Bringing value to the chemical industry from capture, storage and use of CO_2: a dynamic LCA of formic acid production

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Abstract

Low carbon options for the chemical industry include switching from fossil to renewable energy, adopting new low-carbon production processes, along with retrofitting current plants with carbon capture for ulterior use (CCU technologies) or storage (CCS). In this paper, we combine a dynamic Life Cycle Assessment (d-LCA) with economic analysis to explore a potential transition to low-carbon manufacture of formic acid. We propose new methods to enable early technical, environmental and economic assessment of formic acid manufacture by electrochemical reduction of CO_2 (CCU), and compare this production route to the conventional synthesis pathways and to storing CO_2 in geological storage (CCS). Both CCU and CCS reduce carbon emissions in particular scenarios, although the uncertainty in results suggests that further research and scale-up validation are needed to clarify the relative emission reduction compared to conventional process pathways. There are trade-offs between resource security, cost and emissions between CCU and CCS systems. As expected, the CCS technology yields greater reductions in CO_2 emissions than the CCU scenarios and the conventional processes. However, compared to CCS systems, CCU has better economic potential and lower fossil consumption, especially when powered by renewable electricity. The integration of renewable energy in the chemical industry has an important climate mitigation role, especially for processes with high electrical and thermal energy demands.

1. Introduction

At COP21, parties to the UNFCCC reached the Paris Agreement (UN, 2015), which aims to bolster global climate change mitigation efforts in order to keep a global temperature rise this century well below 2 °C. In response, the IPCC published a special report on greenhouse gas emission pathways to limit global warming to 1.5 °C (IPCC, 2018). They conclude that global anthropogenic greenhouse gas emissions must be reduced by 45% from 2010 levels in 2030, and further reduced to net zero by 2050.

Since some emissions are extremely difficult to mitigate, for example from agriculture, achieving net zero emissions will require substantial efforts in all areas where emissions can be avoided or captured, across power generation, homes, industry and transport. GHG emissions from the chemical industry could be reduced by increasing process energy and resource efficiency, and by using low-carbon power and more sustainable feedstocks. For products containing carbon that will be ultimately released to the atmosphere as CO_2, such as formic acid, there will be a need to use sustainable carbon. CO_2 can be a feedstock for some chemical processes including formic acid and could be obtained from fossil fuel electricity generation plants rather than from combusting fossil fuels in the future (Wilmet, 2016), in a process termed carbon capture and utilisation (CCU).

The difference between CCU and carbon capture and storage (CCS) is the final use of the captured CO_2. CCS technologies remove CO_2 from gas streams and transport it to a geological site for long-term storage, including depleted oil and gas reservoirs. CCU instead converts captured CO_2 into commercial products (Mac Dowell et al. 2017).

In spite of the predominance of CCS in most of the mitigation pathways compliant with the Paris target, high investment and operating costs, as well as cross-chain risks have dissuaded its deployment at the required scale (Daggash et al. 2018). CCS technologies face a number of technical and economic barriers that must be overcome before it can be deployed on a large scale (Cuéllar-Franca et al. 2015). At the same time, research shows negligible contribution of CCU to the global CO_2 mitigation challenge and suggests that, from a commercial and policy perspective, CCU should be encouraged when and only when CO_2 is useful as a cheap feedstock, or when it can be robustly and reliably shown that the CO_2-derived product can reasonably displace the incumbent product (Mac Dowell et al. 2017). Yet the European chemical industry could become a key consumer of CO_2 for CCS and/or CCU applications in the future, if the power sector was to become fully decarbonised (Mathy et al. 2018; McDowall et al. 2018). Furthermore, CCU could be critical in the near-term to support the development of early CCS infrastructure. In this overall context, a debate has arisen around the relative benefits of CCU and CCS, introducing divergent perspectives about the role of CO_2 utilization compared to storage in mitigating climate change. Some studies have chosen to group them as carbon capture and storage or utilisation (CCUS) (BEIS, 2018).

