A techno-economic evaluation approach to the electrochemical reduction of CO_2 for formic acid manufacture

M. Rumayor, A. Dominguez-Ramos, P. Perez, 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

Abstract

Efforts to mitigate climate change require technological innovations to reduce greenhouse gas emissions together with the reduction of the consumption of natural resources in an economic way compared to conventional processes. This paper presents a prospective assessment of an alternative for carbon dioxide (CO_2) utilization based on its electrochemical reduction (ER) to produce formic acid (FA). The methodology applied in the present study integrates a techno-economic assessment considering both the use of resources and a set of economic key process indicators versus the fossil-fuel based thermochemical conventional route. The results have demonstrated that the electricity consumption together with the consumables of the process (determined by the cathode lifetime) are the main contributors to the costs of production and therefore, to the profitability of the utilization plant. A sensitivity analysis was carried to evaluate the influence of the specific energy consumption in the profitability under a realistic ER approach. The results will assess the competitiveness of the production of FA by CO_2 ER against the conventional manufacture in terms of economics. The study has demonstrated that the electrification of this kind of commodity production plants through inexpensive surpluses of renewable energy is needed for their future competitiveness.

Introduction

Turning the European Union into a resource-efficient, green, and competitive low-carbon economy is a key objective to meet the targets regarding the reduction of the greenhouse gas (GHG) emissions to 80%-95% below 1990 levels by 2050 (United Nations Framework Convention on Climate Change (UNFCCC), 2016). The insights reveal that the development of new technologies for electric power generation, industrial processes and transportation will play a major role in efforts to reduce the GHG emissions. Among all the non-power industrial sectors, the chemical industry is one of the largest contributors to CO_2. Direct GHG emissions from industrial processes plus the indirect GHG emissions from the generation of electricity accounted for 28% which is equivalent to a staggering figure of 15 Gton CO_2 in 2014 (de Pee et al., 2018).

One of the potential pathways proposed toward the decarbonization of industry is to utilize CO_2. In one hand, it is possible to consider those options with a global relevant market such as those orientated to produce chemicals and fuels or to indirectly support industrial processes such as the enhanced oil recovery (EOR), enhanced gas recovery (EGR), and enhanced geothermal systems (EGS). On the other hand there are small niche commercial applications of CO_2 such as in refrigeration, fire extinguishers and beverage industry (Alper and Orhan, 2017; Barbarossa et al., 2014; Centi and Perathoner, 2009; European Zero Emission Technology and Innovation Platform (ETIP-ZEP), 2018; Meylan et al., 2015; Norhasyima and Mahlia, 2018). Alternatively, it is possible to take into consideration two kinds of routes: i) those involving its direct use, and ii) those alternatives that consider the utilization of CO_2 as a feedstock for chemical reactions. Several CO_2 conversion technologies are being investigated including homogeneous (Pérez-Fortes et al., 2016; Wang et al., 2015), heterogeneous (Maru et al., 2018; Yan and Philippot, 2018; Yang et al., 2015), photochemical (Gunter, 1984; Hu et al., 2013; Kondratenko et al., 2013; Suzuki et al., 2018) and electrochemical (Det Norske Veritas (DNV), 2011; Ganesh, 2016; Jhong et al., 2013; Kauffman et al., 2015; Scibioh and Viswanathan, 2018) catalytic conversion or biochemical conversion (Arends et al., 2017). All of them represent a new kind of economy for CO_2, the so-called "circular carbon economy" in which phasing out of fossil resources and closing the CO_2 loop are considered at the very core of the strategy. To deploy these technologies at industrial scale, they have to be capable to produce fuels and chemicals in a more sustainable manner respect their equivalent conventional routes in terms of: i) environmental requirements (e.g. reduction of the carbon footprint (CF) and resource savings), ii) economic requirements, iii) the market size (Roh et al., 2016), and iv) the social perspective. Indeed, regarding the social aspects, the latest results have indicated that there is a relatively high level of initial acceptance of CO_2 utilization technologies despite the low base of awareness (Perdan et al., 2017).

From a techno-economic perspective, most of these conversion technologies are found in a low technology readiness level (TRL) (Zero Emissions Platform, 2015) within the European Commission classification for TRLs (European Commission, 2015a) which means that they are not as mature as their equivalent fossil-based routes. Their commercial viability remains hampered by market failures, especially due to the absence of a significant CO_2 price that reflects the global constraint on emissions together with the relatively high electricity spot market prices. On one hand, using CO_2 as a suitable feedstock of carbon is an opportunity to use a low-cost or even a negative price carbon source in the event revenues can be derived from the acquisition of allowances e.g. under the EU emissions trading system (European Commission, 2015b). On the other hand, all non-biological CO_2 conversion routes require a noticeable input of energy to revert the oxidation state of the molecule. This involves important associated operating costs. Therefore, the availability of low-cost renewable energy is an imperative prerequisite in order to result in a net carbon uptake, thus it can be commercially competitive versus the conventional processes (Dominguez-Ramos et al., 2015; Zero Emissions Platform, 2015). As it is obvious, the generation of electricity is still dominated by the combustion of fossil fuels (BP Energy Economics, 2018). In the absence of direct taxes schemes, this fact leads to relatively cheap generation electricity costs, which are balanced with high emissions of CO_2 and other pollutants such as SO_2, NO_X and PM_{10}. A true statement is that renewable electricity is now in many places competitive with electricity from coal and its generation cost has deeply decreased in the last years (Bushuyev et al., 2018). The increase of the renewable share in the grid mix involves fluctuating surplus of electricity that limits the operational flexibility of the electricity network. In this context, the concept of power-to-*X (*being *X* power, mobility, heat, fuels or chemicals) is now the focus of the scientific community and its environmental benefits against the traditional storage systems have been demonstrated (Sternberg and Bardow, 2015). A clear example is Carbon Recycling International (CRI): an Icelandic plant of methanol that produces 4000 tons·yr^{-1} of this chemical via CO_2 hydrogenation using surpluses of geothermal energy (Carbon Recycling International (CRI), 2006). A larger plant with an annual capacity of 40,000 t is also being built (Carbon Recycling International (CRI), 2006). Both plants have an advantageous situation as they can access to an inexpensive surplus of renewable electricity and heat.

Another CO_2 conversion technology based on the use of renewables that has attracted a great deal of attention from both research and industry communities is the alternative of electrochemical reduction (ER) of CO_2 (Kumar et al., 2016). It has achieved significant progress in the last decades that pushed the technology towards the demonstration phase. The ER of CO_2 offers the potential of seasonal energy storage in the form of chemical/fuels. It allows the integration of renewable electricity in chemical production. Consequently, it is expected in the foreseeable future that the application of ER of CO_2, together with the trend of global renewable electrification of the industry, may represent a step toward reducing the CF of commodity chemicals (Schiffer and Manthiram, 2017).

Currently, this technology is found in a low technology readiness level (TRL) 3-5 (Jarvis and Samsatli, 2018). Several factors must be still addressed to ensure a potential commercial viability following a sustainable pathway: i) the reduction of the specific energy consumption due to the ER and the associated separation processes, which themselves entails CFs (Roh et al., 2018), and ii) the consumables reduction as electrolytes and also the electrodes, which are directly influenced by the cathode durability and its replacement ratio (Agarwal et al., 2011). Many chemicals can be synthesised by ER of CO_2 such as carbon monoxide (CO) (Lu et al., 2018; Shen et al., 2018; Wang et al., 2018), formic acid (HCOOH) (Del Castillo et al., 2017; Scialdone et al., 2016; Yang et al., 2017), hydrocarbons (e.g., methane CH_4 or ethylene C_2H_4) (Choi et al., 2016; Dinh et al., 2018), and alcohols (e.g., methanol, CH_3OH) (Albo et al., 2015; Malik et al., 2016). Among them, formic acid (FA) has been proposed as one of the most profitable chemicals synthesized by this technology (Agarwal et al., 2011; Jouny et al., 2018). FA can be produced with high faradaic efficiencies on metals with high overpotential for H_2 production (Zhao et al., 2017). Moreover, as FA is a liquid CO_2 ER product, which is particularly desirable thus it can be easy 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 and this growth is estimated to increase in the coming years from 620 kton in 2012 to 1 Mton in 2030 (Global CO2 Initiative and CO2 Sciences Inc., 2016). This fact is mostly motivated by the potential of FA as a storage medium for hydrogen (Eppinger and Huang, 2017; Wang et al., 2015). FA is industrially produced by hydrolysis of methyl formate (Hietala et al., 2000) which represents a fossil-dependant route. No doubt, FA derived from ER of CO_2 using renewable energy offers a potential alternative to the conventional process as it recycles CO_2 (carbon neutral cycle) and provides a method to store/use the excess of renewable energy from intermittent sources while reducing the industry dependence on fossil fuels.

In a recent study carried out by the authors, two of the key environmental metrics associated with this technology have been evaluated: the carbon footprint (CF) and the resource savings (Rumayor et al., 2018). The results made clear the target parameters of the electrocatalytic performance in order to ensure that the technology was environmentally positive compared to the conventional FA manufacture. Briefly, it was concluded that an increment of FA concentration in the outlet stream of ER reactor up to 21% wt. can reduce the steam consumption -requested for the azeotropic distillation- and then the overall CF down to the value of the CF corresponding to the conventional process of FA production (2.2 $kg \cdot kg^{-1}$, expressed as a unit of mass of CO_2 equivalent per unit of mass of FA produced). To the best of our knowledge, the technology is expected to be environmentally positive when compared to the conventional FA manufacture but its feasibility on a techno-economic basis remains unclear yet.

