Feasibility analysis of a CO_2 recycling plant for the decarbonization of formate and dihydroxyacetone production

M. Rumayor*, A. Dominguez-Ramos, A. Irabien

University of Cantabria, Department of Chemical and Biomolecular Engineering, Av. Los Castros s/n, Santander, Spain

*** Corresponding author:** Marta Rumayor

University of Cantabria, Department of Chemical and Biomolecular Engineering

Av. Los Castros s/n, 39005 Santander, Spain;

E-mail: marta.rumayor@unican.es;

Telephone: (+34) 942 20 67 49

KEYWORDS: decarbonization; carbon footprint; carbon recycling plant; carbon dioxide utilization; environmental assessment; techno-economic assessment

Abstract

Renewable-driven CO_2 recycling plants (CO2RPs) to produce chemicals have a certain role to play in the decarbonization of the economy. In recent years, significant progress has been found for the decarbonization of chemicals such as formate/formic acid ($HCOO^-$/HCOOH) by CO_2 electrochemical reduction (CO_2ER). The traditional approach consists of the cathodic CO_2ER coupled to the anodic oxygen evolution reaction (EOR). Current trends appoint alternative anodic processes, as glycerol (GLY) electro-oxidation (EOG), as a powerful alternative to EOR because it can lower noticeably the cell voltage. Also, this recent alternative leads to the formation of products in the anode with more economic value than O_2, for example, the fine chemical dihydroxyacetone (DHA). Until now other factors than just the energy savings in the ER cell have been neglected. Other factors such as the anodic market sizes, the downstream separation energy demand, etc., have to be contemplated in the whole decarbonization picture. In the present study, we analyze the environmental and economic benefits of the integrated production of $HCOO^-$ and DHA by a renewable-driven CO2RP when the traditional EOR is substituted by the EOG alternative. Life-cycle thinking was used to support decision-making. $HCOO^-$ and DHA fossil routes as well as the traditional decarbonization EOR-scheme (that decarbonized the amount of $HCOO^-$) were used for benchmarking. The integrated production in the proposed CO2RP is highly limited by the small market size of DHA compared to $HCOO^-$ and also, by the high energy requirements in the DHA purification step. Anodic DHA concentration over 1.5%wt. is compulsory in short-mid-term developments to achieve a positive decarbonization scenario when the integrated production of DHA and $HCOO^-$ is compared with the traditional route. A noticeable DHA market price reduction would be possible under proper anode developments. In addition, we evaluate the influence of renewable electricity market forecast in the economic figures of the DHA and $HCOO^-$ produced by the co-electrolysis technology.

Introduction

The world's heavy reliance on the limited fossil fuels has caused an excess of anthropogenic CO_2 in the atmosphere overtaking nature's CO_2 recycling capability. This disturbance has resulted in the so-called greenhouse effect[1] and global warming. In the latest decades, policy targets and scientific/technological efforts are focused on reducing CO_2 emissions. In fact, the decarbonization of the economy is at the heart of European Green Deal.[2] In this sense, chemical synthesis using the recycled greenhouse gas (GHG) CO_2, as a feedstock, could open up a complementary strategy for decarbonizing the chemical industry while contributing to close the anthropogenic carbon cycle. CO_2 recycling faces another long-term concern, it can reduce our dependency on the still relatively available fossil resources. With a feasible implementation of carbon recycling plants (CO2RPs), especially if they are integrated into hard-to-abate sectors[3], CO_2 emissions would become an economically attractive resource to produce add-value fossil-free chemicals. The climate benefits of these CO_2-conversion chemicals rely on a substitution effect, which is the reduction in resource consumption and CO_2 emissions elsewhere in the economy when conventional products are finally replaced by them. Of course, the energy needed for the CO_2 conversion to chemicals has to be low-carbon to provide an environmental benefit over the fossil production route. Another advantage is related to the use of intermittent renewable sources (RWs) (i.e. PV solar and wind) that are currently limited by storage possibilities. CO_2RPs could be a powerful strategy to convert this intermittent power to storable carbon-neutral chemicals. Much progress has been achieved in recent years and some projects have already entered the market as the company CRI in Iceland that produces 4000 $t \cdot yr^{-1}$ of methanol via CO_2 hydrogenation using surpluses of geothermal energy.[4]

Several chemicals could be derived from CO_2 and the technologies to convert CO_2 into them are countless and found at different stages of maturity and performance.[5] Among many CO_2 conversion products, we highlight formate or formic acid ($HCOO^-$/HCOOH) as it may be employed as both feedstock chemical and fuel. The conventional production process of $HCOO^-$ involve the heating of fossil raw materials carbon monoxide (CO) and sodium hydroxide (NaOH) under pressure (or methanol (CH_3OH) that replaces NaOH in the HCOOH production route). A clear advantage of $HCOO^-$/ HCOOH is that it is a liquid product so it can be easily stored and distributed according to existing infrastructures. Regarding the global market of this chemical, it has evidenced a linear growth in the past few years, which is estimated to increase in the coming years from 620 kton in 2012 to 1 Mton in 2030 (around 350 kton in EU).[6] This fact is mostly motivated by its potential as a storage medium for hydrogen.[7] Among the CO_2 conversion technologies, electrochemical reduction (CO_2 ER) is currently the most mature technology to produce $HCOO^-$/HCOOH from CO_2 and it is expected a timeframe of only 10 years until deployment.[5] Det Norske Veritas (DNV) [8] and Mantra Venture Group[9] have reported results from a 350 kg HCOOH·yr^{-1} and 35 ton HCOOH·yr^{-1} pilot plants, respectively. These plants are based on the ER CO_2 in conjunction with anodic water oxidation (i.e. with oxygen (O_2) obtained as by-product).

