent power causing precipitation of the product. The suitability of GAP for oxalic acid crystallization depends on the gas–liquid miscibility, the product concentration, and the solubility of oxalic acid in poly-carboante. We have performed a proof-of-principle experiment to study oxalic acid crystallization from poly-carboante using GAP with

compressed CO₂ as anti-solvent. Three different solutions of oxalic acid in poly-carbonate, a saturated solution, a 0.25 M solution and a 0.5 M solution were prepared and loaded into a high pressure sapphire cell. CO2 was gradually added to the cell using a high pressure syringe pump (Teledyne Isco, 260 D model). For the saturated solution and 0.5 M solution, precipitation of oxalic acid was observed around 30 bar. No precipitation of oxalic acid was observed for the 0.25 M oxalic acid solution at pressures up to 50 bar. For oxalic acid precipitation from acetone using CO₂ as the anti-solvent a similar behavior was observed, that is oxalic acid precipitation occurred only at high concentrations. The GAP process for oxalic acid concentrations. More detailed experiments are required to better understand the precipitation characteristics of oxalic acid in non-aqueous sol vents. Nevertheless, these preliminary results can be used for conceptual design purposes. We selected the GAP process for the separation of oxalic acid from poly-carbonate.

Task 1.5 Process design and optimization of integrated process (TT/DMT)

The oxalic acid produced during CO2 reduction in the electrochemical reactor is dissolved in the liquid electrolyte solution. Separation of the oxalic acid from the liquid needs is required to recover the product in a solid state. In order to assess the feasibility of the separation of oxalic acid, several technologies were compared. Liquid-liquid extraction followed by crystallization is a viable option for the separation and recovery of oxalic acid from the liquid catholyte phase. Based on this separation method, a process design is proposed and a techno-economic analysis has been performed. The techno-economic analysis showed a favorable economic potential for this technology if certain key performance indicators can be achieved. Typically, CO2 conversion to oxalate only takes place in an aprotic catholyte solution.

From the experimental work it follows that with the optimal results in terms of faradaic efficiency and current density have been found, using lead as cathode, platinum as anode, propylene carbonate with 0.7 M tetra-ethyl-ammonium chloride as catholyte solution and 0.5 M H₂SO4 as anolyte solution in which the cathodic and anodic compartment are separated by a Nafion 117 membrane. At higher temperatures, higher current densities were obtained by reduction of mass transfer limitations. Within the range of -2.2 V to -2.7 V vs Ag/AgCl, increasing current densities and decreasing faradaic efficiencies were found with increasing applied potential. Typically, two types of anodes are being used: an inert (Pt) anode and a reactive (Zn) anode. The two different types of electrodes give rise to two different process configurations. The zinc anode participates in the reaction, resulting in the formation of solid zinc oxalate and zinc carbonate, while the Pt anode only delivers electrons by the oxygen evolution reaction resulting in dissolved oxalate, glycolate (and probably glyoxylate and formate) as byproducts of the electrochemical process.

A feasibility study has been performed in order to scale-up the electrochemical conversion of CO2 to oxalic acid. A number of options for the downstream processing of oxalic acid are evaluated based on a comparison of a two-compartment and a three-compartment cell configuration, see Figure 10 and Figure 11.

Generally, the costs for 3-compartment cell electrolyser are higher than the two-compartment cell. Furthermore, as Zn anode is consumed during the reaction the downstream section for the zinc anode process is more complex, as this requires a gas-separator, a centrifuge, a crystallizer and a second centrifuge.

The costs for the zinc anode process turned out to be higher compared to the process with the Pt anode electrolyser, as this second process only has a main downstream process consisting of a crystallizer followed by a centrifuge. In the economic evaluation we consider a two-compartment cell with a Pt electrode, see section 6.3.



Figure 10. Basic lay-out for a three-compartment electrolyser and the subsequent downstream section.





Task 1.6 Life-cycle analysis and multi-criteria analysis (DMT/RUG)

Multi-criteria analysis

A house of quality was created for the selection of the best electro-reactor solvent. To create the house of quality the desired properties of the final product (based on an end user perspective) have been stated, prioritized and ranked. Ideally, the solvent used in the electro chemical process will be "green" to maintain the sustainable association of the proposed electrochemical process, so the solvent must

fulfil properties like: availability, non-toxicity, biodegradability, recyclability, flammability, and low price etc. lonic liquids are one such class of green solvent, under which a subclass known as Deep Eutectic Solvents (DES) exists. The results of this exercise are shown in Figure 12.