Even if a lot of potential is in favour of this alternative, it should be undoubtedly stated that there is still a significant gap between laboratory-scale research and industrial processes and the related potential economy of large-scale CO_2 utilization processes. Many issues must be discussed in order to bring light into the real figures associated. Recent studies have presented economic results of the ER technology to produce various chemicals (Jouny et al., 2018; Spurgeon and Kumar, 2018). Therefore, it is only possible to estimate the capital costs of an industrial scale ER of CO_2 system, considering that current ER cells exist only at the lab scale and there is not a standard design for them. It is obvious that there is a lack of any industrial-scale reference for this alternative. Usually, the techno-economic assessments use a high level of aggregation of individual contributors -net use of energy, water, coproducts, etc.-, making hot spots difficult to be analysed. Commercial alkaline water electrolysers are commonly used as proxies for the ER cell in typical models, considering long times of replacement (Jouny et al., 2018; Spurgeon and Kumar, 2018). It is also known that electrochemical components such as catalysts or electrodes have an impact on the cost of these units (Lu et al., 2018). The last figures of merits have suggested lifetimes in the range of thousands of hours under typical cycling loads from renewable energy sources, considering 5,000 h as a first approximation (Martín et al., 2016), thus better stability will reduce the associated maintenance and consumable costs. So far, an early-stage assessment of cell materials covering aspects of cell lifetime is still not available and thus it should be a key consideration to be further studied. A profitability assessment of the process will provide a comprehensive view of the process economy yielding a full picture of the technology's feasibility and sustainability.

In this paper, we aim to carry out a techno-economic assessment of the ER of CO_2 as utilization alternative to produce FA. The novelty of this work is the integration of the currently under development CO_2 ER production infrastructure and its associated chain cost analysis that can potentially fill the gaps due to aggregation obtained in other relevant studies (Jouny et al., 2018; Spurgeon and Kumar, 2018) using the cathode lifetime as one of the main variables. This work can demonstrate the benefits and weakness in terms of economics versus the equivalent FA conventional route. Key performance indicators (KPIs) such as total fixed capital costs (TFCC), net present value (NPV), internal rate of return (IRR) and both variable cost of production (VCP) and fixed cost of production (FCP) will be compared with those KPIs resulted from a conventional FA plant. Sensitivity analyses have been carried out in order to understand the impacts of uncertainty in the mentioned KPIs. Taking into account that ER of CO_2 has been regarded as an energy-intensive process (Bushuyev et al., 2018) and that the accessing to an inexpensive renewable energy source is one of the key facts for its competitiveness, this study will analyse the influence of the energy consumption by ER in the economics of the plant to compete with the conventional process. The results obtained in this study can represent a step towards a successful implementation of the CO_2 ER technology to produce FA on a large scale, which implies that FA must be produced at costs economically competitive with existing commercial prices.

2. Methodology

The present study is focused on the techno-economic comparison between the electrochemical reduction (ER) of captured CO_2 to produce FA and the conventional FA manufacture route. Both the systems description and the methodology applied for the technical and economic analysis are described in the following sections.

2.1. Conventional route to produce FA

The conventional route to synthesize FA was used as the benchmark in this techno-economic assessment. Under current established technology, FA is produced mainly by hydrolysis of methyl formate (Hietala et al., 2000), which is typically a fossil-dependant route consisting of two stages: in the first stage methanol is carbonylated with carbon monoxide ($CH_3OH + CO \rightarrow HCOOCH_3$) and in a second stage, methyl formate is hydrolysed to FA and methanol ($CH_3OOCH + H_2O \rightarrow CH_3OH + HCOOH$). The stages demanding energy in FA synthesis are syngas production (heavy fuel oil is used in the synthesis of CO) and steam needs (also from the combustion of fossil fuels). Some limitations of this route include: i) slow reaction rate, ii) undesirable by-products, iii) relatively high investment cost, and iv) issues related to the environment due to the mentioned high energy requirements (in the separation stage) leading to a noticeable dependence on fossil fuel (Sharma et al., 2018). It should be noted that accordingly to the Ecoinvent database, for the average consumption of heat in a conventional plant of FA, there are two sources: natural gas (14.6 MJ·kg^{-1} of FA) and other sources than natural gas, i.e. waste incineration, coal, oil, diesel, wood, etc. (8.17 MJ·kg^{-1} of FA). In this study, the resource savings was calculated assuming that heat comes exclusively from natural gas. The same assumption was set in the ER route for a fair comparison. The reference scenario will be this conventional route (Conv).

2.2. Electrochemical reduction of CO_2 to produce FA: description of the model

A mass and energy balance model built by the authors in a previous study (Rumayor et al., 2018) was used to determine the inventory of the ER of CO_2 to produce FA. A Life Cycle Inventory (LCI) gathered all the data needed to the inputs and outputs of the hypothetical CO_2 utilization plant. The plant considered an annual FA production rate of 12 kton according to similar CO_2 utilization plants based on the methyl-formate route (Pérez-Fortes et al., 2016).

As previously mentioned, the model consists of mass and energy balances applied to the overall process and the individual process units. The system boundaries include the utilization plant itself (see Figure 1) in order to produce FA such in the conventional process. Transportation from and to the site is not included as it would be the same than in the conventional route. Basically, it includes three main units: i) the ER of CO_2 in the ER cell, ii) the distillation of the azeotropic mixture FA/water to the desired purity (85% wt.), and iii) the compression of by-products H_2 and O_2 to the liquid forms that are ready to transport. The pumping unit process has a minor contribution. The process responsible to capture CO_2 is out of the system boundaries accordingly to similar studies found in the literature (Szima and Cormos, 2018). The functional unit is 1 kg of FA (note that the corresponding amount of water of 0.18 kg is considered in the mass balance to reach a concentration of FA of 85% wt., which is the current standard purity).

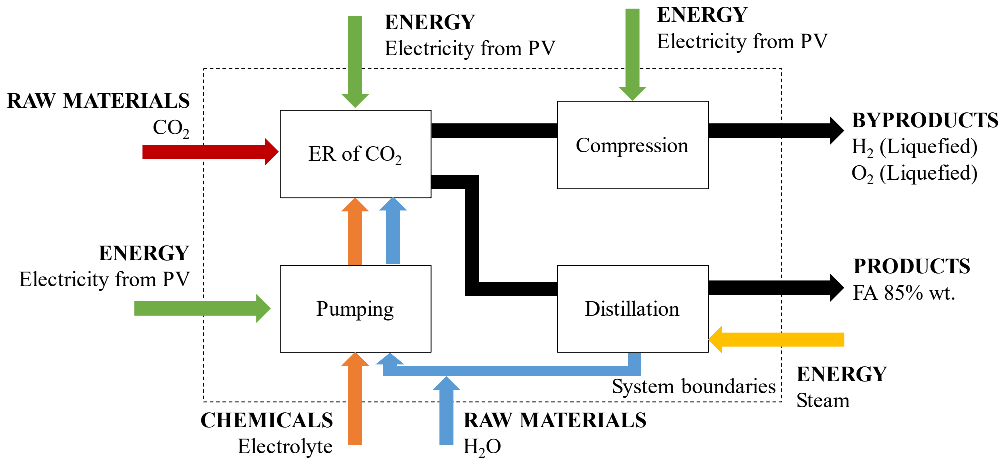

Figure 1. Diagram of the process based on the electrochemical reduction of CO_2 to FA

The electrochemical process was included in the model as a black box unit using a set of parameters. As a result, we define different scenarios (see Table 1). The first scenario labelled as E_{min} was created using the hypothesis of perfect/ideal conditions in the ER. This means the minimum consumption of electrical energy (no overpotential losses) and the maximum Faradaic Efficiency, FE (100%). This scenario E_{min} corresponds to the maximum CO_2 reduction because of all the electricity is effectively employed in the reduction of CO_2 to FA, with no other parallel co-products or overpotential losses. In this context, two E_{min} sub-scenarios were created and used in the techno-economic assessment. These were labelled as E_{min-21} and E_{min-85}. Sub-scenarios E_{min-21} and E_{min-85} represent the situations in which the FA concentration at the outlet stream of the ER cell is 21% wt. (the benchmark value set in our previous study (Rumayor et al., 2018)), and a maximum value of 85% wt. (commercial concentration), respectively. According to that, E_{min-21} will display the influence of the separation step in the resource savings (purity must be raised to 85% wt.) while E_{min-85} will indicate the minimum energy consumption in terms of electrical energy (100% FE and no overpotential losses) and heat (the FA has already the set purity thus no consumption of heat as steam). Then, E_{min-85} represents the absolute maximum CO_2 that could be saved by the option of ER of CO_2 to FA and the minimum production cost.

Table 1. The model assumption in sub-scenarios E_{min-21} and E_{min-85} for the process ER of CO_2 to produce FA.

Parameters	Units	Sub-scenarios	
		E_{min-21}	E_{min-85}
Current density	$mA \cdot cm^{-2}$	300[a]	300[a]
Cell potential	V	1.48[a]	1.48[a]
FE	%	100	100
$[FA]_{out\ ERcell}$	% wt.	21[b]	85
Cathode LT	yr	20	20
Membrane LT	h	20	20
Anode LT	yr	20	20
Electricity supply		From PV solar	From PV solar
Heat supply		Steam from NG	-

[a] (Kauffman et al., 2015)

[b] (Rumayor et al., 2018)

The electrical energy consumption in the process is supplied by photovoltaics (PV solar) electrical energy and heat (as steam) for the purification process unit (distillation). The techno-economic study presented in this study is related to the production of formic acid from CO_2 ER. The ER performance parameters used in the mathematical model (Rumayor et al., 2018) were assumed to be similar to those obtained within the research group of the authors (Del Castillo et al., 2017). It should be mentioned that those ER performance parameters were obtained under neutral to alkaline conditions producing formate. In this study, it was considered that the production of FA under neutral to acid conditions would have a similar performance. Briefly, the mass balances in CO_2 ER unit was solved assuming the main reactions under neutral to alkaline conditions (Li and Oloman, 2006; Oloman and Li, 2008). In the anodic compartment, the O_2 evolution reaction takes place, according to the next reaction R1:

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ (R1)

CO_2 and water are injected in the cathode being the CO_2 solubility considered very high to reach the cathode surface. The mass transfer was not included in the model. It is considered that H_2O is the chemical compound consumed regardless of the pH in the half-cell being acid or basic. Once CO_2 reaches the cathode surface, it is reduced to formate ($HCOO^-$) and H_2O to hydroxide ions (OH^-) (R2) liberating the stoichiometric amount of H_2, in the presence of the correspondent electrolyte in the cathodic compartment of the ER cell (3).

$$CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^- \quad \text{(R2)}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad \text{(R3)}$$

Both the anolyte (KOH) and the catholyte ($KHCO_3$ and KCl) are supposed to be perfectly recirculated thus both were not taken into consideration. A purification process in the form of an azeotropic distillation was included in the model in order to increase the FA concentration from 21% wt. up to 85% wt. (commercial concentration value) when necessary. The unit includes cooling and heating and it was simulated in a previous study carried out by the authors (Dominguez-Ramos et al., 2015) using ASPEN PLUS software (Aspen Technology Inc., 2019). The simulation considers a binary mixture with the presence of water (obtained as a head product) and FA (obtained as the bottom product). The distilled water is recirculated and reinjected to the inlet freshwater stream to the cathode being the net water consumption as the difference between water in the inlet stream and water that is recirculated. The by-product O_2 (considered pure) is separated, liquefied and recovered.