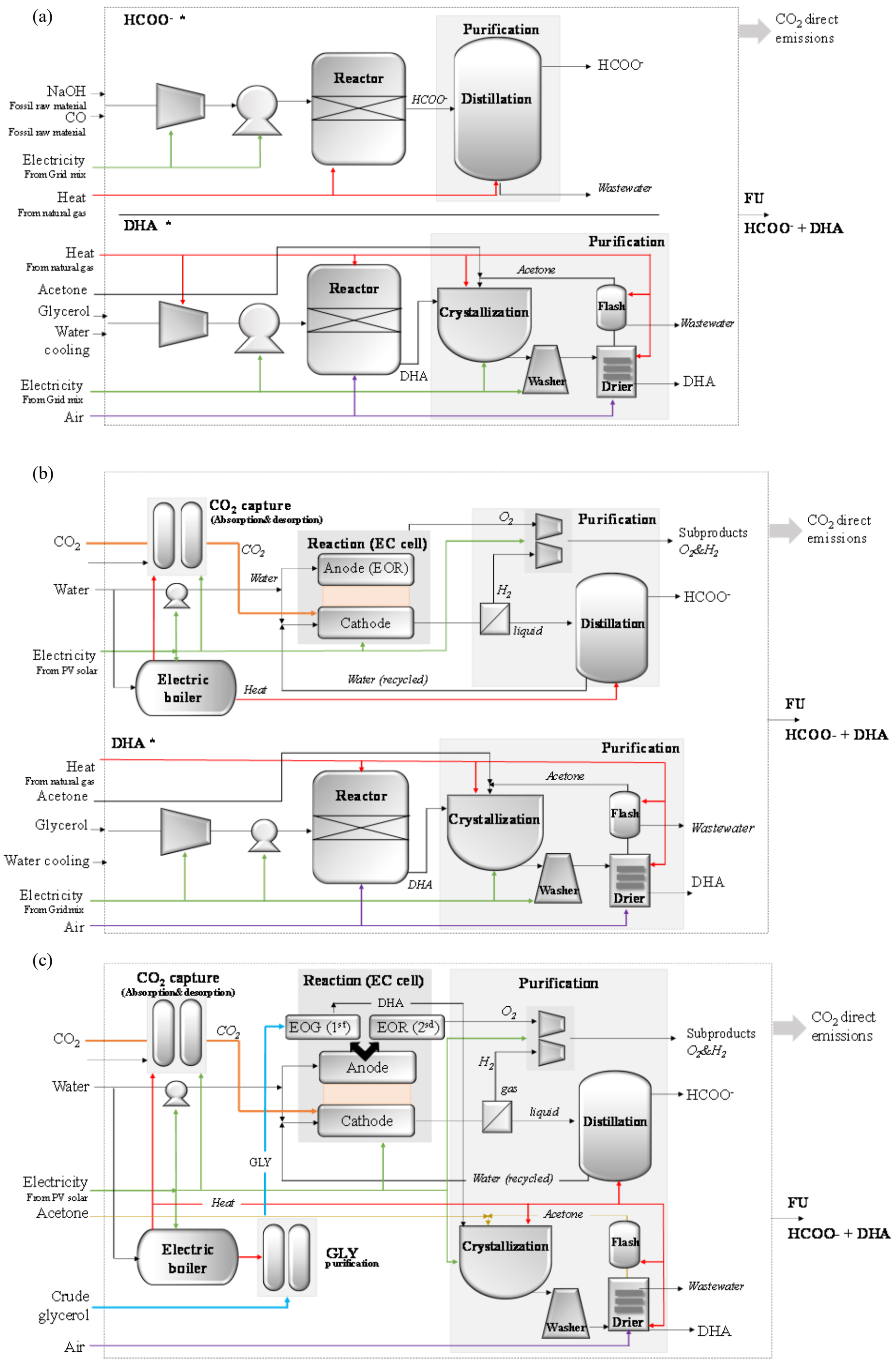
In the latest decades, the CO_2 ER studies have been focused on developing new catalysts, electrolytes and electrochemical reactors.[10] The common configuration scheme found in literature is based on the co-electrolysis of CO_2 (in the cathode) and water (in the anode) by the oxygen evolution reaction (OER). A recent study carried out within the research group of the authors has shown important progress regarding the cathode performance at lab scale[11] reaching energy consumption values as low as 3.92 kWh·kg^{-1} of $HCOO^-$ and $HCOO^-$ concentrations close to 30% wt. Those values are following the last figures of merits found in a recent study carried out by the authors in which low carbon-$HCOO^-$/HCOOH could be achieved by ER of CO_2 (using EOR in the anode).[12] However, OER consumes up to 90% of the electricity input in the electrochemical (EC) cell[13] and recent techno-economic studies suggest the anodic electro-oxidation of glycerol (EOG) as a powerful alternative to the anodic OER resulting in a reduction of the overall electricity consumption by 53%.[13,14] EOG reaction is also an opportunity to produce commercially valuable chemicals in the anode (instead O_2) from widely available wastes, such as glycerol (GLY), making a sound contribution to the circular economy. Several EOG products are possible such as glyceraldehyde (GLAD), dihydroxyacetone (DHA), and glyceric acid (GA). Unlike the sacrificial EOR-based anodes, which produce O_2 and can be valorized or emitted to the air with no-impact, these alternative production-anodes generate mostly liquid products (e.g. DHA, GLAD, GA). Among them, DHA is one of the most economically interesting anodic products due to its high market price (ca. 2 €·kg^{-1})[15]. Despite the high economic value, such liquid products must be purified otherwise, they should be considered as liquid wastes and the benefit from the EOG energy savings will be completely shadowed by the impact of the anode-waste management. As a rule, several factors than just EC cell enegy savings must be considered when assessing this novel approach, such as i) the economic value of the anode product; ii) its market size; iii) the cell voltage; and iv) the complexity of the anode-product separation.[15]

In the present study, we analyze the whole decarbonization picture to determine the environmental and economic feasibility of a CO2RP that is based on the co-electrochemical conversion of CO_2 and GLY into $HCOO^-$ and DHA. The results are compared with the conventional routes and the production by the traditional/first decarbonization approach, which considers the traditional anodic water oxidation. The study addresses: i) the possibilities of carbon footprint (CF) reduction with the proposed joint production in a CO2RP that uses alternative anodic EOG respect the conventional $HCOO^-$ and DHA and the well-knowledge traditional decarbonization approach (using anodic-OER); ii) the economic key performance indicators including the capital expenditure (CAPEX) and operational expenditure (OPEX), the net present value (NPV) and the Total Cost of Production (TCP) of the proposed CO2RP; iii) the possibilities for a near-term DHA market price reduction; and iv) the influence of the renewable electricity market forecast and other variables (cost of EC cell, CO_2 price, etc.) in the overall economic figures. This study may guide the future developments of the innovative processes in CO2RPs in the context of the chemical industry decarbonization.

Methodology

In this paper, we do investigate the environmental benefits (in terms of carbon footprint (CF)) and the impact on economic figures of the recently proposed decarbonization scheme, which is based on renewable-driven electrochemical conversion of CO_2 and GLY (considering anodic-EOG instead of the traditional anodic-EOR) into $HCOO^-$ and DHA. This scheme will permit an integrated decarbonization of $HCOO^-$ and DHA within the same plant. Therefore, authors use for benchmarking the CF for the same amount of these chemical when they are produced by their conventional fossil-based routes as well as the first/traditional approach that decarbonizes the amount of $HCOO^-$ using ER of CO_2 coupled to anodic-EOR. The comparison between these three scenarios (Figure 1) will provide a whole picture of the decarbonization possibilities arising from the recently proposed decarbonization scheme (Figure 1(c)) respect the benchmark, which is conventional routes (Figure 1(a)) and of course, the traditional/first decarbonization approach that was previously assessed (Figure 1(b)).[3,16–18] According to our final objective, which is to produce HCOO- and DHA in the same integrated plant (CO2RP), the chosen functional unit (FU) is a mass combination of $HCOO^-$ and DHA. As was mentioned before, the first restriction is the market capacities of both chemical that will determine the plant capacity and the FU. Both parameters must be established taken into account that $HCOO^-$ and DHA have different markets sizes. It must be taken into account that 1 $Mton\cdot yr^{-1}$ is the global $HCOO^-/HCOOH$ capacity (around 350 $kton\cdot yr^{-1}$ in EU) whereas DHA capacity is limited to only 10 $kton\cdot yr^{-1}$ (in EU) [19]. According to this market limitation, it is not possible to follow just the EOG stoichiometry (shown in the Supporting Information) as it would make no sense to assume a discarding of the excess of DHA. If we considere to dischargue the DHA excess, any benefit from EC energy savings will be shadowed by the impact of waste treatment. Annual capacities of conventional formic acid plants could range between 20kton to more than 50 kton. The production capacity for $HCOO^-$ was fixed in this study at 12 $kton\cdot yr^{-1}$ according to similar CO_2 utilization studies[3,20] and taking into account a local production. DHA capacity in the CO2RP was restricted to 60% of the total EU capacity. A value of 5.7 $kton\cdot yr^{-1}$ was assumed for the DHA capacity in the proposed CO2RP (according to its small market size). Hence, in the proposed CO2RP a switch between EOG and EOR anodes must be done to fulfil the DHA market restriction. Once the DHA capacity (5.7 $kton\cdot yr^{-1}$) is completed, an anode based on EOR (e.g. a commercial dimensionally O_2 stable anode (O_2-DSA)) continues producing O_2 until the plant accomplishes the $HCOO^-$ capacity (12 $kton\cdot yr^{-1}$). An anode switching is possible thanks to the EC modular design.[21] Then, the EOG anode is disengaged (when 5.7 $kton\cdot yr^{-1}$ are produced) and the EOR anode is assembled. Furthermore, the proper electrolyte is pumped. It should be mentioned, that the electrolyte is commonly circulated via an external parallel-feed-manifold arrangement and therefore it can be switched simultaneously with the anode. Accordingly, the chosen FU is a joint amount of 1.00 kg of $HCOO^-$ and 0.47 kg of DHA. Note that the corresponding amount of water of 0.177 kg is considered in the mass balance to reach a $HCOO^-$ concentration of 84% wt., which is the current standard purity.