									/			
							_					
			Impr	ovement Direction			•	▼		▼	▼	
Weight Chart	Relative Weight (%)	Customer Importance (/5)	Customer Requirements	Functional Requirements	Conductivity at 25°C (mS cm ⁻¹)	Carbon Dioxide Solubility (mol _{co2} /mol _{solvent})	Density at Operating Temperature (g/cm ³)] Melting Point (°C)	MSDS Classification	Cost of Hydrogen Bond Acceptor (\$kg ¹)	Cost of Hydrogen Bond Donor (\$kg ¹)	 Chemical Stability (days)
	25	4	Co	ost	0		\bigtriangledown	\vee				\triangle
	13	2	Availa	ability				~		0	0	~
	6	1	Ease of	disposal				V				V
	31	5	Conve	Protects	^	~		V				v
	19	3	Ease	ofuse				×	0			0
		-		Target	0.333	0.3	1	25	-	1	1	365
			Teo	hnicalImportance	57	45	31	38	27	42	42	47
			F	Relative Weight (%)	17	14	9	12	8	13	13	14
				Weight Chart								
Le	gend											
Meaning			Symbol									
Maximise Prop	perty											
Maintain Prog	perty		•									
Minimise Prop	perty		•									
Strong Correla	tion											
Medium Corre	lation		0									
Weak Correla	ition		\bigtriangledown									

Figure 12: House of Quality for the selection of IL/DES

However, taking into account the experimental results, 0.1M Tetrabutylammonium perruthenate (TBAP) in Acetonitrile and 0.7M Tetraethylammonium Chloride (TEACI) in Propylene Carbonate were selected as most promising.

Life-cycle analysis

The goal of the LCA is to obtain an estimation for the total carbon dioxide emissions associated with synthesising oxalic acid from carbohydrates within the Netherlands. Three LCAs are completed, respectively for the theoretical electrochemical process using the proposed electro-reactor as well as two references with conventional oxalic acid production processes based on Glucose and Sodium Formate as feedstock.

The scope includes the emissions generated during the formation of each reactant required in the process and the reactants that are required to synthesis that reactant etc. It also includes the emissions generated from the power requirements of the process (e.g. heating, stirring etc.). Moreover, emissions known to be health and environmental hazards are estimated.

The scope does not include emissions generated as a result of farming crops used as carbohydrate feedstock. This is due to the large differences internationally, nationally and regionally between these emission outputs (e.g. the carbon footprint (2012) of EU sugar beet has been estimated to be between 242-771 kg CO2 per tonne of sugar).

The scope also does not consider the inefficiencies of the processes considered. For example, the regeneration of nitric acid during the carbohydrate to oxalic acid oxidation tends not to be perfect and requires a, comparatively, small continuous input of nitric acid to make up for that which is lost. This is not considered because the amount which is lost can vary greatly depending on age and use. The transport costs associated with moving reactants and products to and from the places they synthesised will also not be considered. Lastly, the sugars of the crop will be made up entirely of carbohydrates; no/negligible glucose present.

The relevant chemical reactions for the three oxalic acids production routes are stated below:

Using the electro-reactor (and a zinc sacrificial anode):

$$2CO_2 + Zn^{2+} \rightarrow (COO)_2^{2-}Zn^{2+}$$

 $(COO)_2^{2-}Zn^{2+} + H_2SO_4 \rightarrow (COOH)_2 + Zn^{2+}SO_4^{-2-}$

Using sugars (glucose):

$$(C_6H_{10}O_5)_xH_2O + (x - 1)H_2O + 6xHNO_3 \rightarrow 3xC_2H_2O_4 + 6xNO + 6xH_2O$$

 $6NO + 3O_2 \rightarrow 6NO_2$
 $6NO_2 + 2H_2O \rightarrow 4HNO_3 + 2NO$

Using sodium formate:

$$\begin{split} NaOH + CO &\rightarrow HCOO^{-}Na^{+} \\ \\ 2HCOO^{-}Na^{+} &\rightarrow (COO)_{2}(Na)_{2} + H_{2} \\ (COO)_{2}(Na)_{2} + Ca(OH)_{2} &\rightarrow Ca(COO)_{2} + 2NaOH \\ \\ Ca(COO)_{2} + H_{2}SO_{4} + 2H_{2}O &\rightarrow CaSO_{4} \cdot (H_{2}O)_{2} + (COOH)_{2} \end{split}$$

The global warming potentials of the sodium formate and carbohydrate routes for oxalic acid production were calculated to be 1.364 kgCO2/kg(COOH)2 and 3.277 kgCO2/kg_{(COOH)2}, respectively. The global warming potential of the electrochemical process (0.467 kg_{(COOH)2};-0.511 kg_{co2}/kg_{(COOH)2}) was also calculated. The theoretical electrochemical process was calculated to have a lower global warming potential relative to the other two contemporary, commercial processes. Provided the electrochemical process is economically viable, it provides a promising opportunity to lower the global warming potential of the oxalic acid industry when applied ².

² Zutphen, Thomas van (2021) <u>Investigation into the use of an Electro-Reactor for Carbon Dioxide to Oxalic Acid</u> <u>conversion</u>. Master's Internship Report, Chemical Engineering. Item availability may be restricted.