We have considered the following set of hypothesis: i) the CO_2 valorisation plant was in the same site of the CO_2 source thus no transport was required, ii) the CO_2 stream was fed to the plant as a pure component and with a suitable pressure for the ER process, iii) the CO_2 feed was assumed free of environmental burdens (no allocated CO_2), and iv) the steam needed for the FA purification is at dry saturated conditions and comes from the combustion of natural gas. No further processes were included, either upstream or downstream of the plant (e.g. CO_2 capture or product distribution and consumption). With the aim of determining the net amount of CO_2 emissions prevented, the ER utilization plant is compared to its equivalent conventional plant by the methyl formate route. While the feedstock to the utilization process to produce FA is CO_2 and water, the feedstock to the benchmark conventional plants is fossil fuel in the form of natural gas.

2.2.1. Evaluation of the influence of the ER cell

It is evident that electrochemical components such as electrocatalysts or electrodes have an influence on the economics of the process. In order to show the potential impact of the cathode lifetime in the capital cost and the cost of consumables a second scenario, named as Baseline, was created (Table 2). In this case, a model that includes ER cell fabrication was used (Rumayor et al., 2018). The ER cell used as reference consists of a filter-press configuration with a geometric surface area of 10 cm^2 being the main components: i) cathode: a Gas Diffusion Electrode with carbon supported Sn nanoparticles (Sn/C-GDE), ii) anode: a commercially available Dimensionally Stable Anode (DSA-O_2 on Platinum), and iii) separation ion-conducting membrane: a commercial Nafion 117. The main components of the cell are clamped by two end plates made from aluminum ($1\cdot10^{-3}$ m as thickness). Steel tie rods are used as well in the assembly process. The influence of the end plates and tie rods have not been included in this study. The LCI data of the cathode was obtained following the hierarchy described in a previous study (Rumayor et al., 2019) carried out by the authors. The lifetime corresponding with the anode was fixed at 10 yr according to the durability proposed in a commercial website ("PolyTechs Technology," 2018) and the corresponding durability of the membrane at 60,000 h (Rozière and Jones, 2003). In this case, two sub-scenarios were created, labelled as $B_{-2.5}$ and $B_{-4.45}$. These two scenarios represent two situations: a high and a low threshold in the percentage that the consumable cost has in the total cost of production. Thus, in sub-scenarios $B_{-2.5}$ and $B_{-4.45}$, the cathode is replaced after 2.5 yr and 4.45 yr, respectively. The mass and energy balances obtained through the process model were the input data for the LCI, which in turn is the basis for the economic feasibility analysis. The key technological variables used for the technical evaluation of the entire CO_2 utilization process are the cathode lifetime and electric power consumption. This latter variable is particularly important, as it accounts for the main percentage of the costs affecting the economics of the plant while the cathode lifetime is crucial in the consumables cost. Moreover, the Baseline scenario corresponds with a realistic situation in which FE is not 100%. The model considered that some part of the applied current density is deviated to other parallel/parasitic reactions (Oloman and Li, 2008) leading to a reduction of the FE to FA production. Specifically, H_2 evolution reaction is recognized as the only parallel/parasitic reaction taking place in the cathode. H_2 is produced and sold as a by-product. The same holds true for O_2 (produced in the anode). FA at the outlet stream of the ER cell is assumed to be 21% wt. according to the benchmark set in our previous study (Rumayor et al., 2018). In the E_{min} sub-scenarios, selling H_2 is not possible due to the FE of 100%.

Table 2. Model assumptions in scenario Baseline for the process ER of CO_2 to produce FA

Parameters	Units	Sub-scenarios		Reference
		$B_{-2.5}$	$B_{-4.45}$	
Current density	$mA \cdot cm^{-2}$	200	200	(Del Castillo et al., 2017)
Cell potential	V	4.3	4.3	(Del Castillo et al., 2017)
FE	%	42.3	42.3	(Del Castillo et al., 2017)
$[FA]_{out\ ERcell}$	% wt.	21	21	(Rumayor et al., 2018)
Cathode LT	yr	2.5	4.45	
Membrane LT	h	60,000	60,000	(Rozière and Jones, 2003)
Anode LT	yr	10	10	
Electricity supply		PV solar	PV solar	
Heat supply		Steam (from natural gas)	Steam (from natural gas)	

2.3. Economic-cost assessment

Economic analysis has been conducted to estimate the production cost required to synthesize 1 kg of FA (plus 0.16 kg of H2O to reach 85% wt. purity) by the ER of CO_2 in order to assess the economic viability and competitiveness of the technology in a substantially extended market.

Based on the input data from the LCI obtained using the model of the process for the E_{min} and Baseline scenarios, the capital (CAPEX) and operational expenditures (OPEX) were estimated. Then, the economic feasibility analysis of the plant includes the calculation of three KPIs: the net present value (NPV), the internal return rate (IRR) and the benefit/cost ratio (B/C). By definition, a project is economically feasible if the B/C ratio is greater than unity and simultaneously the NPV is also greater than zero. As the third KPI, IRR is a metric used in capital budgeting to estimate the profitability of potential investments. The higher the IRR, the greater the profitability of the project will be. The cost of production expressed in units of € per kg of FA synthesised was calculated and compared with an average current FA market price c.a. 650 €·ton^{-1} (Pérez-Fortes et al., 2016). This price for FA represents the one produced by means of the commercial process (selected as the benchmark). The currency exchange rate used in the study is €2017, which was based on Eurostat data (European Commission, 2018). The geographical location of this analysis is North West Europe, the lifetime of the hypothetical ER plant is assumed to be 20 yr, and 2017 is chosen as the reference year. At the current TRL, it is not possible to envisage different lifetimes. The features considered for the utilization plant are shown in Table 3. Prices for raw materials, utilities, products and by-products, are estimated for the year 2017, and they are considered constant for the analysed period.

Table 3. CO_2 utilization plant features

Parameters	Units	Value	References
Production rate	t·yr^{-1}	12,000	
Plant lifetime	yr	20	
Operating time	d·yr^{-1}	350	
Time per shift	h	8	
Operators per shift		4	
Hourly labour cost (EU-28;2017)	€·h^{-1}	26.8	(Eurostat, 2017a)
Discount rate	%	8.1	
€ basis year		2017	
CO_2 price	€·t^{-1}	20	

Electricity price	€·MWh^{-1}	85	(Vartiainen et al., 2015)
Heat price (as steam)	€·t^{-1}	20	(Eurostat, 2017b)
O_2 price	€·kg^{-1}	0.05	
H_2 price	€·kg^{-1}	10	
FA market price	€·kg^{-1}	0.65	(Drury, 2013)

All costs involved in the process were estimated using a bottom-up approach using a factorial method (Towler and Sinnott, 2013). The approach estimates the fixed capital investment as the sum of: i) the inside battery limits (ISBL) investment, which corresponds to the cost of the plant itself, ii) the modifications and improvements that must be made to the site infrastructure, known as offsite or outside battery limits (OSBL) investment, iii) the engineering and construction costs, and iv) the contingency charges. Briefly, the equipment cost of the utilization plant was assumed to be the ER cell cost and the cost of other units involved in the process such as the distillation column (distillation), and the pumps and compressors (pumping and compression). Particularly, the ER cell cost is the critical point as it is still necessary to scale-up the ER reactor (currently lab scale) including the state-of-the-art for the cathode, the anode, and the membrane for an effective mass-transport under high current density (Spurgeon and Kumar, 2018). The ER cell fabrication was incorporated in the economic analysis and estimated by using the commercial market prices of the main chemicals and materials used for its fabrication considering the current lab-scale production procedure. The cost of the cathode, which consists of a Gas Diffusion Electrode with carbon supported Sn nanoparticles (Sn/C-GDE), was estimated following the fabrication procedure described in our previous study (Rumayor et al., 2019). The estimated cost value was 7700 €·m^{-2}. Of course, the cost of production of cathodes at industrial scale would include the influence of other fixed and variable costs. The purchase prices of materials and chemicals are evaluated to fit those from lab scale (i.e.: liters or grams). Of course, bulk purchasing means a lower cost per unit. The cost of distillation, pumping and compression units were calculated using the factorial method found in the literature (Towler and Sinnott, 2013). The operating costs include the costs of: i) raw materials consumed by the process, ii) utilities, and iii) consumables. The fixed costs of production involve: i) operating labour, ii) supervision, iii) direct salary overhead, iii) maintenance, iv) property taxes and insurance, and v) interest. CAPEX includes: i) the total fixed capital costs (TFCC), and ii) the working capital. OPEX consists of fixed and variable operating costs (FCP and VCP, respectively). The KPIs used in this work, such as TFCC, NPV and both VCP and FCP, were estimated as discussed in the Supporting Information.