A mathematical model built in previous studies[18,22] has been expanded to include the decarbonization approach (labelled as S3). The conventional production of HCOO- and DHA (labelled as S1) and the first/traditional HCOO- decarbonization approach by ER of CO_2 coupled to the anodic-EOR (labelled as S2) (updated with the latest performance parameters) are used for benchmarking. Authors analyze the environmental benefit, in terms of CF and then, the influence on economics by comparing the obtained results in the proposed S3 with those coming from the previous well-known scenarios (S1 and S2).



* Conventional HCOO$^-$ route (S1) and DHA chemocatalytic route (S1 and S2) were modelled according to the benchmarking datasets.[23,24] Note that heat and electricity in those datasets comes from steam and grid mix, respectively. Conventional routes powered by renewables will be also assessed by sensitivity analyses.

Figure 1. System boundary of the proposed decarbonization scenarios: a) traditional production (S1); b) first decarbonization approach (S2); and c) new decarbonization approach by the CO2RP to produce both HCOO$^-$ and DHA (S3)

Description of scenarios

Conventional production and first/traditional decarbonization approach (benchmark)

The conventional scenario called S1 integrates the conventional productions of 1.00 kg of sodium formate salt (HCOONa) and 0.47 kg of 1,3-dihydroxyacetone (DHA). Furthermore, authors included the first decarbonization approach labelled as S2. These scenarios will serve in this study as benchmarking to analyze the proposed $HCOO^-$ and DHA joint-production by the renewable driven-CO2RP (S3).

The corresponding amount of $HCOO^-$ (1.00 kg) produced in S1 is modelled using the Ecoinvent dataset for HCOONa [23] while the DHA amount (0.47 kg) has been modelled by the chemocatalytic zeolite-based production route[24,25]. Note that from the environmental perspective HCOONa and HCOOH have almost the same impact on environments.[26] Both chemicals can be produced during the CO_2ER in the cathode (depending on the chemicals involved in the process and the pH) but most ER studies found in the literature report neutral to alkaline conditions. Under these conditions, a formate-based salt is the chemical specie that should be preferentially obtained.[27] Hence, the authors decided to choose the conventional production of HCOONa in the benchmark scenario. On the other hand, the chemocatalytic zeolite-based production is assumed as DHA conventional production route according to the last DHA production trends, which appointed this route as a possible replacement of the currently practised low-productive technology based on the biocatalytic process using the enzyme *Gluconobacter oxydans*[19]. Note that authors are performing a prospective or ex-ante feasibility assessment so the time at which the comparison is made must be aligned to the same development stage for all modelled technologies.[28] Despite, HCOONa conventional route is mature with a high productivity, the currently biocatalytic system practised for DHA production has very low productivity and a high carbon footprint impact (around 5 kg CO_2 eq·kg^{-1}).[24] For this reason, the chemocatalytic zeolite-based process was assumed in the conventional benchmark to achieve a fair prospective comparison. Both biocatalytic and chemocatalytic DHA production inventories are detailed in the Supporting Information.

The first decarbonization approach (S2) includes the common EC configuration in which CO_2 is captured from a hard-to-abate source and reduced in the cathode to produce low carbon-$HCOO^-$ while water is oxidized in the sacrificial EOR-anode to produce O_2 that can be emitted to the air with a negligible impact. The amount of DHA (0.47 kg) in S2 comes from its conventional route as until now, there is no CO_2-based route to produce DHA. The first decarbonization approach (for 1 kg of $HCOO^-$) has been previously modelled and assessed by the authors.[16,17] However, as a novelty, in this study authors have used the latest ER performance parameters[11] for modelling and DHA production has been integrated in the model.

Decarbonization alternative using a CO_2 recycling plant (CO2RP)

In the proposed scenario, called S3, a CO2RP employs the co-electrolysis technology achieving a joint production of $HCOO^-$ and DHA. The scenario S3 allows us for evaluating the influence of the recent anode alternative (anodic-EOG) for the integrated decarbonization of these chemicals. On one hand, the feasibility of EOG (using glycerol, an abundant by-product of the biodiesel production) coupled to the oxygen reduction reaction has been effectively proved. [29–31] On the other hand, Verma et al., [13] has recently proposed to couple the anodic EOG to the cathodic ER of CO_2 in order to reduce the cell voltage. According to that, the benefit of S3 respect the S2 is not only the reduction of the EC energy consumption but also, the possibility to decarbonize the amount of DHA (together with $HCOO^-$) and to reduce the fossil resource consumption recycling CO2 and GLY a by-product from biodiesel production as raw materials, which makes a sound contribution to the circular economy. Authors aim to assess the conditions in which this alternative decarbonization approach could be considered feasible from the environmental and economic perspectives.

The system boundary of S3 includes: (i) the capture technology that is based on absorption using MEA[32] (a well-established end-of-pipe technology; the capture inventory can be found in the Supporting Information); (ii) the electrochemical process (EC cell); (ii) purification of formate-based products by distillation; (iii) the compression of gas by-products and pumping for liquids; and (iv) an electric heat unit to supply thermal energy from renewable electricity to the capture, purification and compression steps. In addition, we include: (v) a crude GLY purification step; and (vi) DHA purification (by crystallization technology). A detailed process simulation including the corresponding mass flows, compositions, P&T in the involved streams is out of the scope of the present study.

The CO_2 captured and water are injected into the cathode compartment. As the solubility of CO_2 is assumed to be high enough, the soluble CO_2 reaches the cathode surface. The reaction is assumed in neutral to alkaline conditions.[27] CO_2 is reduced to $HCOO^-$ and H_2O to hydroxide ions (OH^-), in the presence of the correspondent electrolyte in the cathodic compartment of the EC cell. Simultaneously, when EOG is working the reaction taking place in the anode considers the formation of the mentioned amount of DHA ($C_3H_6O_3$) (limited by its market size) and then, a sacrificial-EOR anode (the same as that used in S2) continues producing O_2. Note that an ideal EC reactor, a perfect electrode would lead to a value of 100% for the faradaic current efficiency (FE) in both compartments. This would correspond with the formation of pure $HCOO^-$ in the cathode and pure O_2/DHA in the anode. However, a fraction of the applied current density is deviated to other parallels/parasitic reactions[27], reducing the FE to $HCOO^-$ production. In this study, H_2 evolution reaction (HER) is assumed as the unique parallel reaction in the cathode. The O_2 evolution reaction (in OER anode) and the DHA production (in EOG anode) are the only reactions taking place in the anodic compartment in each case. Within the electrochemical process, the cathode performance is entirely modelled by the latest lab-scale parameters obtained within the research group of the authors, which are the same in S2.[11] In S3 an EOG anode (Pt-Bi/C) produces the limited amount of DHA and then, it is switched by a sacrificial EOR-anode (a commercial DSA-O_2 that produces O_2) while the cathode performance scenario is kept (Bi-GDEs). The DHA production rate by the EOG anode was linearly estimated from the values found in the literature[31] and considering compatible current densities between cathode and anode (j, 45 $mA \cdot cm^{-2}$). A detailed cathode and anodes (both EOR and EOG) performances description is shown in the Supplementary Information.

Table 1. Performance of the CO2RP and the traditional decarbonization approach (more information is available in Supplementary material)

Parameter	Traditional approach	Alternative approach	
	S2	S3	
		1st stage	2^{o} stage
Cathode	Bi-GDEs	Bi-GDEs	Bi-GDEs
Anode	DSA-O$_2$	Pt-Bi/C	DSA-O$_2$
Production HCOO$^-$ (kton·yr^{-1})	12.0	3.0	9.0
Production DHA	*	5.7	-

* The DHA amount (5.7 kton·yr^{-1}) is produced by the chemocatalytic process in the traditional decarbonization approach

The energy consumption is considered as PV solar electricity for the EC step, compression of gas by-products and purification DHA and GLY. The thermal energy to the CO$_2$ capture and desorption, the unit for the distillation of HCOO$^-$ and DHA purification (crystallization) were supplied by renewable heat instead of using fossil heat (i.e. steam from natural gas). Authors considered an electric boiler to produce electric-steam with a 99% heat/electricity efficiency driven by PV solar electricity[33] as electric boilers have demonstrated to be suitable for larger installations using higher voltages and power capacities at lower installation expenses.[34] Mass and energy balances, including the pumping of liquids, compression of gas subproducts, the distillation of HCOO$^-$, crystallization of DHA and purification of the required amount of GLY are described in the Supplementary Information.