6.2. WP2 Construction of prototype unit (TNO)

Task 2.1 Construction of lab-scale unit (TNO)

The lab-scale set-up employed for the scaled-up testing of the Integrated CO_2 capture and conversion towards oxalic acid has been designed and build by TNO and is shown in Figure 13.



Figure 13. Pictures of the lab-scale set-up employed for CO₂ capture and conversion

The process flow diagram of the lab-scale se-up is presented on Figure 14. The set-up consist of:

- 1. **Feeding system** where the CO2 absorption takes place
- 2. Recirculation system where the electrochemical reaction takes place
- 3. Control system to control pressure, temperature and current applied
- 4. Sampling system to measure liquid and gas products formed
- 5. Ventilation system to operate in a safe environment

In the feeding system, the reactant CO_2 is fed into the catholyte vessel were the CO_2 capture step takes place with the use of physical CO_2 capture solvents. The control systems allows to pressurize the vessel where the capture takes place to enhance the absorption step and therefore increase the amount of CO_2 absorbed. Once the solvent is completely loaded with CO_2 , the CO_2 -rich solvent is flowed into the electrochemical reactor, where the CO_2 is electrochemically reduced. The CO_2 -lean solvent is recirculated back to the absorption vessel, where it will be reloaded with CO_2 . In the reactor, the electrochemical reaction is controlled by the power supply by applying a certain current that allows to operate in the adequate voltage range for the desired reaction. A gas and liquid sampling systems allows for monitoring of all the products formed during electrolysis.



Figure 14. Process flow diagram of the lab-scale set-up for Integrated CO₂ capture and conversion.

Task 2.2 Testing of prototype unit (TNO)

With the selected electrolyte consisting of a 0.7M TEACI solution in Propylene carbonate, further scale up of the technology was investigated increasing Pb electrode area form 10 cm² to 100 cm² and intensifying the process from batch reactors to flow reactors.

Additionally, in order to increase the current density and productivity of the process, several ideas were explored such as increasing the active area of the Pb cathode (by using nanoparticulated electrodes), and increasing the working pressure of the system, to augment CO₂ catholyte concentration and accessibility to the electrode surface. The results of the

Electrolysis experiments were performed at atmospheric pressures and at high pressures. An overview of the most representative experiments is showed in the following paragraphs. 2.2.1) CO_2 electrolysis at elevated pressures, and 2.2.2) CO_2 electrolysis at atmospheric pressures.

CO₂ electrolysis at elevated pressures (10 bar)

Figure 15 shows the results of CO₂ electrolysis at different applied current densities under the following conditions:

- Cathode: 100 cm² flat Pb electrode
- Catholyte: 0.7 M TEACL in PC
- Anode: 100 cm² flat Pt electrode
- Anolyte: 0.5 M H₂SO₄
- Membrane : CEM- Nafion 117
- Temperature: 20 °C
- Pressure: 10 bar
- Current applied: -10, -20, -30 and -40 mA/cm²
- Cathode pre-treatment: Mechanical polishing and reductive current (-25 mA/cm²) to reduce surface oxides



Figure 15. A) Applied current density as a function of time during CO_2 electrolysis on a Pb electrode in a 0.7 M TEACL in propylene carbonate solution at 10 bar. B) Faradaic efficiency of measured products as a function of time. C) Productivity of measured products as a function of time and related to the applied current density. Formic acid is plotted in a different graph due to values being an order of magnitude larger than other products.

The main product formed during CO₂ electrolysis was formic acid. Other products such as oxalic acid, glycolic acid and glyoxylic acid, were detected in small amounts.

After 4 hours of electrolysis, oxalic acid production increased, with a faradaic efficiency close to 30%. This selectivity towards oxalic acid presents after substantial reductive charge has been applied into the system. Additionally, it is also at this final hour where the complete charge was accounted for (Total FE ~100%). All these effects point towards a big component of the initial charge being used to reduce surface oxides.

With this information, a subsequent test was performed, where for the first two hours a high reductive current was applied to the system. However, no oxalic acid was detected, and faradaic efficiency towards formic acid was low (<20%). UPLC samples showed a big peak of an unknown compound appearing after the first 10 minutes. This unknown compound is expected to come from catholyte decomposition under reductive current. Therefore applying a high initial reductive current to reduce surface oxides is not feasible and it was not used in follow-up tests.

It was also during this experiment where it was noted that the coloration of the electrolytes was changing during electrolysis. This effect was investigated, and it was discovered to be caused by corrosion of the metal vessels and components in the setup, brought upon by the contact of the solvent with the stainless steel parts. Analysis of the electrolyte samples showed a gradual increment of metal particles in the anolyte, and in a smaller proportion, in the catholyte. The reduction of these metallic ions might also explain some of the unaccounted charge in previous experiments. Given all these negative effects in this set up, it was decided to not continue the high pressure experiments in this reactor, and proceed in a non-metal based set up, where electrolytes are not in contact with metal parts of the setup and thus no corrosion occurs.