The economic analysis of the conventional plant of FA was carried out using a reference CAPEX value of 17 M€ from the 20 kton capacity expansion of a FA plant (Solutions, 2003). In order to compare that plant fairly with the CO_2 based ER plant described here, the CAPEX value had to be scaled down to the equivalent 12 kton of capacity. We used the 0.6 rule economic scale procedure (Tribe and Alpine, 1986). Therefore, the reference CAPEX value calculated for a conventional plant of 12 $kton \cdot yr^{-1}$ is estimated at 12.5 M€. The operating cost of the conventional plant was estimated using the same market prices of the utilities (i.e. electricity, heat and water) and the factorial method used for the cost estimation of the utilization plant. The prices for other raw materials such as carbon monoxide and methanol were set as 70 $€ \cdot ton^{-1}$ (Jouny et al., 2018) and 380 $€ \cdot ton^{-1}$ ("Methanex Corporation," 2015), respectively.

The break-even productions corresponding with each ER scenario and the conventional plant were determined in order to show the minimum level of production capacity that ensure these plants would be profitable under the hypotheses of the study. The break-even production was calculated as the value that even the revenue to the total cost of production.

2.4. Sensitivity analysis

Sensitivity analyses are completed to account for the uncertainty of the main variables that influence on the techno-economic results and the project profitability. On one hand, the NPV, as KPI that is used to evaluate the profitability of the studied plants, is considerably sensitive to the interest rate. It should be mentioned that the interest rate varies widely within the EU members

(Fernandez et al., 2018). Then, a sensitivity analysis of the influence of the interest rate in the NPV value was carried out in each scenario. Additionally, it was determined the NPV evolution with the period of time for a fixed interest rate of 8.1% in order to determine and compare the payback periods of the studied scenarios. By definition, the payback period is the length of time required to recover the investment, or also the period of time that makes the NPV equal to zero.

On the other hand, the electricity consumption is expected to be the variable of the process performance that influences the most on the associated operating cost and therefore on the total cost of production and profitability. As it was previously mentioned, this kind of electricity-intensive plants should be self-supplied by means of a surplus or inexpensive renewable source integrated into the plant for its industrial competition. A sensitivity analysis of the influence of the electricity consumption by the ER of CO_2 in the IRR was determined in a realistic scenario. This scenario is based on the ER performance parameters of $B_{-4.45}$ assuming the current CO_2 market price of 20 $€\cdot ton^{-1}$ (European Commission, 2015b) and a reasonable lower cost of electricity of 20 $€\cdot MWh^{-1}$, predicted in the foreseen. The electricity market price was chosen in this study (20 $€\cdot MWh^{-1}$) based on the prospective levelised cost of electricity (LCOE) of large-scale PV solar electricity in Europe by 2050. Briefly, the LCOE includes only the generation cost, this it was predicted to decrease in the range from 25 $€\cdot MWh^{-1}$ to 45 $€\cdot MWh^{-1}$ by 2030, reaching a value as low as 20 $€\cdot MWh^{-1}$ by 2050 (Vartiainen et al., 2015).

3. Results and discussion

3.1. Technical assessment

Table 4 shows the use of resources obtained from the mass and energy balance used in our model in the sub-scenarios E_{min-20} and E_{min-85} that consider a concentration of FA at the outlet stream of the ER cell of 21% wt. and 85% wt. respectively. The use of resources corresponds to the LCI of the utilization process. The LCI values of the commercial process were included for comparison purposes and they were collected from Ecoinvent database v3.2 (Swiss Centre for

Life Cycle Inventories, 2016). As it was previously mentioned, the steam for the separation step in the conventional manufacture was assumed to come 100% from natural gas (the same assumption was taken in the case of the alternative ER of CO_2). However, it should be recalled that, accordingly to the Ecoinvent dataset for the average conventional FA route, there are two sources for the requested heat: natural gas (14.6 $MJ \cdot kg^{-1}$); and other sources different than natural gas (i.e. waste incineration, coal, oil, diesel, wood, etc.) (8.17 $MJ \cdot kg^{-1}$).

Table 4. Life cycle inventory (LCI) of the FA manufacture alternatives: ER of CO_2 and conventional per unit of mass of FA (Note that an amount of H_2O of 0.18 kg is not shown in the table as it is considered in the 85%wt. FA product)

	Unit	Conventional	ER of CO_2	
			E_{min-20}	E_{min-85}
Raw materials				
CO_2	kg	-	0.957	0.957
H_2O	kg	0.600	0.570	0.570
CO	kg	0.610	-	-
CH_3OH	kg	0.040	-	-
By-Products				
O_2	kg	-	0.348	0.348
H_2	kg	-	0.000	0.000
Electricity consumption				
ER	kWh	-	1.75	1.75
Pumping	kWh	-	<0.01	<0.01
Compression	kWh	-	<0.01	<0.01
TOTAL	kWh	0.290	1.75	1.75
Heating needs	MJ	22.8	17.1	0.00

As shown in Table 4, E_{min-20} and E_{min-85} scenarios require an amount of H_2O of 0.570 $kg \cdot kg^{-1}$ (expressed as the amount of water consumed per unit of mass of FA produced) together with CO_2 per unit of mass of FA produced of 0.957 $kg \cdot kg^{-1}$. In the case of the conventional route, the feed to the process consists of the fossil-derived CO and CH_3OH. The effect of producing FA from renewable CO and/or MeOH do not belong to the scope of this work. In the alternative ER of CO_2, there is an amount of O_2 produced in the anode (0.348 $kg \cdot kg^{-1}$) that can be sold as a by-product. It must be considered that in the case of both ideal scenarios, a FE of 100% is achieved and consequently H_2 is not produced. The total electricity consumption can take into account from the needs of compression (O_2) and pumping (water recirculation) but it is totally controlled by the needs of the electrolyser, highlighting that the process is an electrical intensive process. A value of 1.75 $kWh \cdot kg^{-1}$ is obtained as the electrical energy consumption of the ER cell in both E_{min} sub-scenarios. This value corresponds with the theoretical minimum consumption of energy to produce FA through the ER of CO_2 (Kauffman et al., 2015). It can be observed that the conventional process displays an electric energy consumption value as low as 0.29 $kWh \cdot kg^{-1}$. For the heating needs, 17.1 $MJ \cdot kg^{-1}$ are consumed in the distillation unit in E_{min-20}. No heating needs are required in E_{min-85} (as the FA reaches the commercial purity at the reactor outlet). The resource savings of the ER route respect the conventional alternative are displayed in Table 5. It must be highlighted that 0.405 kg of heavy fuel oil (assumed as the basis for the CO as listed in Table 4) and 1.25 kg of natural gas at high pressure can be saved per kg of FA produced through this CO_2 utilization alternative. Natural gas consumption due to the heat requirement in E_{min-20} was 0.314 kg while a value of 0.419 kg of natural gas is the consumption obtained in the separation step of the conventional plant. These savings are direct savings from the direct use thus they do not account for savings regarding the substitution of the source of electricity.

Table 5. Consumption of raw materials (per unit of kg of FA)

	Unit	E_{CONV} (Swiss Centre for Life Cycle Inventories, 2016)	E_{min-20}	E_{min-85}
Heavy fuel oil	kg	0.405	-	-
Natural gas *(heating purposes)*	kg	0.419*	0.314*	-
Natural gas, at high pressure**	kg	1.25	-	-

*The value was calculated assuming that heat comes exclusively from natural gas

**At 60 bar, 15 °C, the natural gas density used is 48 $kg \cdot m^{-3}$ (original value was expressed as m^3)

Table 6 shows the LCI for the Baseline scenario. It is required a feed stream of 1.1 $kg \cdot kg^{-1}$ of H_2O (expressed as the amount of H_2O consumed per unit of mass of FA produced) together with 0.957 kg·kg^{-1} of CO_2. This is a realistic scenario in which FE is considered low, and therefore below the 100% shown in the previous E_{min} sub-scenarios. Then, H_2 is produced by the parallel reaction in the cathode (0.06 kg·kg^{-1}), and it is compressed and sold as by-product together with the O_2 produced in the anode. From the point of view of natural resources consumption, the consumption of natural gas calculated in the separation step is 0.314 kg·kg^{-1} (expressed as a unit of mass of natural gas per unit of mass of FA produced).

Table 6. LCI of the FA by ER of CO_2 in the Baseline scenario per unit of mass of FA (Note that an amount of H_2O of 0.18 kg is not shown in the table as it is considered in the 85%wt. FA product)

	Unit	ER of CO_2 (Baseline)
Raw materials		
CO_2	kg	0.957
H_2O	kg	1.10
CO	kg	-
CH_3OH	kg	-
By-Products		
O_2	kg	0.82
H_2	kg	0.06
Electricity consumption		
ER	kWh	11.8
Pump	kWh	<0.01
Compression	kWh	0.150
TOTAL	kWh	12.0
Heating needs	MJ	17.1

3.2. Economic assessment

Table 7 displays the economic key performance indicators (KPIs) of both E_{min-20} and E_{min-85} and the conventional plant. The capital costs of the utilization plant in terms of CAPEX are 13.1 M€, with distillation, and 12.1 M€ without distillation. Those values are in the same order of magnitude of the CAPEX obtained for a conventional FA plant of the same annual capacity (12.5 M€) (see section 2.3). TCP values calculated for both E_{min} scenarios are in the range of 20%-23%

lower than the TCP value calculated for the conventional FA plant indicating the maximum economic gap that could be achieved by the ER of CO_2 route respect the conventional route in future developments.

Table 7. Economic KPIs of the utilization FA plant and the conventional FA plant

KPI	UNIT	Utilization (ER of CO_2)		Conv
		E_{min-21}	E_{min-85}	
ISBL	M€	6.01	5.60	5.63
OSBL	M€	2.40	2.24	2.25
TFCC	M€	12.0	11.0	11.0
CAPEX	M€	13.1	12.1	12.5
ACC	M€	1.22	1.13	1.13
VCP	€·kg^{-1}	0.26	0.15	0.23
FCP	M€·yr^{-1}	2.16	2.14	2.14
CCOP	M€·yr^{-1}	4.9	3. 51	4.93
Gross margin	M€·yr^{-1}	8.2	8.23	7.09
Gross profit	M€·yr^{-1}	2.93	4.29	2.87
TCP	€·kg^{-1}	0.51	0.38	0.50
NPV	M€	15.4	29.7	16.9
IRR	%	25	39	26
BCR		1.28	1.68	1.29
Break-even production	kton	46.1	30.5	52.2

As it was expected, the value of the indicator NPV is doubled in E_{min-85} (29.7 M€) respect both scenarios E_{min-20} (15.4 M€) and Conv (16.9 M€). Those values were calculated using an *i* of 8.1% in 2018.