Carbon footprint assessment

In this study, CFs of the FU in the benchmarks S1 and S2 and the CF of the proposed decarbonization alternative in S3 were determined through the admittedly ex-ante LCA tool, which is the best tool to assess the projected future of emerging technologies before their large-scale implementation.[35] The procedure evaluates the technology using scenarios that detail a future in which the technology system can operate at a full operational scale. This does allow for estimating and simulating the technology in the target scenarios, in particular those with maximum energy efficiency and better production rates for both $HCOO^-$ and DHA conversion products. The scenarios have been evaluated using a cradle-to-gate approach. The LCA assessment was performed using GaBi Professional software by Sphera[36]. The mid-point method CML 2001 was used to calculate the CFs. The method restricts quantitative modelling to early stages in the cause-effect chain to limit uncertainties.[37] This method allows the assessment of impact grouped in midpoint categories according to common environmental mechanisms (e.g. global warming, abiotic depletion, etc.) or commonly accepted groupings (e.g. ecotoxicity). It must be highlighted that global warming impact (evaluated in terms of CF) was the only impact category shown in this study because the viability of the suggested technology should be fulfilled at least for the impact category indicator that is intended to benefit from this decarbonization process. Of course, a complete LCA study (including other environmental impact categories) must be considered as future work when this technology reaches a higher TRL. Furthermore, in this study, we have considered transport as a negligible impact in comparison with the parameters that are inherent to the decarbonization technology (e.g. electricity consumption, CO_2 capture, GLY purification, etc.). Regarding GLY, we have only considered the impact that comes from the concentration upgrading (the inventory and purification details of crude GLY can be found in the Supporting Information). But GLY is assumed as burden-free. In any case, this assumption is pessimistic as it could have even negative CF value (-0.27 kg CO2·kg FU^{-1}) because biomass absorbs CO_2 in the cultivation stage.[38] Certainly, other influences such as transport, geographical location, renewables sources, specific origin of CO_2 or GLY etc. must be also considered and studied for each particular solution before the implementation of the emerging technology in CO2RPs. In the scenarios S2 and S3 a system expansion was carried out following the ISO 14040-series[39,40] to quantify the effect of minor sub-products on emissions of the CO2RP when necessary (i.e. H_2 and O_2 that are produced in the cathode and anode, respectively). H_2 and O_2 could be valorized and included as avoiding emissions or emitted to the atmosphere with a neglected environmental impact. Their CFs, calculated using their Ecoinvent datasets, are 1.75 kg·kg^{-1} and 0.702 kg·kg^{-1} of H_2 and O_2 respectively (expressed as the amount of CO_2 eq per unit of mass of H_2/O_2 produced. The following additional hypothesis were assumed in this study:

i. The CO_2 valorization plant is close to the CO_2 and GLY sources and then no transport is considered. CO2RP are intended to be implemented in industrial clusters. .

ii. The feed of CO_2 to the plant is assumed to be pure and with a suitable pressure for the ER process.

iv. The crude GLY as waste coming from biodiesel production is assumed to be free of environmental burdens.

iv. The vapour steam (from the electric boiler) needed for the purification units is at dry saturated conditions.

v. Electrolytes used in the process can be perfectly separated and recirculated and therefore their impacts are neglected.

Economic assessment

An economic analysis has been conducted to estimate the Total Cost of Production (TCP) required to synthesize $HCOO^-$ and DHA in S2 and S3 that can be compared with the reference conventional market prices 0.65 €·kg^{-1} ($HCOO^-$) and 2 €·kg^{-1} (DHA). The economic impact in S3 caused by the DHA co-electrolysis (including its purification cost) was also evaluated.

The capital (CAPEX) and operational expenditures (OPEX) of each scenario were estimated together with the calculation of the key performance indicator (KPI) of net present value (NPV). OPEX consists of Fixed and Variable Operating Costs (FCP and VCP, respectively). VCP includes the costs of: i) raw materials consumed by the processes, ii) utilities, and iii) consumables. FCP involves: i) operating labour, ii) supervision, iii) direct salary overhead, iii) maintenance, iv) property taxes and insurance, and v) interest.

The currency exchange rate used in the study is €$_{2020}$, which was based on Eurostat data.[41] The preferred geographical location of the analysis is the EU-27. The lifetime of the plant is assumed to be 20 yr. The reader must note that at the current low TRL values of the co-electrolysis technology, it is not suitable to envisage larger plant lifetimes. Most of these prices and costs were assumed constant for the analyzed period. However, a sensitivity analysis was performed in order to investigate the sensitivity of the NPV to the expected variation of some affecting parameters. We chose the economic parameters that are likely to change in the short/mid-term such as energy price, CO_2 price and of course, the market price of DHA. The plant features, cost of equipment and market price of utilities that were considered in the assessment are shown in the Supplementary Information. The assessment of the market penetration of the emerging technology (scenario S3) is out of the scope of the present study. It must be taken into account that this technology is its infancy (proof of concept and lab-scale) and there is a restriction marked by the lack of data.

Results and discussion

Carbon footprint assessment

The operating inventories obtained from the mathematical model for the production of the FU (1.00 kg of $HCOO^-$ + 0.47 kg of DHA) are shown in the Supplementary Information. Briefly, raw materials for the first/traditional decarbonization approach (scenario S2) are 0.957 kg of CO_2 and 1.025 kg of H_2O while 0.631 kg of GLY is required in the proposed S3. The inventory includes the values for the main utilities (heat and electricity) as well as the raw materials used in the processes. Other utilities displayed include the needs in both DHA and GLY purification processes such as air compressed, acetone, process water, etc. It must be highlighted the noticeable energy consumption by the DHA purification process. In particular, in S3 a value of heat consumption of 104 $MJ\cdot kg^{-1}$ (per mass of FU) is required in this stage while 17.02 $MJ\cdot kg^{-1}$

(per mass of FU) is required for the purification of the amount of $HCOO^-$. It was expected due to the current low concentration of DHA in the anode outlet stream (0.4% wt.).

Figure 2 displays the CFs results of the production of the FU (1.00 kg of $HCOO^-$ + 0.47 kg of DHA) by the conventional S1, the traditional decarbonization scenario, S2, as well as the proposed joint decarbonization alternative in S3. By this comparison, authors aim to demonstrate the decarbonization possibilities of S3 respect the conventional (S1) and its competitiveness and hot spots when comparing with the traditional decarbonization approach, S2. The CF of the conventional production is around 2.8 kg $CO_2 \cdot$kg FU^{-1}. S2 achieves a considerable CF decline. The CF value in S2 is 1.5 kg $CO_2 \cdot$kg FU^{-1} considering no commercialization of by-products H_2 and O_2 neither the CO_2 amount recycled (0.957 kg), which would be assumed as allocated to the main product of the CO_2 source (e.g. a hard-to-abate sector). If H_2 and O_2 would be considered (i.e. commercialization) and the amount of CO_2 recycled allocated to the recycling plant, the CF value could be as low as 0.25 kg CO_2 eq per kg of FU. Note that in scenario (S2), DHA comes from its conventional production (blue bars). In any case, the CF range is lower than CF of S1 (2.8 kg $CO_2 \cdot$kg FU^{-1}). The green bars represent the joint DHA and HCOO- production by the co-electrolysis in S3. In this case, DHA is synthesized in the EC cell, avoiding its conventional route. As was expected, the CF results are higher than those obtained in S2 due to the high impact that comes from the DHA purification step. In the proposed alternative, and under the co-electrolysis assumptions, the obtained CF is 2.9 kg $CO_2 \cdot$kg FU^{-1} with no commercialization of the subproducts (H_2 and O_2) and the amount of CO_2 recycled is allocated to the main product of the source. Nonetheless, the value is quite close to CF value from S1 (2.8 kg $CO_2 \cdot$kg FU^{-1}) but higher than CF from S2. As it was expected, the CF values obtained from S2 shows the great improvement of this traditional approach comparing with our previous studies[12,22]. It should be mentioned that this kind of decarbonization approaches would be competitive only if they are based on renewables (i.e. on a low carbon electricity) while the main constraint to the conventional route (S1) is the fossil resource consumption. Notice that these fossil resources that are comsumed as raw materials in S1 are avoided in the decarbonized pathway, which is in agreement with the recent LCA guidelines for decarbonization technologies.[42] Note that the conventional HCOO$^-$+DHA routes has only 0.581 kWh·kg FU^{-1} of electricity consumption (from the Grid mix) while the HCOO$^-$ +DHA produced in the CO2RP, under our assumptions, can consume more than 4.0 kWh·kg FU^{-1}. In addition, heat consumption (as steam) represents an overall value of 3.633 MJ·kg FU^{-1} in the traditional S1. For a fair comparison, authors have also considered the same renewable background in S1. If both heat and electricity consumption were supplied by renewables (from PV solar) the overall CF of S1 would decrease to 2.53 kg CO2 eq·kg FU^{-1}.