CO₂ electrolysis at atmospheric pressures (1 bar)

Figure 16 shows the results of CO₂ electrolysis at different applied current densities under the following conditions:

- Cathode: 100 cm² flat Pb electrode
- Catholyte: 0.7 M TEACL in PC
- Anode: 100 cm² flat Pt electrode
- Anolyte: 0.5 M H₂SO₄
- Membrane : CEM- Nafion 117
- Temperature: 20 °C
- Pressure: 1 bar
- Potential applied: -2.5 V vs Ag/AgCl
- Cathode pre-treatment: Mechanical polishing and reductive current (-25 mA/cm²) to reduce surface oxides



Figure 16. a) Current density b) water content and concentration of products formed and c) Faradaic efficiency of products formed during CO₂ electrolysis at -2.5 V vs Ag/AgCL on Pb electrode in a 0.7 M TEACL in PC at atmospheric conditions.

Oxalic acid was the main product detected in the first hour of electrolysis. The concentration of formic acid increased after 1 h, to reach a plateau after 2 h of electrolysis. No gas products were detected in any substantial amount, neither was there any solid product formation. Water content on the catholyte gradually increased over time at a rate of approximately 1%/hour. At the 2.5h time oxalic acid production stopped, the catholyte water content was ~3%w.

The total Faradaic efficiency was not close to 100%. Given neither gas nor solid products were detected, unaccounted electrochemical processes that could explain the rest of the reductive current include surface oxide reduction, or transfer of the products formed in the cathode- to the anolyte and its reoxidation.

Task 2.3 Integration with renewable energy source (TNO)

This activity aimed to couple the electrochemical set-up with a wind turbine or a solar panel to study the influence of intermittency of electricity during the electrochemical conversion of CO₂.

Due to the lack of equipment and to the fact that the development of the desired reaction did not reach the expected mature level in a big scale, the effect of electricity intermittency was considered out of scope in this stage of the project.

Although the influence of the stability of the energy supply is a very relevant topic to study for electrochemical reactions, the technology must have a certain maturity level in order to be able to extract conclusion from this type of studies. In this project, we were able to produce oxalic acid in a relatively stable way but only in small scale (10cm² electrode active area and batch configuration). When the reaction was scaled up to 100cm² and changed from batch to flow process, the stability and the performance of the reaction decayed drastically. Therefore, further research and work is needed in order to first achieve a stable operation of the system at large scale, with acceptable faradaic efficiencies towards oxalic acid (>80%) and stability (weeks) before we can test the effect of electricity intermittency.

6.3. WP3 Valorisation: System integration and Techno-economic evaluation (TT)

Task 3.1 System integration based on P2C, CCU, and source-sink matching (MvF/DMT)

In order to advance electrification of the process industry, recycling of carbon dioxide through electrochemical reduction is an interesting way. Basically, this is a combination of carbon capture and utilization (CCU) and power-2-chemiclas (P2C) concepts. One of the advantages is that this can already be implemented on a relatively small scaler by producing locally some added-value chemicals, using CO2 from for example biogas and locally produced green electricity. The only other 'feedstock' is then related to the electrolyte solution, to provide for the required hydrogen molecules.

In terms of source-sink matching, here we start with the removal of (biogenic) CO2 from biogas and the option of coupling with a renewable energy source, like solar panels or wind turbines that will produce the electric power to run the CO2 electrolyser. Furthermore, considering the wide range options that are available for storage and transport for CO2, electricity, and chemicals our focus is on relatively small-scale applications. For CO2, transport only makes sense for large scale and relatively long-distance transport, and when there is permanent underground storage of the CO2

Local production and use of CO2 and renewable electricity for the synthesis of oxalic acid is a clear alternative to all kind of transmission issues. Local, decentralized production does not require a dedicated transport infrastructure for the long-distance transport of CO2 either by pipeline or by ship. Additionally, considering the congestion of the Dutch power grid that is already taking place in several regions in the Netherlands, local use of electricity to store energy in chemicals is also a feasible option to mitigate some of the current (and expected future) issues associated with the transport of large quantities of electricity.

Based on some existing industrial CCU applications as operated by Covestro and Carbon Recycling International, a relevant scale where local production of a chemical will be feasible is based on the use of CO2 in the order of 5 to 10 kton CO2 per year. A typical medium-size digester in the Netherlands produces 500 to 1000 Nm3 of biogas per hour, which corresponds to 3.5 to 7.0 kton of CO2 per year. So, a relatively simple way forward is to start with the CO2 from two digesters or consider a large-scale digester that produce well in excess 10 kton of CO2 per year.