Figure 2 displays the contributions of the purchase and installation of different units to the total equipment investment of 6.01 M€ (as ISBL). Figure 2 only displays the breakdown of the cost of purchasing and installing the equipment in the scenario E_{min-21}. Please note that the ISBL indicator in the scenario E_{min-85} was as low as 5.60 M€ being the cost gap (around 450 k€) allocated to the absence of the distillation unit. It should be reminded that in scenario E_{min-85}, FA is supposed to be synthesized in the ER cell at its commercial purity.

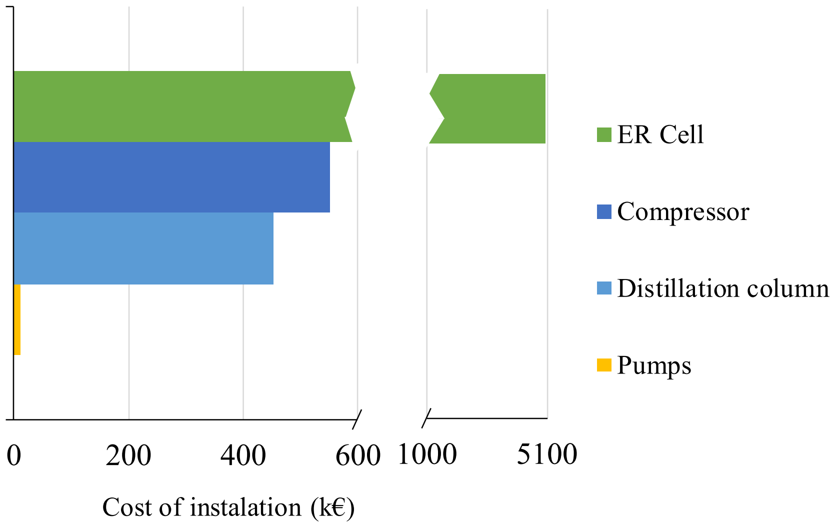

Figure 2. Distribution of the installation cost (ISBL) in the scenario E_{min-21}

The overall VCP obtained in the conditions of E_{min-21} scenario was 0.26 €·kg^{-1}. The contributions of different variable costs to the overall VCP in E_{min-21} scenario is shown in Figure 3. It should be highlighted electricity being the utility contributing the most to the VCP followed by the steam consumption. It is remarkable that the electricity consumption in both E_{min} sub-scenarios is set at its minimum theoretical value, and of course, the real electricity consumption will be always higher than that value. As it was mentioned previously, the gap between the VCP values in the scenarios E_{min-21} and E_{min-85}, which is 0.11 €·kg^{-1}, is attributed to the absence of steam consumption in E_{min-85} because no purification step is needed. The results obtained underscored the high impact in the TCP of the utilization processes due to the commercial price of electricity as a result of the high contribution of electricity in VCP.

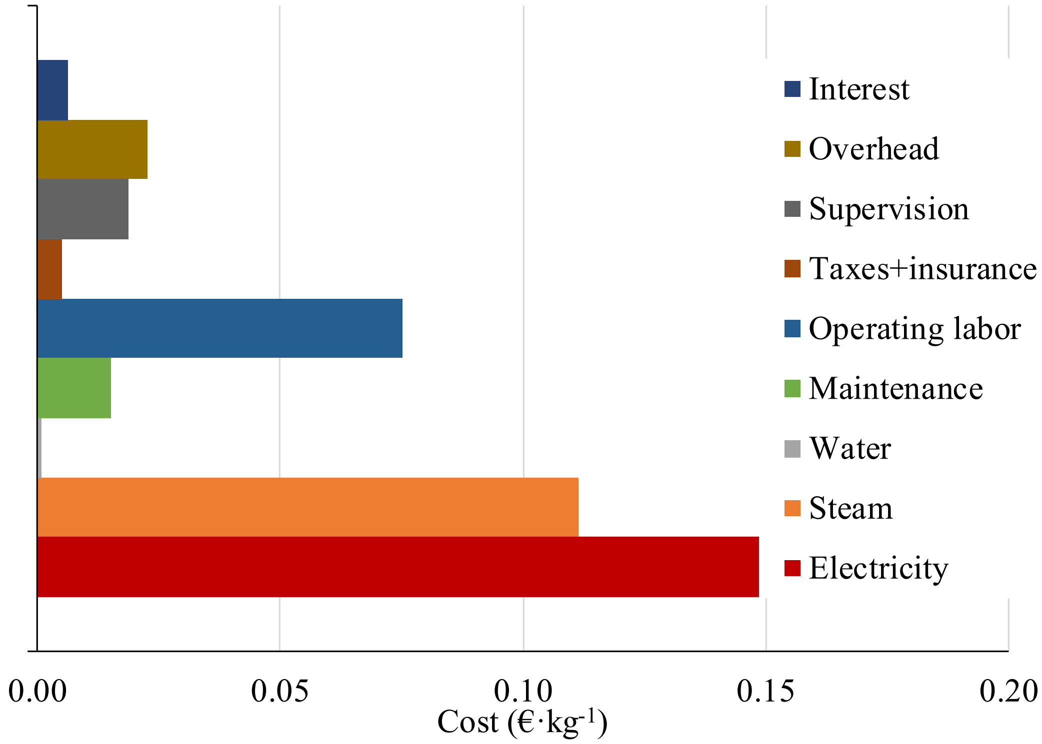

Figure 3. Distribution of the variable cost of production (VCP) in the scenario E_{min-21}

The economic results obtained from both scenarios E_{min-21} and E_{min-85} have not considered the influence of the consumables cost in the VCP because the lifetimes of the cathode, anode and membrane were supposed to be 20 years (the lifetime of the plant). However, this assumption is far from reality because it is well-known that the cost of consumables could have a potential influence on the overall cost of production (Kondratenko et al., 2013). Following the parallelism with hydrogenation-based technologies for CO_2 utilization to produce FA, consumables can be the main contribution to the VCP, even higher than the cost of electricity consumed by the typical electrolysers found in these plants (Jarvis and Samsatli, 2018). In addition, it has been claimed that cathode durability is one of the least studied parameters in the ER of CO_2 literature (Martín et al., 2016). In order to demonstrate the influence of the cost of consumables in the profitability of the ER process, economic KPIs were calculated once again under the conditions of the conservative sub-scenarios $B_{-2.5}$ and $B_{-4.45}$, which consider cathode lifetimes of 2.5 yr and 4.45 yr, respectively. According to the methodology section, the durability of the DSA-O_2 anode was set at 10 yr (PolyTechs Technology, 2018), while the lifetime of the perfluorosulfonic acid (PFSA) membrane was 60,000 h (Rozière and Jones, 2003). The economic KPIs calculated for both scenarios are shown in Table 8. As it was expected, both situations are negative from the point of view of economics. A CAPEX value of 13.1 M€ was estimated, which could be compared with the one obtained in the conventional plant (12.5 M€). However, NPV values are negative and IRR lower than 8.1% in both cases, thus the proposed plant is not economically feasible under the assumptions made in the conservative sub-scenarios. TCPs calculated in the two scenarios are 1.5 €·kg^{-1} and 1.4 €·kg^{-1}, respectively, which tripled the estimated TCP in the conventional route (0.50 €·kg^{-1}).

Table 8. Economic KPIs of the CO_2 utilization plant in the sub-scenarios $B_{-2.5}$ and $B_{-4.45}$

KPI	UNIT	$B_{-2.5}$	$B_{-4.45}$
ISBL	M€	6.0	6.0
OSBL investment	M€	2.4	2.4
TFCC	M€	12.0	11.9
CAPEX	M€	13.1	13.1
ACC	M€	1.22	1.22
VCP	€·kg^{-1}	1.3	1.2
FCP	M€·yr^{-1}	2.2	2.2
CCOP	M€·yr^{-1}	17.3	15.2
Gross margin	M€·yr^{-1}	8.8	8.8
Gross profit	M€·yr^{-1}	-9.5	-7.6
TCP	€·kg^{-1}	1.5	1.4
NPV	M€	<0.0	<0.0
IRR	%	<8.1	<8.1
BCR		0.4	0.5

Figure 4 demonstrates that consumables present a noted contribution to the VCP together with the electricity, which remains as the main contributor in both scenarios, being the steam for the purification step the third contributor. The positive values obtained for the gross profit demonstrated that the benefits for selling FA and by-products are higher than the cost of raw materials; however, the TCP is now as high as twice the revenues. This fact is demonstrated by the values of BCR obtained in the assessment, which are below 0.5 in both scenarios. Therefore, the production costs need to be reduced to become the ER plan profitable. Then, a series of sensitivity analyses are needed in order to know the situations in which the project could become profitable.