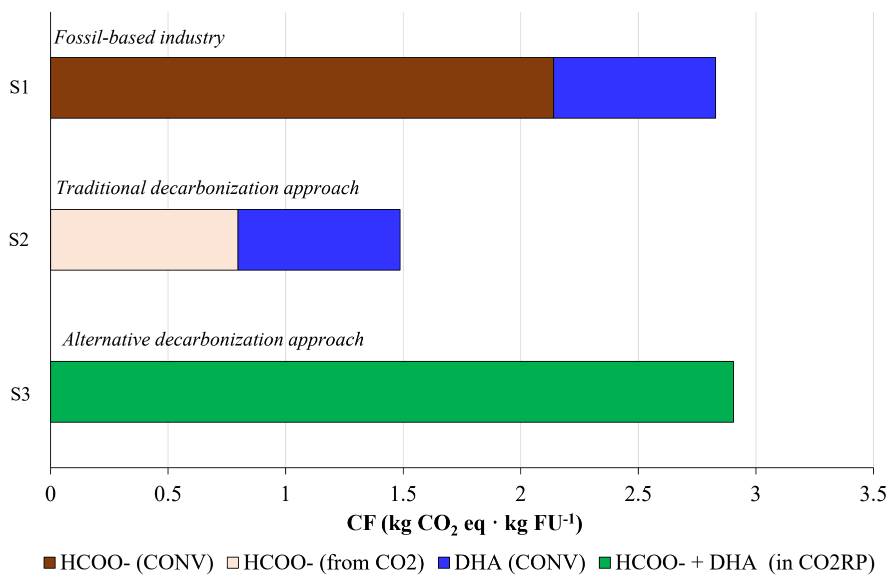


Figure 2. CF results of conventional route (S1) the traditional decarbonization scenario (S2) and the joint production in the alternative scenario (S3) (CF values are expressed as unit of mass of CO$_2$ eq per unit of FU (1.00 kg of HCOO- + 0.47 kg of DHA))

A breakdown of the CFs in both decarbonization approaches is carried out to identify the hotspots and then, to evaluate the challenges of the recent alternative decarbonization route (S3) by the comparison with the traditional approach (S2). Essentially, author aim to assess the window of opportunity of S3 in relation with the traditional approach (S2) in order to guide future developments of the electrochemical technology. According to the breakdown results (Figure 3(a)), the electricity consumption by the HCOO$^-$ purification step and the EC cell are important contributors to the CF value from S2 accordingly to our previous results.[16] Of course, now the highest impact in the traditional scenario is the DHA, which comes from its conventional route. Its contribution represents the 46% of the overall CF value. Note that in S2 approach the amount of DHA is not decarbonized being still produced by its conventional route. The results indicate that certainly, co-electrolysis technology could open an opportunity to reduce the CF of such alternative anodic-chemicals, as DHA, avoiding effectively the impact from their conventional production routes. The analysis of the breakdown results from S3 (Figure 3(b)) shows the unbalanced compromise between the EC cell energy savings (achieved by the cell potential reduction when EOG replace EOR) with the energy consumption by the purification of the anodic DHA. It can be seen that this consumption of energy by the purification step represents 74% of CF value. Actually, DHA purification is the main hot spot of the novel decarbonization approach. Further research should be focused now on the anode EOG performance to achieve higher DHA concentration (i.e. new catalyst, electrolytes…). Other contributions such as the $HCOO^-$ purification, the EC cell electricity consumption and CO_2 capture step have a similar influence on the value. Processes such as pumping or GLY purification are negligible in both scenarios.

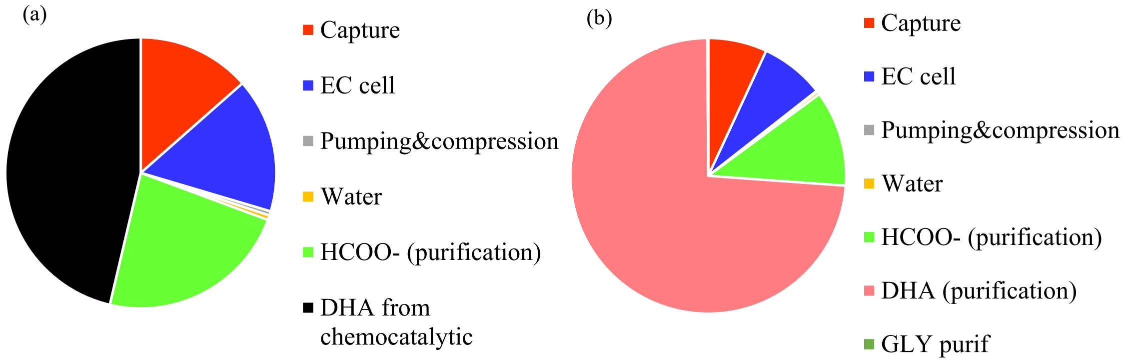


Figure 3. CF breakdown results of CF in scenarios S2 (a) and S3 (b)

In agreement with the previous results, the next step is to establish the target DHA concentration that should be achieved at the anode compartment to ensure the environmental competitiveness of S3. A sensitivity assessment of the CF versus DHA anode concentration was performed (Figure 4). Note that $HCOO^-$ concentration in the cathode compartment is fixed in this study at 30.0% wt. (in S2 and S3, according to the latest lab concentration achievements). A concentration of DHA over 1.5% wt. would be needed to achieve CF equal to S2, i.e. carbon-free $HCOO^-$ compared with the conventional route. If we consider the comerciallization of H_2 and O_2 and the amount of CO_2 recycled (0.957 kg of CO_2) was allocated to the recycling plant, a concentration of DHA over 2.4% wt. would suggest a net-zero emissions of the joint production in the CO2RP (CF=0.0 kg $CO_2 \cdot kg^{-1}$).

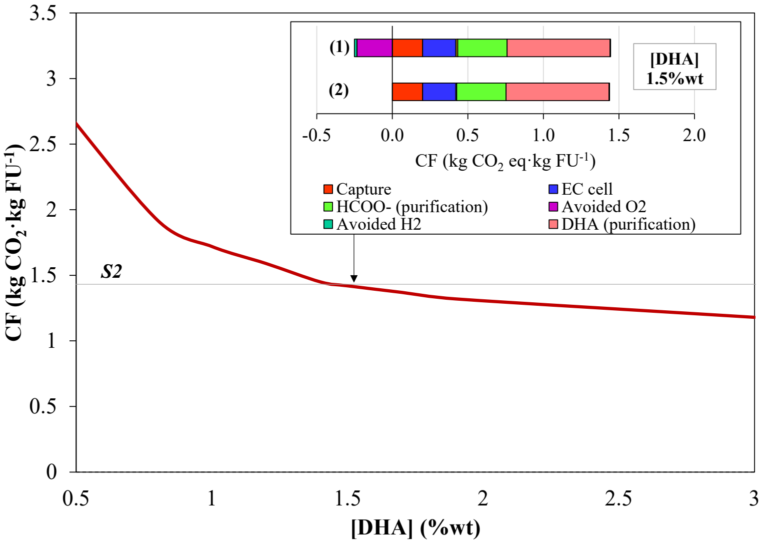


Figure 4. Sensitivity analysis of the influence of DHA concentration (in the anode) on the CF of S3 and the breakdown CF analysis in the target anode performance (DHA, 1.5%wt.)