On the other hand, there are number of small-scale applications of oxalic acid, mainly related to cleaning or bleaching, especially for the removal of rust (iron complexing agent). It is used commercially as a laundry rinse, wood-bleaching agent, and calcium remover. Oxalic acid can remove some paints and varnishes. It is available in packages of 1 to 10 kg, and asl liquid sprayer at the liter scale. The main applications of oxalic acid can be classified as around 30% for metal treatment, 25% for textile treatment, 20% as bleaching agents, and around 25% for chemical uses.

Power-2-chemicals approach for synthesis of oxalic acid

As an example for the economic evaluation, we started with the availability of 1 ton of biogas per hour, with a typical gas composition of CO2 : CH4 of 40 : 60 on a vol% basis. These values for the flow rate and the gas composition then correspond to around 600 kg of CO2 per hour, and on an annual basis this gives then 5 kton of CO2.

From the other parameters for electrochemical conversion, including a Faraday efficiency of 80% toward oxalic acid, the current density of 100 Ma / cm2, and the ratio of the molar mass of oxalic acid to CO2 of 2.4 (from 96/44) around 200 kg of oxalic acid can be produced from 600 kg CO2. These numbers also mean that in order to produce 1 ton of oxalic acid in the range of 4.5 to 5 MW orf power is required. So, around 1 MWh is required to produce 200 kg of oxalic acid per hour from 600 kg of CO2 per hour.

One of the options to provide the green electricity is to use a small-scale wind park of a few MW to produce the renewable power to operate a CO2 electrolyser. Typical investment cost for a single 1 MW wind turbine is in the order of \in 1.5 to 2 M. An investment of \in 2 M for 1 MW gives a Levelized Cost of Electricity (LCOE) in the order of 30 to 35 \in per MW. This is for a 15 year depreciation period with an interest rate of 5% per year. In the economic evaluation, see Table 5, an electricity price of \in 30 per

Task 3.2 Techno-economic analysis and business case (DMT, TT, TNO, TUD)

Economic analysis

The profitability of a process can be judged based on different metrics like the payback time (PBT), the return on investment (ROI), or the discounted cash flow or net present value (NPV) approach. We employed the NPV criteria to evaluate the economic feasibility of the electrochemical reduction of CO2 to oxalic acid process. The NPV was calculated by summing the discounted cash flows over the lifetime of the process:

$$NPV = \sum_{n} \frac{C(n)}{(1+ir)n}$$

where C_0 is the initial investment, C_n is the cash flow, n the year, and ir the interest rate.

A nominal interest rate of 5% and an income tax rate of 25% was assumed. The straight-line depreciation method was applied over a depreciation period of 10 years using a salvage value of 10% of the total capital investment. The working capital was assumed to be 5% of the capital investment, which was recovered at the end of the project. The total CAPEX was obtained as the sum of the capital cost of all process units. The yearly profit was calculated from the revenues generated by selling the products (oxalic acid and H2) minus the annual OPEX of the process. The value of anodic oxygen and purified methane was not considered in the economic analysis. The lifetime of the process was assumed to be 20 years with 8000 h/y of operation.

Capital Cost Estimation

The capital cost (CAPEX) of the CO2 electrolyser, including the balance of plant (BOP), was taken from our previous work as \$20,000/m₂. Note that this cost was derived from related electrolysis technologies due to the lack of commercial scale CO2 electrolysers. The required electrolyser area was calculated from the current density and the set CO2 conversion rate. The CAPEX of the CO2 absorber was obtained from the Aspen Economic Analyzer after optimizing the number of stages, solvent flow rate, and the pressure. The CAPEX of the compressor, which is required to compress the biogas, was obtained from a correlation. The CAPEX of the GAP unit was obtained from a capacity scaling equation:

$$C_2 = C_1 (F_2/F_1)^n$$

where C_i is the total battery limit capital cost, F_i the mass flow of CO₂ for process *i*, and *n* the scaling exponent (a value of 0.7 was used here). The reference cost of the GAP unit was taken from M. Rantakyla, Particle production by supercritical anti-solvent processing techniques, 2004.

Operating Cost Estimation

The operating cost (OPEX) of the electrolyser and the compressor was estimated from the power consumption using a base case electricity price of \$30/MWh. The power of the electrolyser is computed from:

$$P_i = I_i A V$$

where P_j is the power required to produce component j, I_j is the partial current density for component i, A the electrode area, and V the cell voltage.

The power of the compressor is obtained from a model for adiabatic compression of an ideal gas, see the Supporting Information. The power required for pumping the solvent through the absorber and the reactor is neglected, since this is typically very small compared to the compression of a gas. The cost for CO_2 is included in the CAPEX and OPEX of the absorber. The costs of water and recyclable chemicals (e.g., electrolytes and solvents) were neglected in the economic analysis.