In recent years, the interest for researching CCUS systems has grown as evidenced by several published reviews of the available techniques and technologies. Tabbi et al. (2019) include an evaluation of the most modern technologies used in CO_2 capture, reviewing the main capture strategies, including post-combustion, pre-combustion and oxy-combustion. In the same line, Al-Mamoori et al. (2017) present various carbon-capture routes, reviewing the technological and the economic performance extensively studied in last years. These routes include absorption-based CO_2 capture by chemical or physical solvents, membranes, and chemical looping. These works discuss the latest advances made by the research community to support the development of affordable CCS systems. On the other hand, Norhasyima and Mahlia (2018) methodically review patents on CO_2 utilization technologies for CCUS application over last 20 years. Recent advances include enhancements to the state-of-the-art technologies, including enhanced oil recovery (EOR) and enhanced coal-bed methane (ECBM), chemical and fuel, mineral carbonation, biological algae cultivation and enhanced geothermal system (EGS), and hybrid concepts such as in photobioreactor in algae cultivation, chemical reaction and EGS. All these studies present as a common basis the recommendation to move towards methods and technologies that meet economic needs, security, non-dependence on location and respect for the environment.

The full potentials of CCU and CCS are unclear as most CCUS technologies are in early stage of development and neither their potential, cost-effectiveness, nor their impact on CO_2 emission reductions are well understood. A number of studies assessed the environmental impacts of CCS and CCU technologies using an attributional life cycle approach. Cuellar-Franca and Azapagic (2015) and (2017) undertook a critical analysis and comparison of the life cycle environmental impact of carbon capture, storage, and utilization technologies. Their analysis is an excellent starting point for understanding the methodological challenges and the main impacts of these technologies, as well as to identify the remaining research gaps. According to these authors, the attributional analyses are difficult to compare, as they have different goals and scopes, system boundaries, allocation methods and functional units against which the impacts are estimated. Moreover, the data quality is uncertain since most systems are still at the development stage and real operational data are not available (Cuellar-Franca and Azapagic, 2015).

One disadvantage of attributional LCA is that it does not account for CO_2 variations over time. For example, under decarbonisation pathways compatible with the Paris target, the power sector should undergo a significant decarbonisation, affecting the emissions of all the sectors using electricity. An alternative "dynamic" approach to LCA enables us to understand the efficiency of CCS and CCU technologies to reduce atmospheric CO_2 emissions over time. This paper proposes a dynamic LCA as a tool to analyse the potential benefits of CCS vs. CCU technologies for producing formic acid (FA).

In this paper, we explore dynamic CO_2 emissions, fossil resource consumption and economic profiles of producing formic acid (FA) by electrochemical reduction (ER) of CO_2 (ER FA). Accordingly, this work addresses two research questions:

1. How do different configurations of the ER FA process (CCUS) compare in terms of emissions, fossil resource consumption and economic costs to conventional ways of producing FA?
2. What are the environmental and economic trade-offs between using captured CO_2 for ER FA vs. sending it to permanent geological storage (CCS)?

In answering these questions, we focus on two key LCA methodological challenges: (i) how to include the time dimension in LCA; and, (ii) how the system boundaries should be set around chemical processes to include the influence of the whole energy system. The paper is structured in two main parts. Section 2 describes in detail the CCU and CCS systems and scenarios we analyse, as well as the dynamic approach to LCA enabling to assess the efficiency of CCS and CCU technologies to reduce CO_2 emissions under two global climate mitigation scenarios. Section 3 and Section 4 introduce the main results and discussion of the study. In particular, the first part includes a full discussion of the technology performance, the energy assessment, the carbon footprint and the techno-economic evaluation. The last part reviews the overall d-LCA results in order to determine environmental performance and expected improvement measures. The paper ends with the main conclusions and the future challenges.

2. Materials and methods

2.1. Goal and scope

The goal and scope of the study is to estimate the change in greenhouse gas emissions and fossil resource consumption caused by the implementation of an emergent CCU technology, i.e. ER process for the synthesis of FA from captured CO_2. As a benchmark for comparison is the current commercial FA production by hydrolysis of methyl formate. An additional goal of this analysis is to investigate whether the implementation of CCU in combination with partial carbon storage (CCS) is a viable option for further reducing the carbon emissions from FA production. The results are expected to provide an interesting field for discussion on the suitability of using CCU vs. CCS with a dynamic energy and greenhouse gas emissions approach.