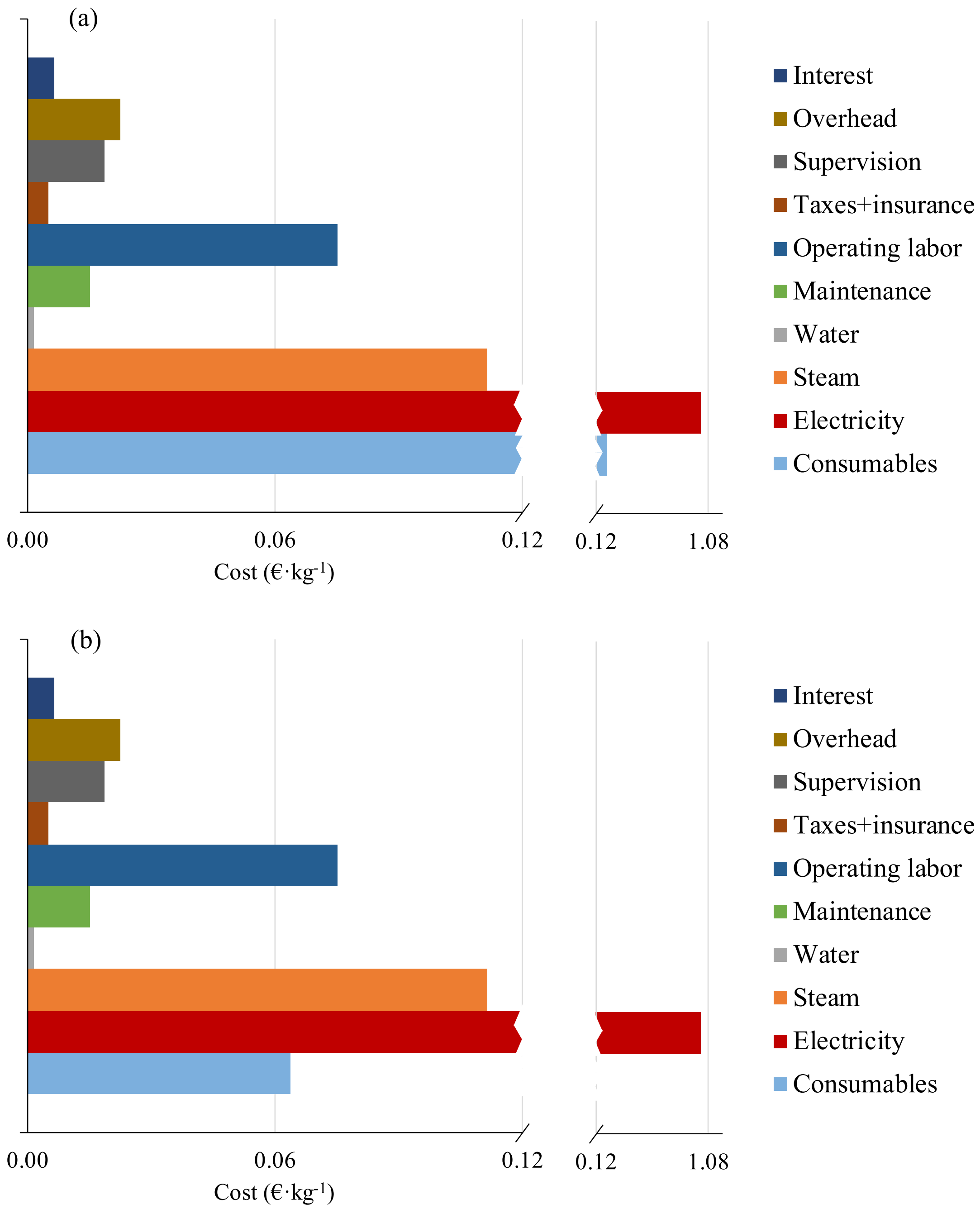

Figure 4. Breakdown of the variable cost of production (VCP) in the scenarios: (a) $B_{-2.5}$ and (b) $B_{-4.45}$

3.3. Sensitivity analysis

As mentioned above, the interest rate *i* varies widely within the EU medium and large member states (Fernandez et al., 2018) reaching values between 10.4% in Portugal and 6.7% in Germany in 2018. Figure 5 displays the results of the sensitivity analysis of the influence of the *i* rate in the NPV of the project for different scenarios. The range analysed is between the minimum and maximum values of 6.7% and 10.4% that are those corresponding to Germany and Portugal, respectively. According to the results obtained in the analysis, the influence of the *i* rate in the project profitability under the conditions of E_{min-20}, $B_{4.45}$ and Conv are almost the same as the three lines are overlapped. Note that the project $B_{-4.45}$ was not economically viable under the current electricity market price (85 €·MWh^{-1}). Then, the sensitivity analysis carried out here for $B_{-4.45}$ (green line) assumes the accessibility of the plant to an inexpensive energy source. Then, the electricity price was set using a LCOE value of 20.0 €·MWh^{-1}. Interest rates higher than 11.5% means a negative value of the NPV for the realistic ER scenario. As a result, it is clear that under the hypothesis formulated in $B_{-4.45}$ supposing the access to an inexpensive renewable source, similar environmental and economic results would be obtained for the FA production by the ER or the conventional routes highlighting the relevant savings in fossil resources such as fuel oil and natural gas of the ER route.

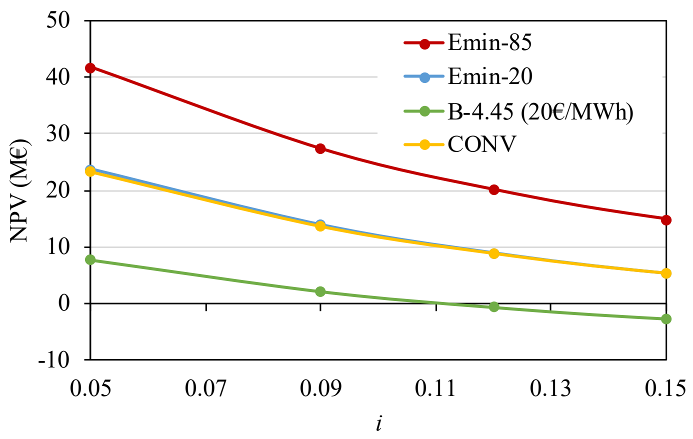

Figure 5. Sensitivity analysis of the NPV to the interest rate (*i*)

The NPV evolution with the period of time for a fixed interest rate of 8.1% is displayed in Figure 6. The payback periods of the studied scenarios E_{min-85}, E_{min-20}, Conv and $B_{-4.45}$ are 3.4 yr, 5.9 yr, 5.7 yr and 12.7 yr, respectively. This latter value is of relevance, as it states that more than 12 yr are needed for the return of the investment under the consideration of a 21% wt. FA at the outlet of the ER under the interest rate *i* of 8.1%.

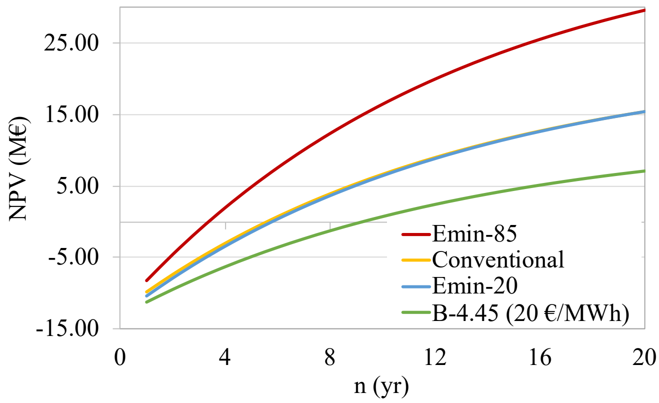

Figure 6. Evolution of the NPV with the period of time (n)

Despite the payback period of the scenario $B_{-4.45}$ (when it uses an inexpensive energy source) is under 20 years, the value doubles the corresponding payback period of the conventional plant. This fact was initially expected considering the low TRL of the ER route, being the high consumption of electricity per unit of mass of FA the main consequence. As it was previously mentioned, the current energy consumption by ER of CO_2 to produce 1 kg of FA (together with 0.16 kg of H_2O to reach 85% wt.) is in the order or 11.8 kWh (please see Table 5). In contrast, the minimum theoretical value of energy consumption in ER per kg of FA produced is as low as 1.75 kWh. Note that 1.75 kWh is the minimum theoretical energy and it cannot be achieved in practice. Being the gap 11.8 kWh to 1.75 kWh, a remarkable margin of improvement of the ER technology does exist in the medium/long term. A sensitivity analysis of the influence of the electricity consumption in the IRR of the plant was carried out. It was analysed the influence of the specific energy consumption ratio respect the minimum theoretical specific energy (ratio E/E_{min}) in the IRR. The scenario considered here employed the realistic ER features of $B_{-4.45}$ (cathode lifetime of 4.45 yr; membrane lifetime of 6.84 yr; anode lifetime of 10 yr; FA concentration at the outlet stream of ER of 21% wt.) using a fixed CO_2 market price of 20 €·ton^{-1} and a LCOE of 20.0 €·MWh^{-1} for the electricity price. According to the results obtained in the sensitivity analysis (Figure 7), it could be then predicted that the ER of CO_2 route could be profitable in a mid-term horizon under proper technological developments regarding the energy efficiency together with the cathode durability and FA concentration at outlet stream of ER. Moreover, the access to an inexpensive energy source or even the employ of mechanisms as the application of Power Purchase Agreements (PPAs) could introduce a new possibility for a risk-controlled agreement to purchase and to sale energy between the utility and the PV electricity generator (Bruck et al., 2018). These could help to become these CO_2 utilization FA plants less sensitive to the cost of renewable energy.

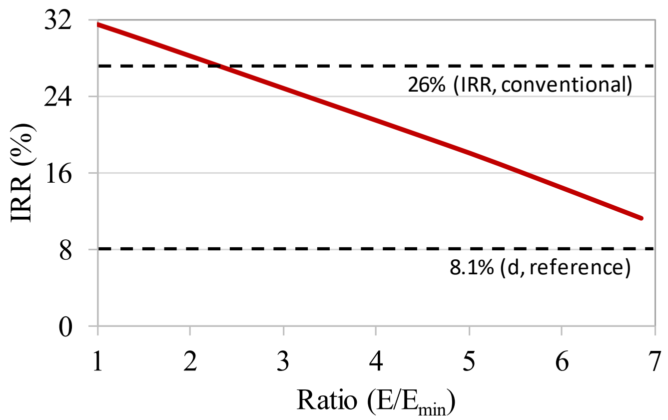

Figure 7. Analysis of the influence of the ratio between the ER energy consumption respect the minimum theoretical energy (1.75 kWh) in the IRR of the plant.