Base Case Assumptions

In Table 6 the data used in the techno-economic analysis for the base case is given.

Table 6.	Base	case	data	used	in	techno-	economic	anal	lysis
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Parameter	Value
Cell voltage (V)	4
Current Density, CD (mA/cm ²)	100
Faraday Efficiency, FE (%)'	80
CO ₂ conversion (%)	60
Concentration oxalic acid (M)	0.5
Oxalic acid price (\$/ton)	1000
Hydrogen price (\$/ton)	1000
Electricity price (\$/MWh)	30
CAPEX electrolyser (\$/m ²)	20 000

The parameters of the electrolyser are based on the latest developments in the field of CO_2 electrolysis to oxalic acid. Thus, the base case data is not necessarily derived from the experiments of this work. The concentration of oxalic acid is limited by the solubility of CO2 in poly-carbonate. At 10 bar and 298.15 K, the solubility is around 0.15 mol CO^2 / mol poly-carbonate or 1.76 mol CO2 / L of poly-carbonate. This means that at a CO2 conversion of 60%, an oxalic acid concentration of only 0.5 M can be obtained in single-pass, since 2 moles of CO2 are required per mol of oxalic acid. The poly-carbonate stream with the dissolved oxalic acid can be re-circulated for higher concentrations, but the concentration cannot be too high to avoid precipitation in the reactor and pipelines. For this reason, we have assumed a concentration of 0.5 M for the base case calculations. The prices of chemicals and electricity are based on the European market. It is important to note that the bulk price of oxalic acid in China or India is almost a factor two lower than in Europe. For this reason, the European Union (EU) is imposing an anti-dumping duty on oxalic acid imports from these countries. The electricity price is based on recent estimates of the U.S. Energy Information Administration for renewable energy from solar and wind. Most of the base case assumptions are subjected to some uncertainty, which will be taken into account in a sensitivity analysis.

Results for Techno-Economic Analysis

In Table 7, the CAPEX and OPEX of the electrochemical CO2 conversion process shown in Figure 3 are reported. The total CAPEX and OPEX of the process are roughly \$ 7.5 M and \$ 0.5M / y. The CO2 electrolyser accounts for >70% and >50% of the CAPEX and OPEX, respectively. The CAPEX and the OPEX of the downstream separation of oxalic acid is relatively low and accounts for <20% of the total costs. The revenues from selling oxalic acid and hydrogen are around \$ 2.9 M / y. The sales income of hydrogen is negligible small compared to oxalic acid, since the amount of hydrogen produced is small. The NPV for the base case scenario is positive (\$ 16 M) and the PBT is 4 years. These results show that the electrochemical CO2 conversion process can be profitable under the base case assumptions.

Process step	Capex	Opex	Capex	Opex	
	\$M	\$M / year	%	%	
CO2 absorption	0.9	0.14	13	28	
CO2 electrolyser	5.3	0.26	72	52	
Oxalic acid separation	1.2	0.10	16	20	
Sum	7.4	0.50	100	100	

Table 7. Data the Capex and Opex for the main process steps: CO2 capture by absorption, the electrochemical conversion of CO2 in the electrolyser to oxalic acid, and the cost for the downstream separation of the oxalic acid

A sensitivity analysis is performed to check the effect of different parameters on the economics of the process. In Figure 17 the results of the sensitivity analysis are shown. Note that only a single input parameter was varied, while keeping other variables constant at the base case values. The relative change of the input parameters is with respect to the base case values (in Table 6Table 5).

It is clear that the product price has the largest impact on the NPV. The price of oxalic acid should be at least \$ 550 / ton to have a positive NPV and a PBT of less than 10 years. As expected, the cell voltage and the electricity price have a similar effect on the economics, since both are related through the power equation. The current density, the Faraday Efficiency, and electrolyser CAPEX seems to have a marginal effect on the NPV. It is remarkable that the process has a positive business case for a current density of 50 mA / cm² with a NPV of \$ 12 M and PBT of 7 years. Electrochemical conversion of CO₂ to oxalic acid seems to have a very favourable economics, which is related to the high market value of oxalic acid and the low number of electrons input per mole of product.



Figure 17. Sensitivity analysis fro the economics of CO2 to oxalic acid. Effect of relative changes to current density, cell voltage, Faraday Efficiency, CAPEX, electricity price and product price on Net present Value (NPV). Values in brackets refer to the base case.

This can easily be understood by computing the value of 1 mol of supplied electrons, according to:

$$V_e = P_p M W / n$$

where V_e is in \$/mol electrons, P_p the market price of the product in \$/g, MW the molecular weight in (g/mol), and n the mole of electrons required to produce 1 mol of product.