Economic assessment

Once the feasible/target performance scenario for S3 from the environmental perspective has been found, an economic assessment must be carried out. The objective is to evaluate the chance of S3 for being deploy under a future market perspective. The target performance scenario (found in the previous section) is that in which DHA is produced in the anode compartment at concentrations around 1.5%wt. Taking this assumption, S3 could achieve the same decarbonization degree as the traditional decarbonization approach (S2). In this section, the economic viability of the investment for the installation of a CO_2 capture and utilization plant is investigated for both S2 and S3 decarbonization scenarios. The KPIs values are displayed in Table

2. It was estimated a CAPEX increment of 18% with the consideration of the EOG reaction instead of the OER in the anode, which is mainly due to the DHA purification infrastructure investment and the higher price of EOG anode that is under development comparing with the traditional DSA-O_2 (that is commercially available). Figure 5 shows the VCP distribution for both scenarios. The overall annual production cost expenditure (OPEX) for S2 and S3 are about 9.2 M€ and 17 M€, respectively. The most important contributor is represented by energy costs for $HCOO^-$ distillation (37%), consumables (37%) and the electricity consumption by EC cell (25%) in S2. On the contrary, the cost for DHA purification (42%) and consumables (28%) are the main cost contribution in S3 (Figure 5); it is worth noting that other costs are negligible such as pumping of or GLY purification costs.

Table 2. Results of economic assessment for scenarios S2 and S3

KPIs	UNIT	S2	S3
CAPEX	M€	27.0	32.0
VCP	€·kg^{-1}	0.55	1.2
FCP	M€·yr^{-1}	2.6	2.7
OPEX	M€·yr^{-1}	9.2	17
TCP $_{HCOO^-}$	€·kg^{-1}	0.90	0.67
TCP ^{DHA}	€·kg^{-1}	-	1.40
NPV	M€	-31.0 (no feasible)	-5.00 (no feasible)

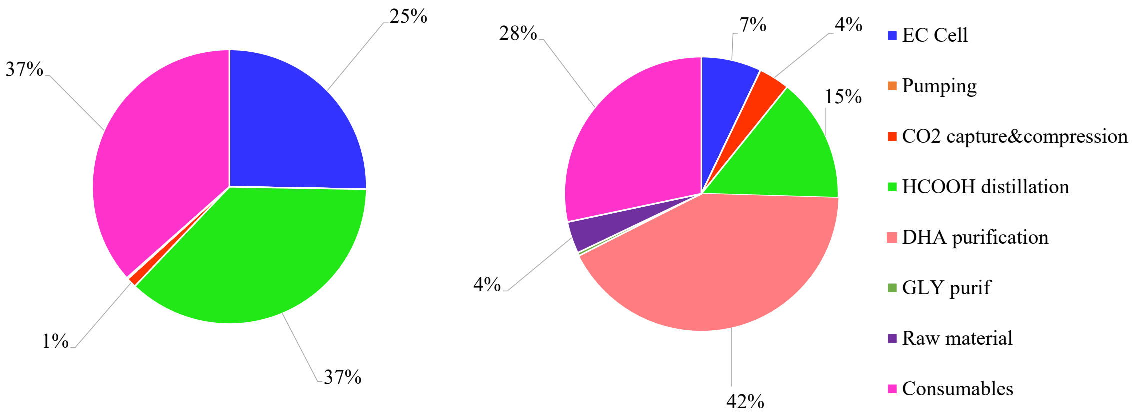


Figure 5. Annual variable cost breakdown for S2 and S3

Both scenarios can be positive from the environment perspective, however, the NPV values obtained in the economic assessment indicate that both decarbonization approaches are still unfeasible under current market conditions. In order to know the situations in which these projects could become profitable, different sensitivity analyses have been performed for both S2 and S3. The influences of $HCOO^-$ market price, CO_2 price (as benefits from a tax on emissions) and electricity market price in the NPV indicator of the traditional approach are displayed in Figure 6. At current $HCOO^-$ market prices (0.65 $€\cdot kg^{-1}$) the project will be profitable for electricity market prices under 10 $€\cdot MWh^{-1}$. Electricity market prices higher than 20 $€\cdot MWh^{-1}$ would require increasing the current price for $HCOO^-$ in the market up to 0.85-1.00 $€\cdot kg^{-1}$. The results show that CO_2 price (considered as a tax on direct emissions from the source plant) is the less-sensitive parameter to the economics. Even though the CO_2 market price is expected to vary considerably in the short/mid-term, the variation in the economic figures of the plant will be mild in comparison with the influence of the electricity or $HCOO^-$ prices. The results indicate that a price of electricity lower than 10 $€\cdot MWh^{-1}$ would be necessary under current CO_2 price (0.033 $€\cdot kg^{-1}$) while prices over 15 $€\cdot MWh^{-1}$ would allow positive NPVs considering an income from CO_2 higher than 0.1 $€\cdot kg^{-1}$. This CO_2 income price (0.100 $€\cdot kg^{-1}$) is found in the range of those CO_2 tax values predicted in EU ETS by 2050 [43]. On the hand, PV solar prices were predicted to decrease in the range from 25 €·MWh^{-1} to 45 €·MWh^{-1} by 2030, reaching a value as low as 10 €·MWh^{-1} by 2050.[44,45]

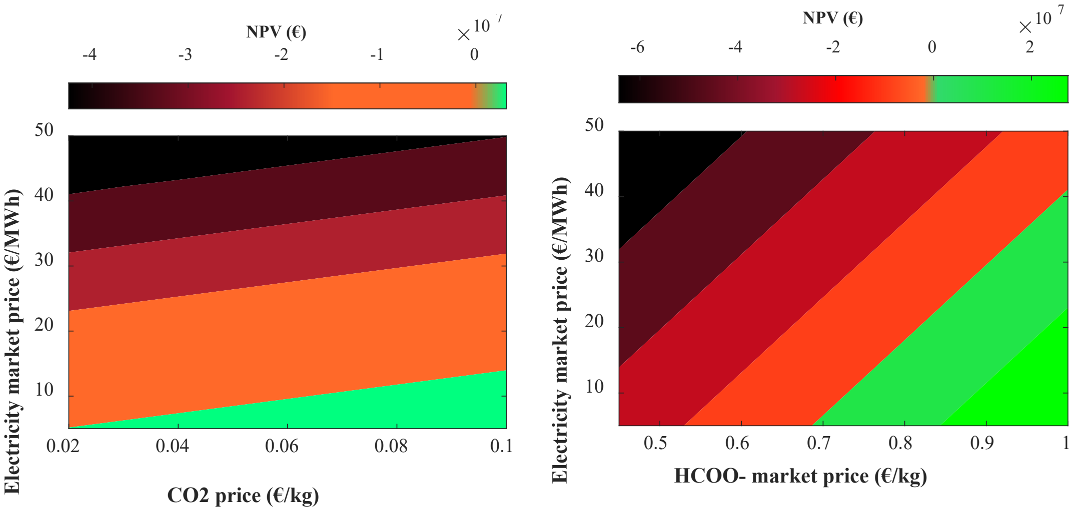


Figure 6. Sensitivity analysis of the influence in NPV of S2 of: (a) $HCOO^-$ and electricity market prices; and (b) CO_2 price and electricity market price