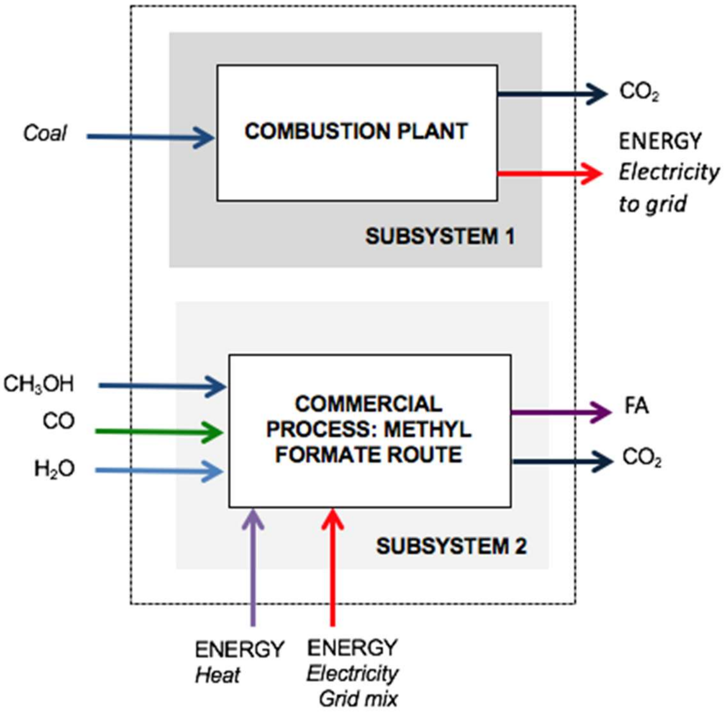


Figure 1. Conventional process system flowchart, including combustion plant (subsystem 1) and FA conventional process (subsystem 2).

2.2.Function, functional unit and system boundaries

The ER process for the synthesis of FA from captured CO_2 includes two main parts: the capture of CO_2 emissions from a coal power plant, and the use of this CO_2 as feedstock for FA. Therefore, the function of the benchmark and alternative systems is FA production and electricity supply. In order to define the functional unit of the work, we chose the current European production rate of FA as reference, and a coal combustion plant of 500 MW capacity to supply energy to the grid. In this context, the benchmark system produces 350 kt FA at a commercial concentration of 85% wt (Perez-Fortes et al. 2016a). To obtain the necessary amount of CO_2 and energy to produce 350 kt FA by the conventional process, we considered a 500 MW capacity coal plant. Note that these plants are hypothetical ones, chosen for simplicity in this study to provide the energy and CO_2 necessary for producing the full amount of FA currently produced within the EU. In practice, CO_2 could be captured from smaller fossil plants and transported to the ER FA plant, but these scenarios are out of scope in this study. Nevertheless, the methods we describe below can be used for analysing the latter scenario.

The benchmark system (Figure 1) comprises the coal combustion and FA manufacture plants. The power plant is assumed to supply electricity to the grid. Conventional FA plants use the hydrolysis of methyl formate. The process has two stages: (i) carboxylation of methanol with carbon monoxide ($CH_3OH + CO \rightarrow HCOOCH_3$); and, (ii) hydrolysis of methyl formate to FA and CO_2 ($CH_3OOCH + H_2O \rightarrow CO_2 + HCOOH$) (Hietala et al., 2000).