The 'value per mol electrons', V_e, is for oxalic acid \$ 0.045 /mol of electrons. This is a factor 10 to 15 higher than for example CO_2 reduction toward ethylene or ethanol. From a market perspective, oxalic acid is the only CO_2 electro-reduction product that can compete with the fossil-based route under the base case scenario. The economics of electrochemical oxalic acid production from CO2 can be

improved even further if higher current density and Faraday Efficiency, and lower cell voltages are achieved, and better oxalic acid separation methods are developed.

Future studies should focus on improving the mass transfer by using gas diffusion electrodes, the elimination of water in the catholyte by for example using hydrogen oxidation at the anode, and increasing the electrical conductivity of the solvent/electrolyte mixtures to decrease ohmic losses and the cell voltage.

7. Conclusions

Solvent properties for CO2 capture and conversion (TUD)

Recently, deep eutectic solvents (DES) have been considered as possible electrolytes for the electrochemical reduction of CO₂ to value-added products such as formic and oxalic acid. The applicability of pure DES as electrolytes is hindered by high viscosities. Mixtures of DES with organic solvents can be a promising way of designing superior electrolytes by exploiting the advantages of each solvent type. In this study, densities, viscosities, diffusivities and ionic conductivities of mixed solvents comprising DES (i.e., reline and ethaline), methanol and propylene carbonate were computed using molecular simulations. To provide a quantitative assessment of the affinity and mass transport of CO₂, oxalic and formic acid in the mixed solvents, the solubilities and self-diffusivities of these solutes were also computed.

Our results show that the addition of DES to the organic solvents enhances the solubilities of oxalic and formic acid, while the solubility of CO_2 in the ethaline–containing mixtures are in the same order of magnitude with the respective pure organic components. A monotonic increase in the densities and viscosities of the mixed solvents is observed as the mole fraction of DES in the mixture increases, with the exception of the density of ethaline–propylene carbonate which shows the opposite behaviour due to the high viscosity of the pure organic component. The self–diffusivities of all species in the mixtures significantly decrease as the mole fraction of DES approaches unity. Similarly, the self–diffusivities of the dissolved CO_2 , and the oxalic and formic acid also decrease by at least one order of magnitude as the composition of the mixture shifts from the pure organic component to pure DES. The computed ionic conductivities of all mixed solvents show a maximum value for mole fractions of DES in the range of 0.2 to 0.6, and decrease as more DES is added to the mixtures. Since for most mixtures studied here no prior experimental measurements exist, our findings can serve as a first data-set based on which further investigation of DES containing electrolyte solutions can be performed for the electrochemical reduction of CO_2 to useful chemicals.

Electrolyte-capture solvent optimisation (TNO)

A 0.7M solution of tetraethylammonium chloride in propylene carbonate showed the best performance towards oxalic acid production in small scale. During CO₂ electrolysis on a Pb electrode in a 0.7 M TEACL in PC at a potential of -2.5 V vs Ag/AgCl, the following KPIs were obtained:

- Current density: ~10 mA/cm2
- Faradaic Efficiency towards oxalic acid: (>90%)
- Concentration oxalic acid after 3h: ~1.5 mg/ml

The ionic liquids tested in this project are not a suitable media to function as catholyte in this electrochemical process. High decomposition rates, low activity towards CO₂ reduction, and low oxalic acid selectivity lower their application as feasible solvents for oxalic acid production.

Choline chloride based deep eutectic solvents show higher activity towards CO₂ reduction than the ionic liquid tested, but low selectivity towards oxalic acid formation, and therefore are also discouraged as catholytes for this electrochemical process

Presence of water negatively affects the formation of oxalic acid and promotes formic acid production.

Further research is needed to understand the challenges of scaling-up this technology in order to reach the same KPIs that were obtained in smaller scale.

Product recovery (TUD)

The recovery of oxalic acid from non-aqueous solutions like propylene carbonate is challenging. The state of the acid (dissociated or undissociated), which depends on the pH and the requirement of waterfree solvent in the electrolyser significantly complicates the downstream processing. We have considered liquid-liquid extraction, electrodialysis, cooling crystallization, and gas antisolvent precipitation (GAP) for oxalic acid separation. We show that only GAP with CO2 as antisolvent can be used for oxalic acid separation from propylene carbonate. Liquid-liquid extraction with water cannot be used because this contaminates the solvent with water, which is not desired as this trigger by-product formation in the reactor. Electrodialysis cannot be used because in our experiments the acid was present in an undissociated state. Cooling crystallization cannot be used for oxalic separation from propylene carbonate because no crystallization behaviour is observed when the solution is cooled from 333 K to 263 K. Our preliminary GAP experiments showed that oxalic acid can be precipitated from saturated and 0.5M solutions using 30 bar CO2 pressure.