Conclusions

This study has carried out a techno-economic evaluation of a CO_2 utilization process based on the electrochemical reduction (ER) of captured CO_2 to produce formic acid (FA). The technical evaluation has shown the potential of this route to reduce the fossil resource consumption within the CO_2 abatement objectives. Despite the environmental benefits of this utilization option in terms of resources savings as the CF is made even, the economic KPIs obtained have indicated that it is not yet profitable and competitive under current market conditions considering the FA commercial process as a benchmark. The technology needs further R&D considering its low associated TRL, especially to decrease the notable influence of the electricity consumption and the electrodes durability in the cost of operation and consumables, respectively, which results in high production costs. Under the set of hypotheses considered in this study, a cathode lifetime over 4.45 yr would keep the influence of the consumable cost in the total cost of production below 10%. No doubt, favourable market conditions such as the access to low-cost renewable electricity and the application of a meaningful price regarding CO_2 emissions (e.g. within the EU emissions trading system (EU ETS)) are essential to make this process profitable. A sensitivity analysis was carried out to demonstrate the noticeable influence of the electrical power consumption by ER in the profitability of the plant. The results obtained in this study indicate that the ER of CO_2 route could be potentially profitable in a mid-term horizon under certain improvements in the specific energy consumption, and under proper technological developments regarding the cathode durability. The study has demonstrated that the electrification of this kind of commodity production plants through inexpensive surpluses of renewable energy is a requirement for their future competitiveness.

Acknowledgments Authors thank to Spanish Ministry of Economy and Competitiveness (MINECO) for the financial support through the project CTQ2016-76231-C2-1-R. We would like also to thank MINECO for providing Marta Rumayor with a Juan de la Cierva postdoctoral contract (FJCI-2015-23658).

References

Agarwal, A.S., Zhai, Y., Hill, D., Sridhar, N., 2011. The electrochemical reduction of carbon dioxide to formate/formic acid: Engineering and economic feasibility. ChemSusChem 4, 1301–1310. https://doi.org/10.1002/cssc.201100220

Albo, J., Sáez, A., Solla-Gullón, J., Montiel, V., Irabien, A., 2015. Production of methanol from CO 2 electroreduction at Cu 2 O and Cu 2 O/ZnO-based electrodes in aqueous solution. “Applied Catalysis B, Environmental” 176–177, 709–717.

https://doi.org/10.1016/j.apcatb.2015.04.055

Alper, E., Orhan, O.Y., 2017. CO2 utilization: Developments in conversion processes. Petroleum 3, 109–126. https://doi.org/10.1016/j.petlm.2016.11.003

Arends, J.B.A., Patil, S.A., Roume, H., Rabaey, K., 2017. Continuous long-term electricity-driven bioproduction of carboxylates and isopropanol from CO 2 with a mixed microbial community. Journal of CO2 Utilization 20, 141–149. https://doi.org/10.1016/j.jcou.2017.04.014

Aspen Technology Inc., 2019. ASPEN PLUS v9.

Barbarossa, V., Vanga, G., Viscardi, R., Gattia, D.M., 2014. CO2as carbon source for fuel synthesis. Energy Procedia 45, 1325–1329. https://doi.org/10.1016/j.egypro.2014.01.138

BP Energy Economics, 2018. 2018 BP Energy Outlook 2018 BP Energy Outlook, 2018 BP Energy Outlook. https://doi.org/10.1088/1757-899X/342/1/012091

Bushuyev, O.S., De Luna, P., Dinh, C.T., Tao, L., Saur, G., van de Lagemaat, J., Kelley, S.O., Sargent, E.H., 2018. What Should We Make with CO2and How Can We Make It? Joule 2, 825–832. https://doi.org/10.1016/j.joule.2017.09.003

Centi, G., Perathoner, S., 2009. Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. Catalysis Today 148, 191–205. https://doi.org/10.1016/J.CATTOD.2009.07.075

Choi, J., Kim, M.J., Ahn, S.H., Choi, I., Jang, J.H., Ham, Y.S., Kim, J.J., Kim, S.K., 2016. Electrochemical CO2reduction to CO on dendritic Ag-Cu electrocatalysts prepared by electrodeposition. Chemical Engineering Journal 299, 37–44. https://doi.org/10.1016/j.cej.2016.04.037

de Pee, A., Pinner, D., Roelofsen, O., Somers, K., Speelman, E., Witteveen, M., 2018. Decarbonization of industrial sectors: the next frontier.

Del Castillo, A., Alvarez-Guerra, M., Solla-Gullón, J., Sáez, A., Montiel, V., Irabien, A., 2017.

Sn nanoparticles on gas diffusion electrodes: Synthesis, characterization and use for continuous CO2 electroreduction to formate. Journal of CO2 Utilization 18, 222–228. https://doi.org/10.1016/j.jcou.2017.01.021

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

Dinh, C.-T., Burdyny, T., Kibria, G., Seifitokaldani, A., Gabardo, C.M., Pelayo García De Arquer, F., Kiani, A., Edwards, J.P., De Luna, P., Bushuyev, O.S., Zou, C., Quintero-Bermudez, R., Pang, Y., Sinton, D., Sargent, E.H., 2018. CO2 electroreduction to ethylene via hydroxide-mediated copper catalysis at an abrupt interface. Science 360, 783–787. https://doi.org/10.1126/science.aas9100

Dominguez-Ramos, A., Singh, B., Zhang, X., Hertwich, E.G., Irabien, A., 2015. Global warming footprint of the electrochemical reduction of carbon dioxide to formate. Journal of Cleaner Production 104, 148–155. https://doi.org/10.1016/j.jclepro.2013.11.046

Drury, D.J., 2013. Formic acid, in: Kirk-Othmer Encyclopedia of Chemical Technology. John Wiley & Sons, Inc., pp. 1–9. https://doi.org/https://doi.org/10.1002/0471238961.0615181304182118.a01.pub2

Eppinger, J., Huang, K.-W., 2017. Formic Acid as a Hydrogen Energy Carrier. ACS Energy Letters 2, 188–195. https://doi.org/10.1021/acsenergylett.6b00574

European Commission, 2018. ECU/EUR exchange rates versus national currencies [WWW Document]. URL http://ec.europa.eu/eurostat/web/products-datasets/product?code=TEC00033 (accessed 6.5.18).

European Commission, 2015a. Technology readiness levels (TRL). HORIZON 2020 – WORK PROGRAMME 2014-2015 General Annexes, Extract from Part 19 - Commission Decision C 4995.

European Commission, 2015b. The European Commission’s welcome page on the EU ETS

[WWW Document]. URL http://ec.europa.eu/clima/policies/ets/index_en.htm (accessed 10.25.18).

European Zero Emission Technology and Innovation Platform (ETIP-ZEP), 2018. Role of CCUS in a below 2 degrees scenario.

Eurostat, 2017a. Wages and labour costs [WWW Document]. URL http://ec.europa.eu/eurostat/statistics-explained/index.php/Wages_and_labour_costs#Labour_costs (accessed 7.12.18).

Eurostat, 2017b. Statistics Explained [WWW Document]. URL http://ec.europa.eu/eurostat/statistics-explained/index.php?title=Energy_price_statistics&redirect=no (accessed 6.5.18).

Fernandez, P., Pershin, V., Fernández Acín, I., 2018. Market Risk Premium and Risk-Free Rate used for 59 Countries in 2018: A Survey, Market Risk Premium and Risk-Free Rate used for 59 countries in 2018. https://doi.org/10.2139/ssrn.3155709

Ganesh, I., 2016. Electrochemical conversion of carbon dioxide into renewable fuel chemicals - The role of nanomaterials and the commercialization. Renewable and Sustainable Energy Reviews. https://doi.org/10.1016/j.rser.2016.01.026

Global CO2 Initiative, CO2 Sciences Inc., 2016. Global Roadmap for Implementing CO2 Utilization. https://doi.org/10.1007/s11661-016-3882-z

Gunter, D., 1984. Photochemical Machining. Engineering (London) 224. https://doi.org/10.1002/14356007.o13

Hietala, J., Vouri, A., Pekka, J., Ilkka, P., Reutemann, W., Heinz, K., 2000. Formic Acid, in: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH, Weinheim, Germany, pp. 1–22. https://doi.org/10.1002/14356007.a12_013

Hu, B., Guild, C., Suib, S.L., 2013. Thermal, electrochemical, and photochemical conversion of CO2to fuels and value-added products. Journal of CO2 Utilization 1, 18–27.

https://doi.org/10.1016/j.jcou.2013.03.004

Jarvis, S.M., Samsatli, S., 2018. Technologies and infrastructures underpinning future CO2 value chains: A comprehensive review and comparative analysis. Renewable and Sustainable Energy Reviews 85, 46–68. https://doi.org/10.1016/j.rser.2018.01.007

Jhong, H.-R. "Molly," Ma, S., Kenis, P.J., 2013. Electrochemical conversion of CO2 to useful chemicals: current status, remaining challenges, and future opportunities. Current Opinion in Chemical Engineering 2, 191–199. https://doi.org/10.1016/j.coche.2013.03.005

Jouny, M., Luc, W.W., Jiao, F., 2018. A General Techno-Economic Analysis of CO_2 Electrolysis Systems. Industrial & Engineering Chemistry Research acs.iecr.7b03514. https://doi.org/10.1021/acs.iecr.7b03514

Kauffman, D.R., Thakkar, J., Siva, R., Matranga, C., Ohodnicki, P.R., Zeng, C., Jin, R., 2015. Efficient Electrochemical CO2 Conversion Powered by Renewable Energy. ACS Applied Materials and Interfaces 7, 15626–15632. https://doi.org/10.1021/acsami.5b04393

Kondratenko, E. V., Mul, G., Baltrusaitis, J., Larrazábal, G.O., Pérez-Ramírez, J., 2013. Status and perspectives of CO2 conversion into fuels and chemicals by catalytic, photocatalytic and electrocatalytic processes. Energy & Environmental Science 6, 3112–3135. https://doi.org/10.1039/c3ee41272e

Kumar, B., Brian, J.P., Atla, V., Kumari, S., Bertram, K.A., White, R.T., Spurgeon, J.M., 2016. New trends in the development of heterogeneous catalysts for electrochemical CO2reduction. Catalysis Today 270, 19–38. https://doi.org/10.1016/j.cattod.2016.02.006

Li, H., Oloman, C., 2006. Development of a continuous reactor for the electro-reduction of carbon dioxide to formate – Part 1: Process variables. Journal of Applied Electrochemistry 36, 1105–1115. https://doi.org/10.1007/s10800-006-9194-z

Lu, X., Wu, Y., Yuan, X., Huang, L., Wu, Z., Xuan, J., Wang, Y., Wang, H., 2018. High-Performance Electrochemical CO2Reduction Cells Based on Non-noble Metal Catalysts.