The obtained NPV value for S3 (-5 M€) is much closer to the feasibility (NPV>0) than the NPV from S2 (-31 M€). This fact denotes that the needed market conditions to ensure economic feasibility in the proposed decarbonization approach could be mild in comparison with the needed market conditions needed under the traditional approach (S2). The main advantage in the economic figures of S3 is the benefit that comes from the commercialization of the fine chemical DHA. However, this benefit should be balanced with the DHA purification cost, which is the main contributor to the operation cost of this novel decarbonization approach. Authors carried out a sensitivity analysis to display the influence of the most affecting parameters in the economics of S3 (Figure 7). As it can be seen in Figure 7 the window opportunity for economic feasibility is much broader than the feasibility window obtained in the previous traditional approach (seen in Figure 6). The analysis of the influence of the DHA concentration (obtained in the anode compartment of the EC cell) on the NPV indicator (Figure 7(a)) shows that DHA concentrations over 3%wt. improve noticeably the economic figures, even at the current electricity market price (40 €·MWh^{-1}). One of the parameters that affect the most to the economic figures is the DHA market price (Figure 7(b)). In this study, it was investigated the price reduction possibilities since the current DHA market price is still significantly high (2 €·kg^{-1}). Despite the small current size of the DHA market in the EU, with the ongoing development of new cheaper production alternatives, it is expected that its market spreads and hence its market price could sharply decrease.[19] The results obtained in the sensitivity assessment indicate that under electricity market prices lower than 20 €·MWh^{-1}, DHA market price could be reduced up to 1.6 €·kg^{-1} (considering that 5.7 kton·yr^{-1} of DHA are effectively sold in the market). Of course, the further expected future reduction of the electricity market price will promote DHA market price reductions. Other influences, such as the expected EC cell cost reduction (Figure 7(c)) in a short/mid-term and the rising CO_2 price (Figure 7(d)) have been analysed. The influence of these parameters are much slighter than the influence of DHA market price or even the anodic DHA concentration, nevertheless, in combination with a reduction of the electricity market price, these could also improve the overall economic figures. Strong policies are expected in the coming years to create incentives for achieving a decarbonization roadmap including direct incentives or adjustments to the financial requirements for investment or utilities incentives for companies that consider CO_2 recycling, among other decarbonization solution (e.g hydrogen, biomass, electrification, etc.). [46,47]

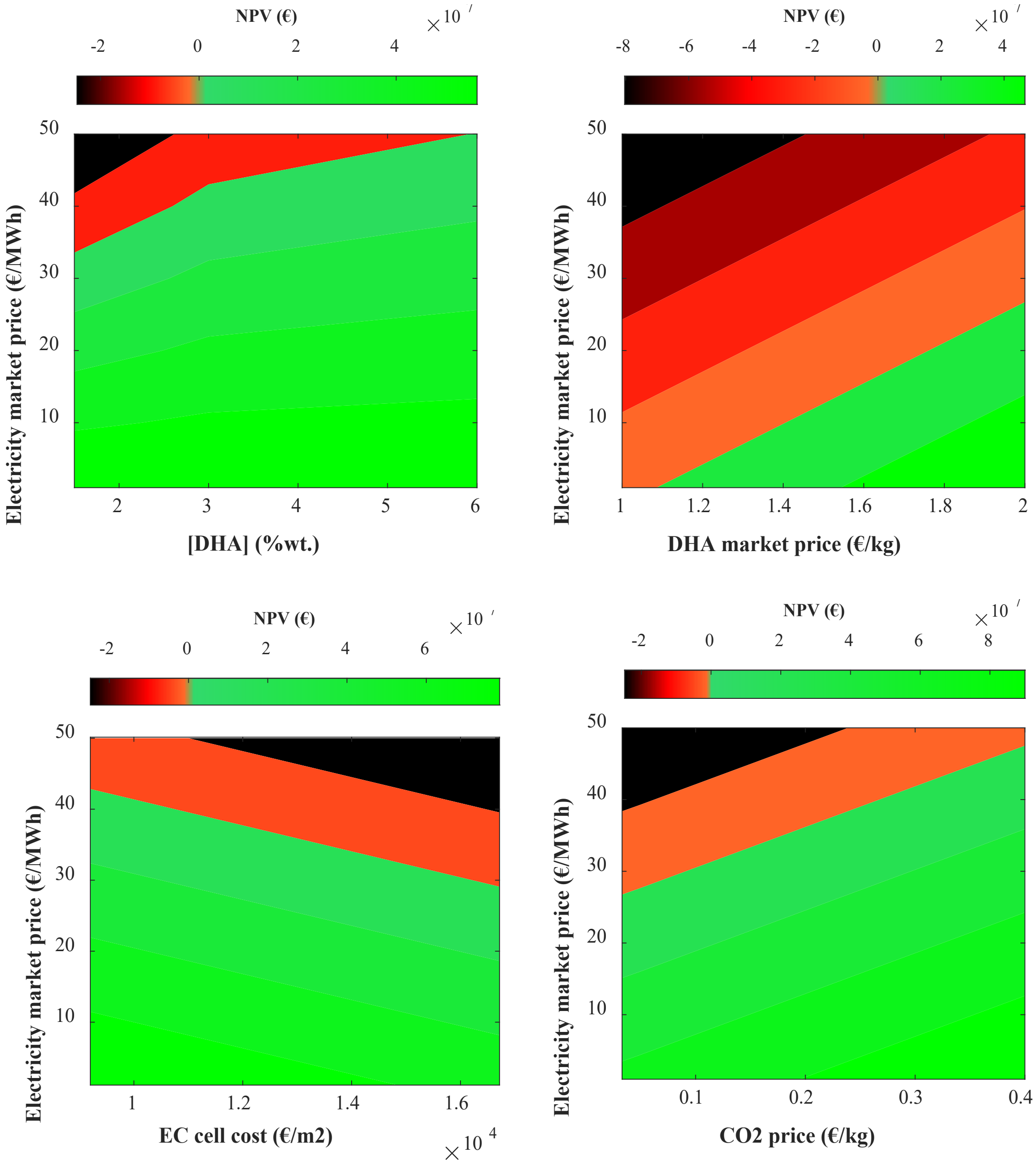


Figure 7. Sensitivity analysis of the influence in the economics of S3 of the electricity market price and the variation of: (a) DHA concentration; (b) DHA market price; (c) EC cell cost; and (d) CO_2 price

Conclusions

This paper has investigated the possibilities of a joint decarbonization of $HCOO^-$ and DHA manufacture using a carbon recycling plant (CO2RP), which is based on the renewable-driven co-electrochemical conversion of CO_2 and glycerol (GLY). This study has shown the environmental and economic benefits when alternative oxidation reactions as GLY electro-oxidation (EOG) are considered in the anodic compartment instead of the traditional decarbonization approach, which is based on the anodic oxygen evolution reaction (EOR). The environmental assessment results of the $HCOO^-$ and DHA production in the reference scenario (based on the traditional decarbonization approach that used anodic-OER) displayed CF values for the joint production in the range of 1.5-1.2 $kg \cdot kg\text{-}^1$. The integrated production in the proposed CO2RP is highly limited by the small market size of DHA compared to $HCOO^-$ and also, by the high energy requirements in the DHA purification step. The proposed joint decarbonization approach in the CO2RP could represent a 10% of energy savings in the EC cell consumption as well as a benefit from the DHA production in the anode instead of traditional low-value O_2. EC cell energy savings can be shadowed by the large amount of energy consumed by the DHA purification, which is currently synthesized at low concentrations in the anode compartment (0.4% wt.). A sensitivity analysis has appointed a target DHA concentration of 1.5%wt. to achieve a carbon-neutral synthesis comparing with the traditional decarbonization approach. The economic assessment results for the traditional EC performance indicated that the project would be feasible when the electricity market price is under 10 $€\cdot MWh^{-1}$ while the feasibility window obtained for the proposed joint HCOO- and DHA production in the CO2RP is much broader. The proposed decarbonization alternative would be economically feasible from electricity market prices values of 20 $€\cdot MWh^{-1}$ or lower. The CO_2 price (considered as a tax on direct emissions from the source plant) that is expected to vary considerably in the short/mid-term, is less sensitive to the economics. The market price of DHA could be noticeably reduced under proper developments of the co-electrolysis technology. The results obtained in this study have demonstrated the environmental and economic benefits of the novel EC scheme of considering the EOG to DHA (in the anode) with the ER of CO_2 to $HCOO^-$ (on the cathode). The study represents a step forward in the electrochemical CO_2 conversion, proposing the new figures of merits regarding the concentration of the alternative anodic product DHA as well as the possibilities for DHA market price reduction and the expected short-mid term feasibility under electricity market price reduction.