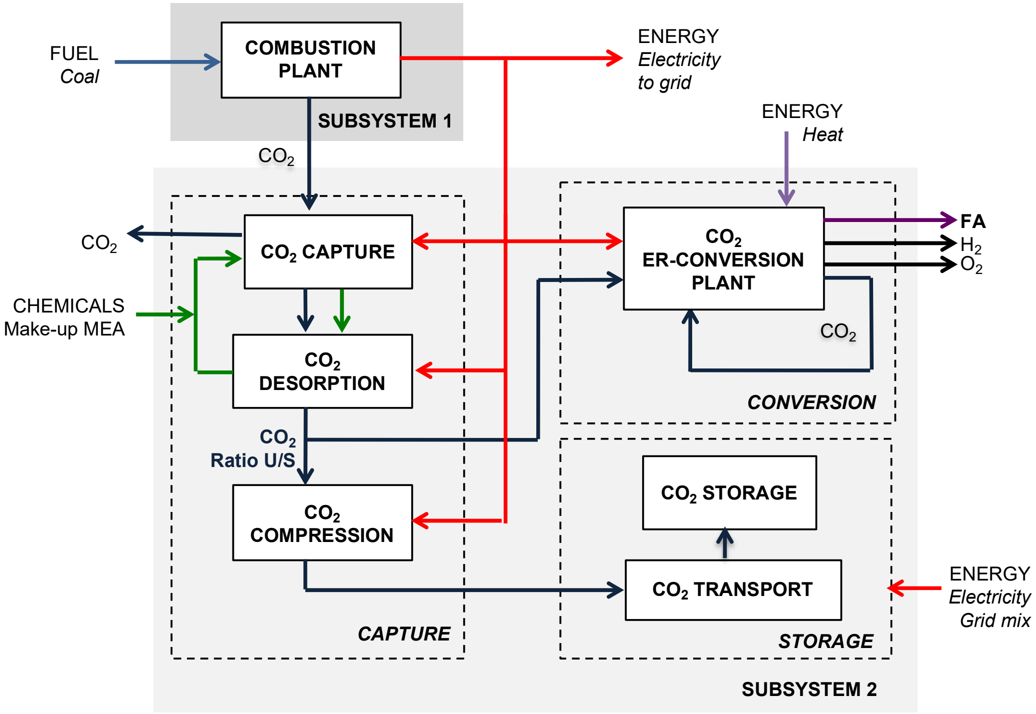


Figure 2. Process flowchart of the suggested process structure for the combustion plant with post combustion capture, and the CCS and CCU units, the latter including the ER FA plant.

Alternative low-carbon approaches that convert CO_2 to formic acid (FA) include homogeneous (Wang et al. 2015, and Perez-Fortes et al. 2016a) and heterogeneous catalysis, photocatalytic reduction, and electrochemical reduction (Rumayor et al. 2018). These technologies are currently found at different stages in terms of maturity, but they should be economically viable, safe, and sustainable for their final industrial**.** Among them, catalytic synthesis of FA from CO_2 and H_2 presents the highest technology readiness levels (TRL) as it is based on available technology. However, the hydrogen synthesis is the weak spot of this option (Perez-Fortes et al. 2016a). Hydrogen synthesis involves an input of energy if it is carried out on an in-situ electrolyser or a consumption of fossil resources if it is produced by conventional processes. Despite ER of CO_2 is still behind to catalytic ways in terms of TRLs, it has the advantage that can be fully developed at atmospheric temperature and pressure, while surpluses of electricity from renewable sources are used (Ganesh, 2016 and Kauffman et al., 2015). Recently, the use of carbon dioxide in microbial electrosynthesis has gained many interest due to its capability to produce FA (Ganigue et al., 2015), reducing the energy used and leading higher environmental and economical sustainability. Current efforts are mainly focused on (i) decreasing the overall energy consumption of the ER process (electricity) and the separation process (heat) (Rumayor et al. 2018; Roh et al. 2018), and (2) improving the economic feasibility by developing more efficient catalysts and reducing the consumables use (i.e. electrolytes and electrodes) (Agarwal et al, 2011).

In this paper, we examine electrochemical reduction (ER) of CO_2 captured from a coal power station, assuming post-combustion based on amine as solvent. Power plants offer meaningful opportunities for CCU and CCS options as main sources of CO_2 (Markewitz et al. 2012). A flowchart of the process structure for the carbon dioxide capture, transport, storage and utilization (CCU-CCS) is presented in Figure 2, which shows three main sections: (1) combustion; (2) capture, transport and storage; and, (3) CO_2 conversion to FA production, based on a design suggested by Rumayor et al. (2018).

2.2.1. Capture

We assume that monoethanolamine (MEA)-based solvent would be used to capture CO_2 from flue gas. In a packed absorption column, the MEA reacts with and absorbs CO_2 to form an MEA carbonate soluble salt. This CO_2-rich MEA solution is then sent to a heat exchanger and fed to a stripping column where the MEA is regenerated and recycled, while the concentrated CO_2 stream is captured for further processing. The efficiency of the capture technology is assumed to be 89% (IEA, 2009). The current research on CO_2 absorption using MEA is mainly focused on the minimization of energy consumption during solvent regeneration. The desorption step implies an important amount of heat, incurring a severe penalty to the overall efficiency of the plant. Luis (2016) mentions several technological options, e.g. a CO_2 absorption-desorption system based on MEA with capacitive deionization (CDI) to minimize the heat duty requirement of the stripper; a two steps desorption consisting in removing a reaction product (mainly the bicarbonate ion) and the simultaneous amine deprotonation, as well as the integration of solar-assisted post combustion CO_2 capture into a power plant with amine-based chemical absorption for CO_2 capture. Although the conventional absorption-desorption process can still be optimized and improved by modifying the operating conditions or by integration with other emerging technologies, currently the energy requirement for solvent regeneration is lower that the energy consumption of the MEA production process (Rumayor et al., 2018).