Process design of integrated process (TT/DMT)

A feasibility study has been performed in order to scale-up the electrochemical conversion of CO2 to oxalic acid. A number of options for the downstream processing of oxalic acid are evaluated based on a comparison of a two-compartment and a three-compartment cell configuration. Generally, the costs for 3-compartment cell electrolyser are higher than the two-compartment cell. Furthermore, as Zn anode is consumed during the reaction the downstream section for the zinc anode process is more complex, as this requires a gas-separator, a centrifuge, a crystallizer and a second centrifuge.

The costs for the zinc anode process turned out to be higher compared to the process with the Pt anode electrolyser, as this second process only has a main downstream process consisting of a crystallizer followed by a centrifuge.

Life-cycle analysis and multi-criteria analysis (DMT/RUG)

The global warming potentials of the sodium formate and carbohydrate routes for oxalic acid production were calculated to be 1.364 kgCO2/kg(COOH)2 and 3.277 kgCO2/kg_{(COOH)2}, respectively. The global warming potential of the electrochemical process (0.467 kg_{(COOH)2};-0.511 kg_{co2}/kg_{(COOH)2}) was also calculated. The theoretical electrochemical process was calculated to have a lower global warming potential relative to the other two contemporary, commercial processes. Provided the electrochemical process is economically viable, it provides a promising opportunity to lower the global warming potential of the oxalic acid industry when applied.

Techno-economic analysis and business case (DMT, TT, TNO, TUD)

The Faraday Efficiency, current density, and product concentration were investigated for the electrochemical conversion in a non-aqueous solvent of CO_2 to oxalic acid. All these parameters influence the performance, but the Faraday Efficiency of oxalic acid and by-production formation are mostly affected by the water content of the catholyte. The liquid by-products glycolic acid, glyoxylic acid, and formic acid are formed in the presence of minor amounts of water. We show that a high Faraday Efficiency for oxalic acid can be obtained (up to 90%), but the current density is relatively low (10-20 mA/cm2) at a cathode potential of -2.5 V vs. Ag/AgCI.

A process design and techno-economic evaluation of the value chain for electrochemical conversion of CO2 to oxalic acid is presented. An integrated process is designed where CO2 is captured from biogas (1 ton/h scale) using propylene carbonate, which serves as non-aqueous solvent in the subsequent step for electrochemical conversion of CO2 to oxalic acid. It is shown that the requirement of a water-free solvent is significantly complicating the downstream separation of oxalic acid from propylene carbonate. We have investigated liquid- liquid extraction, electro-dialysis, cooling crystallization, and gas anti-solvent precipitation for the downstream separation. The latter process, gas anti-solvent precipitation, is the only separation method that seems to work for oxalic acid separation from propylene carbonate. An economic analysis of the integrated process, which includes CO_2 capture, CO_2 conversion, and the downstream separation for oxalic acid is presented.

We have shown that the process has a positive NPV (\$ 16 M) and a PBT of 4 years under the base case scenario, with: a current density of 100 mA/ cm², an oxalic acid Faraday efficiency of 80%, a cell voltage of 4 (V), an electrolyser CAPEX of $\$20000 / m^2$, electricity price of \$ 30 /MWh, and an oxalic acid price of \$ 1000 / ton).

A sensitivity analysis shows that the market price of oxalic acid has a huge impact on the economics. A market price of at least 550/ton is required to have a positive NPV and a PBT of <10 years. Compared with other CO₂ electro-reduction products, oxalic acid has extremely favourable economics due to the relatively high market price and the low number of electrons input per unit of product.

8. Dissemination & communication

The project released the following publications:

Noura Dawass, Jilles Langeveld, Mahinder Ramdin, Elena Pérez-Gallent, Angel A. Villanueva, Erwin J. M. Giling, Jort Langerak, Leo J. P. van den Broeke, Thijs J. H. Vlugt, and Othonas A. Moultos, 2022, *Solubilities and Transport Properties of CO2, Oxalic Acid, and Formic Acid in Mixed Solvents Composed of Deep Eutectic Solvents, Methanol, and Propylene Carbonate*, Published as part of The Journal of Physical Chemistry virtual special issue "Doros N. Theodorou Festschrift".

Boor, V., Frijns, J. E. B. M., Laitinen, A. T., Goetheer, E. L. V., Van Den Broeke, L. J. P., Kortlever, R., De Jong, W., Moultos, O. A., Vlugt, T. J. H., Ramdin, M., & More Authors (2022). *Electrochemical Reduction of CO2 to Oxalic Acid: Experiments, Process Modeling, and Economics.* Industrial and Engineering Chemistry Research, 61(40), 14837-14846. https://doi.org/10.1021/acs.iecr.2c02647

Zutphen, T. van, 2021, *Investigation into the use of an Electro-Reactor for Carbon Dioxide to Oxalic Acid conversion*. Master's Internship Report, Chemical Engineering. Item availability may be restricted. URL: <u>http://fse.studenttheses.ub.rug.nl/26205/</u>

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