ACS Energy Letters 2527–2532. https://doi.org/10.1021/acsenergylett.8b01681

Lu, Y., Han, B., Tian, C., Wu, J., Geng, D., Wang, D., 2018. Efficient electrocatalytic reduction of CO2 to CO on an electrodeposited Zn porous network. Electrochemistry Communications 97, 87–90. https://doi.org/10.1016/J.ELECOM.2018.11.002

Malik, M.I., Omar, Z., Atieh, M., Abussaud, B., 2016. Electrochemical reduction of CO 2 to methanol over MWCNTs impregnated with Cu 2 O. Chemical Engineering Science 152, 468–477. https://doi.org/10.1016/j.ces.2016.06.035

Martín, A.J., Larrazábal, G.O., Pérez-Ramírez, J., Mailänder, V., 2016. Towards sustainable fuels and chemicals through the electrochemical reduction of CO2: lessons from water electrolysis. https://doi.org/10.1039/x0xx00000x

Maru, M.S., Ram, S., Shukla, R.S., Khan, N. ul H., 2018. Ruthenium-hydrotalcite (Ru-HT) as an effective heterogeneous catalyst for the selective hydrogenation of CO2 to formic acid. Molecular Catalysis 446, 23–30. https://doi.org/10.1016/j.mcat.2017.12.005

Methanex Corporation [WWW Document], 2015. URL https://www.methanex.com (accessed 6.5.18).

Meylan, F.D., Moreau, V., Erkman, S., 2015. CO2utilization in the perspective of industrial ecology, an overview. Journal of CO2 Utilization 12, 101–108. https://doi.org/10.1016/j.jcou.2015.05.003

Norhasyima, R.S., Mahlia, T.M.I., 2018. Advances in CO2utilization technology: A patent landscape review. Journal of CO2 Utilization 26, 323–335. https://doi.org/10.1016/j.jcou.2018.05.022

Oloman, C., Li, H., 2008. Electrochemical processing of carbon dioxide. ChemSusChem 1, 385–391. https://doi.org/10.1002/cssc.200800015

Perdan, S., Jones, C.R., Azapagic, A., 2017. Public awareness and acceptance of carbon capture and utilisation in the UK. Sustainable Production and Consumption 10, 74–84.

https://doi.org/10.1016/j.spc.2017.01.001

Pérez-Fortes, M., Schöneberger, J.C., Boulamanti, A., Harrison, G., Tzimas, E., 2016. Formic acid synthesis using CO2 as raw material: Techno-economic and environmental evaluation and market potential. International Journal of Hydrogen Energy 41, 16444–16462. https://doi.org/10.1016/j.ijhydene.2016.05.199

PolyTechs Technology [WWW Document], 2018. URL https://www.polytechs.co.jp/en_index.html (accessed 11.19.18).

Roh, K., Lee, J.H., Gani, R., 2016. A methodological framework for the development of feasible CO2conversion processes. International Journal of Greenhouse Gas Control 47, 250–265. https://doi.org/10.1016/j.ijggc.2016.01.028

Roh, K., Lim, H., Chung, W., Oh, J., Yoo, H., Al-Hunaidy, A.S., Imran, H., Lee, J.H., 2018. Sustainability analysis of CO2capture and utilization processes using a computer-aided tool. Journal of CO2 Utilization 26, 60–69. https://doi.org/10.1016/j.jcou.2018.04.022

Rozière, J., Jones, D.J., 2003. Non-Fluorinated Polymer Materials for Proton Exchange Membrane Fuel Cells. Annual Review of Materials Research 33, 503–555. https://doi.org/10.1146/annurev.matsci.33.022702.154657

Rumayor, M., Dominguez-Ramos, A., Irabien, A., 2019. Environmental and economic assessment of the formic acid electrochemical manufacture using carbon dioxide : Influence of the electrode lifetime. Sustainable Production and Consumption 18, 72–82. https://doi.org/10.1016/j.spc.2018.12.002

Rumayor, M., Dominguez-Ramos, A., Irabien, A., 2018. Formic Acid Manufacture: Carbon Dioxide Utilization Alternatives. Applied Sciences 2018, Vol. 8, Page 914 8, 914. https://doi.org/10.3390/APP8060914

Schiffer, Z.J., Manthiram, K., 2017. Electrification and Decarbonization of the Chemical Industry. Joule 1, 10–14. https://doi.org/10.1016/j.joule.2017.07.008

Scialdone, O., Galia, A., Nero, G. Lo, Proietto, F., Sabatino, S., Schiavo, B., 2016. Electrochemical reduction of carbon dioxide to formic acid at a tin cathode in divided and undivided cells: effect of carbon dioxide pressure and other operating parameters. Electrochimica Acta 199, 332–341. https://doi.org/10.1016/J.ELECTACTA.2016.02.079

Scibioh, M.A., Viswanathan, B., 2018. Electrochemical Reduction of CO2, Carbon Dioxide to Chemicals and Fuels. https://doi.org/10.1016/B978-0-444-63996-7.00007-9

Sharma, S., Patle, D.S., Gadhamsetti, A.P., Pandit, S., Manca, D., G S, N., 2018. Intensification and performance assessment of the formic acid production process through a dividing wall reactive distillation column with vapor recompression. Chemical Engineering and Processing: Process Intensification 123, 204–213. https://doi.org/10.1016/j.cep.2017.11.016

Shen, F. xia, Shi, J., Chen, T. you, Shi, F., Li, Q. yuan, Zhen, J. zheng, Li, Y. fei, Dai, Y. nian, Yang, B., Qu, T., 2018. Electrochemical reduction of CO2to CO over Zn in propylene carbonate/tetrabutylammonium perchlorate. Journal of Power Sources 378, 555–561. https://doi.org/10.1016/j.jpowsour.2017.12.078

Solutions, I., 2003. ABB's Industrial sets the pace for formic acid production in Kemira, ABB Inc. https://doi.org/10.1038/224826b0

Spurgeon, J.M., Kumar, B., 2018. A comparative technoeconomic analysis of pathways for commercial electrochemical CO2 reduction to liquid products. Energy & Environmental Science 0–18. https://doi.org/10.1039/C8EE00097B

Sternberg, A., Bardow, A., 2015. Power-to-What?-Environmental assessment of energy storage systems. Energy and Environmental Science 8, 389–400. https://doi.org/10.1039/c4ee03051f

Suzuki, T.M., Takayama, T., Sato, S., Iwase, A., Kudo, A., Morikawa, T., 2018. Enhancement of CO2 reduction activity under visible light irradiation over Zn-based metal sulfides by combination with Ru-complex catalysts. Applied Catalysis B: Environmental 224, 572–578. https://doi.org/10.1016/j.apcatb.2017.10.053

Swiss Centre for Life Cycle Inventories, 2016. The ecoinvent database Version 3 [WWW Document]. URL http://www.ecoinvent.org (accessed 5.3.18).

Szima, S., Cormos, C.C., 2018. Improving methanol synthesis from carbon-free H2and captured CO2: A techno-economic and environmental evaluation. Journal of CO2 Utilization 24, 555–563. https://doi.org/10.1016/j.jcou.2018.02.007

Towler, G., Sinnott, R., 2013. Chemical Engineering Design, Principles, practice, and economics of plant design.

Tribe, M.., Alpine, R.L.., 1986. Scale economies and the “0.6 rule.” Engineering Costs and Production Economics 10, 271–278.

United Nations Framework Convention on Climate Change (UNFCCC), 2016. The Paris Agreement [WWW Document]. URL http://unfccc.int/paris_agreement/items/9485.php (accessed 10.31.17).

Vartiainen, E., Masson, G., Breyer, C., 2015. PV LCOE IN EUROPE 2014-30 - Final Report 23 June 2015 1–15.

Wang, C., Cao, M., Jiang, X., Wang, M., Shen, Y., 2018. A catalyst based on copper-cadmium bimetal for electrochemical reduction of CO2to CO with high faradaic efficiency. Electrochimica Acta 271, 544–550. https://doi.org/10.1016/j.electacta.2018.03.156

Wang, W.-H., Himeda, Y., Muckerman, J.T., Manbeck, G.F., Fujita, E., 2015. CO2 Hydrogenation to Formate and Methanol as an Alternative to Photo- and Electrochemical CO2 Reduction. Chemical Reviews 115, 12936–12973. https://doi.org/10.1021/acs.chemrev.5b00197

Yan, N., Philippot, K., 2018. Transformation of CO2 by using nanoscale metal catalysts: cases studies on the formation of formic acid and dimethylether. Current Opinion in Chemical

Engineering 20, 86–92. https://doi.org/10.1016/j.coche.2018.03.006

Yang, H., Kaczur, J.J., Sajjad, S.D., Masel, R.I., 2017. Electrochemical conversion of CO2 to formic acid utilizing Sustainion™ membranes. Journal of CO2 Utilization 20, 208–217. https://doi.org/10.1016/j.jcou.2017.04.011

Yang, Z.-Z., Zhang, H., Yu, B., Zhao, Y., Ji, G., Liu, Z., 2015. A Troger's base-derived microporous organic polymer: design and applications in CO2/H2 capture and hydrogenation of CO2 to formic acid. Chemical Communications 51, 1271–1274. https://doi.org/10.1039/C4CC08295H

Zero Emissions Platform, 2015. CCU – carbon capture and utilisation 1–23.

Zhao, S., Guo, S., Zhu, C., Gao, J., Li, H., Huang, H., Liu, Y., Kang, Z., 2017. Achieving electroreduction of CO_2 to CH_3OH with high selectivity using a pyrite–nickel sulfide nanocomposite. RSC Adv. 7, 1376–1381. https://doi.org/10.1039/C6RA26868D