Conflicts of interest

There are no conflicts to declare.

Acknowledgment

Authors thank to Spanish Ministry of Economy and Competitiveness (MINECO) for the financial support through the project PID2019-108136RB-C31. We would like also to thank MINECO for providing Marta Rumayor with a Juan de la Cierva postdoctoral contract (IJCI-2017-32621).

References

1 S. Arrhenius, *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 1896, **41**, 237–276.

2 European Comission, *European Commission*, 2019, 24.

3 M. Rumayor, A. Dominguez-Ramos and A. Irabien, *ACS Sustainable Chemistry and Engineering*, 2020, **8**, 11956–11966.

4 Carbon Recycling International (CRI), Carbon Recycling International, http://www.carbonrecycling.is/, (accessed 11 March 2019).

5 R. Chauvy, N. Meunier, D. Thomas and G. De Weireld, *Applied Energy*, 2019, **236**, 662–680.

6 Global CO2 Initiative and CO2 Sciences Inc., *Global Roadmap for Implementing CO2 Utilization*, 2016.

7 J. Eppinger and K.-W. Huang, *ACS Energy Letters*, 2017, **2**, 188–195.

8 Det Norske Veritas (DNV), *Carbon dioxide utilisation: Electrochemical conversion of CO2: Opportunities and challenges*, 2011.

9 M. V. Group, Mantra releases update on demonstration projects, http://mantraenergy.com/mantra-releases-update-on-demonstration-projects/, (accessed 3 March 2021).

10 M. Jouny, W. W. Luc and F. Jiao, *Industrial & Engineering Chemistry Research*, 2018, acs.iecr.7b03514.

11 G. Díaz-Sainz, M. Alvarez-Guerra, B. Ávila-Bolívar, J. Solla-Gullón, V. Montiel and A. Irabien, *Chemical Engineering Journal*, 2021, **405**, 126965.

12 M. Rumayor, A. Dominguez-Ramos and A. Irabien, *Applied Sciences*, 2018, **8**, 914.

13 S. Verma, S. Lu and P. J. A. Kenis, *Nature Energy*, 2019, **4**, 466–474.

14 J. Na, B. Seo, J. Kim, C. W. Lee, H. Lee, Y. J. Hwang, B. K. Min, D. K. Lee, H. S. Oh and U. Lee, *Nature Communications*, , DOI:10.1038/s41467-019-12744-y.

15 Vass, B. Endrődi and C. Janáky, *Current Opinion in Electrochemistry*, 2021, **25**, 1–9.

16 M. Rumayor, A. Dominguez-Ramos, P. Perez and A. Irabien, *Journal of CO2 Utilization*, 2019, **34**, 490–499.

17 M. Rumayor, A. Dominguez-Ramos and A. Irabien, *Sustainable Production and Consumption*, 2019, **18**, 72–82.

18 M. Rumayor, A. Dominguez-Ramos and A. Irabien, *Applied Sciences 2018, Vol. 8, Page 914*, 2018, **8**, 914.

19 R. Ciriminna, A. Fidalgo, L. M. Ilharco and M. Pagliaro, *ChemistryOpen*, 2018, **7**, 233–236.

20 M. Pérez-Fortes, J. C. Schöneberger, A. Boulamanti, G. Harrison and E. Tzimas, *International Journal of Hydrogen Energy*, 2016, **41**, 16444–16462.

21 A. S. Agarwal, Y. Zhai, D. Hill and N. Sridhar, *ChemSusChem*, 2011, **4**, 1301–1310.

22 M. Rumayor, A. Dominguez-Ramos and A. Irabien, *Sustainable Production and*

Consumption, 2019, **18**, 72–82.

23 Swiss Centre for Life Cycle Inventories, The ecoinvent database Version 7, http://www.ecoinvent.org, (accessed 3 May 2018).

24 G. M. Lari, C. Mondelli, S. Papadokonstantakis, M. Morales, K. Hungerbühler and J. Pérez-Ramírez, *Reaction Chemistry and Engineering*, 2016, **1**, 106–118.

25 M. Morales, P. Y. Dapsens, I. Giovinazzo, J. Witte, C. Mondelli, S. Papadokonstantakis, K. Hungerbühler and J. Pérez-Ramírez, *Energy and Environmental Science*, 2015, **8**, 558–567.

26 A. Dominguez-Ramos, B. Singh, X. Zhang, E. G. Hertwich and A. Irabien, *Journal of Cleaner Production*, 2015, **104**, 148–155.

27 C. Oloman and H. Li, *ChemSusChem*, 2008, **1**, 385–391.

28 N. Thonemann, A. Schulte and D. Maga, *Sustainability (Switzerland)*, 2020, **12**, 1–23.

29 M. Simões, S. Baranton and C. Coutanceau, *ChemSusChem*, 2012, **5**, 2106–2124.

30 A. Talebian-Kiakalaieh, N. A. S. Amin, K. Rajaei and S. Tarighi, *Applied Energy*, 2018, **230**, 1347–1379.

31 Y. Kwon, Y. Birdja, I. Spanos, P. Rodriguez and M. T. M. Koper, *ACS Catalysis*, 2012, **2**, 759–764.

32 L. Giordano, D. Roizard and E. Favre, *International Journal of Greenhouse Gas Control*, 2018, **68**, 146–163.

33 Hasan Ümitcan Yilmaz, R. Hartel, D. Keles, R. McKenna and W. Fichtner, *Analysis of the potential for Power-to-Heat/Cool applications to increase flexibility in the European electricity system until 2030*, 2017.

34 D. Schüwer and C. Schneider, *Eceee Industrial Summer Study Proceedings*, 2018, **2018-June**, 411–422.

35 S. Cucurachi, C. Van Der Giesen and J. Guinée, *Procedia CIRP*, 2018, **69**, 463–468.

36 Sphera, 2019.

37 J. B. Guinée, M. Gorrée, R. Heijungs, G. Huppes, R. Kleijn, A. de Koning, L. van Oers, S. Wegener Sleeswijk, A. Suh, H. A. Udo de Haes, H. de Bruijn, R. van Duin and M. A. J. Huijbregts, *Handbook on life cycle assessment. Operational guide to the ISO standards. I: LCA in perspective. IIa: Guide. IIb: Operational annex. III: Scientific background*, Kluwer Academic Publishers, Dordrecht, 2002.

38 S. Galera and F. J. Gutiérrez Ortiz, *Energy Conversion and Management*, 2015, **96**, 637–645.

39 International Organization for Standardization, ISO 14040:2006. Environmental management- Life cycle assessment- Principles and framework, https://www.iso.org/standard/37456.html, (accessed 12 February 2018).

40 International Organization for Standardization, ISO 14044:2006. Environmental management- Life cycle assessment- Requirements and guidelines, https://www.iso.org/standard/38498.html, (accessed 10 February 2018).

41 European Commission, ECU/EUR exchange rates versus national currencies, https://ec.europa.eu/eurostat/web/products-datasets/-/tec00033, (accessed 1 February 2021).

42 M. Finkbeiner and V. Bach, *International Journal of Life Cycle Assessment*, , DOI:10.1007/s11367-021-01902-4.

43 P. Y. Oei and R. Mendelevitch, *Energy Journal*, 2016, **37**, 171–194.

44 E. Vartiainen, G. Masson and C. Breyer, 2015, 1–15.

45 EIA, *AEO2020*, 2020.

46 A. de Pee, D. Pinner, O. Roelofsen, K. Somers, E. Speelman and M. Witteveen,

Decarbonization of industrial sectors: the next frontier, 2018.

47 Energy Transitions Commission, *Mission possible: Reaching net-zero carbon emissions from harder-to-abate sectors by mid-century*, 2018.