The combination of partial CO_2 utilisation with partial CO_2 storage could be an interesting CO_2 mitigation option for industrial sources (Fernández-Dacosta et al. 2018). To investigate this hypothesis, we assume that a fraction of the captured CO_2 is sent to the

ER process, while the remaining is sent to storage. The fraction sent to the ER process, here called the derivation ratio (DR), is assumed to be pure CO_2 with sufficient pressure for the ER process. The CO_2 fraction for storage is sent to compression, transport and storage. High DR implies that virtually all CO_2 is diverted to CCU while a low DR means the CCS option is carried out.

2.2.2. CO_2 conversion

There are three main steps in the CO_2 conversion: (i) ER of CO_2; (ii) distillation of the products, and, (iii) compression of valuable by-products, such as H_2 and O_2, to liquid form ready to transport. Rumayor et al. (2018) and (2019), Dominguez-Ramos et al. (2015), Del Castillo et al. (2017) and Dominguez-Ramos et al. (2019), have studied the ER FA process, including a comprehensive technical analysis, in order to select the process variables and configurations to increase the performance of CO_2 conversion. In this work, we have selected those CO_2 conversion scenarios that lead to higher results.

Energy consumption is in form of electricity or steam according to the nature of each individual process. The CO_2 is reduced to FA at the cathode in the presence of chemicals acting as supporting electrolytes. A parallel cathode reaction produces hydrogen. At the anode, the main reaction is the production of oxygen. Usually, the catholyte is an aqueous solution of 0.45 M $KHCO_3$ and 0.5 M KCl saturated with Ar or with CO_2. The anolyte is a 1.0 mol/L KOH aqueous solution. In this work, both the anolyte (KOH) and the catholyte ($KHCO_3$ and KCl) are supposed to be recirculated and then, they were not taken into consideration when compiling the inventory stage.

The electricity for the electrochemical reactor could come exclusively from the coal power plant, or supplemented from a low-carbon generation. To investigate the potential benefit of utilizing renewable energy, we analysed a scenario with process electricity generated by photovoltaic solar power (PV). However, for the remaining electricity consuming processes in the ER FA unit, we assumed that the source would be only the electricity from the coal power plant. This is in agreement with the plans to utilise renewable power in the energy-intensive production of base chemicals (Riese et al. 2014). Several works theorize about the potential availability of the process industry to function as an energy sink for excess energy generated from the discontinuous renewable sources wind and sun (Riese et al. 2014; Jens et al. 2016). However this is unlikely in practice, because the high capital costs of an ER FA plant would demand high capacity factor operation. Capturing excess generation means not having the plant operating for long periods, so something cheaper (e.g. an electrolyser for hydrogen production) makes more sense. Our work is aiming to contribute to this debate by integrating not only the renewable energy production and the chemical process industry, but also the CCU and CCS technologies.

2.2.3. Compression, transport and storage

For CO_2 storage, the CO_2 flow is assumed to be compressed to 11 MPa for transport by means of a compression train formed by several compression stages with intercoolers and a final pump. The compressed CO_2 is transported through a pipeline with a diameter of 95 cm, thickness of 10 mm (Koornneef et al. 2008). We assume that CO_2 is transported in a supercritical state 5 km onshore and 95 km to an offshore aquifer, where it is stored in a permanent storage (Fernández-Dacosta et al. 2018). An alternative case with CCS but without CCU enables us to understand potential climate benefit of CCS over time, i.e. CO_2 potential reduction.

2.3. Description of scenarios

The scenarios described in Table 1 have been designed based on different published works. For example, Rumayor et al. (2018) note that future deployment of ER process is conditioned by the performance technology; Koornneef et al. (2008) assess the environmental impacts of three pulverized coal fired electricity supply chains with and without carbon capture and storage (CCS), and Fernández-Dacosta et al. (2018) refers to the combination of multi-product CCU with CO_2 storage; Dominguez-Ramos et al. (2015) conclude that integration of renewable energy and alternative purification process are required to ensure a sustainable process to obtain FA from CO_2 . Beside these we further argue that that the degree of decarbonisation of the global energy system also influences the configuration of the ER FA system. Therefore, we also investigate the case when the EU grid electricity supply is decarbonised to meet the Paris Agreement targets vs. the case when no climate action is implemented. The latter could lead to increased emissions towards 2040, which is the time horizon considered in this study.

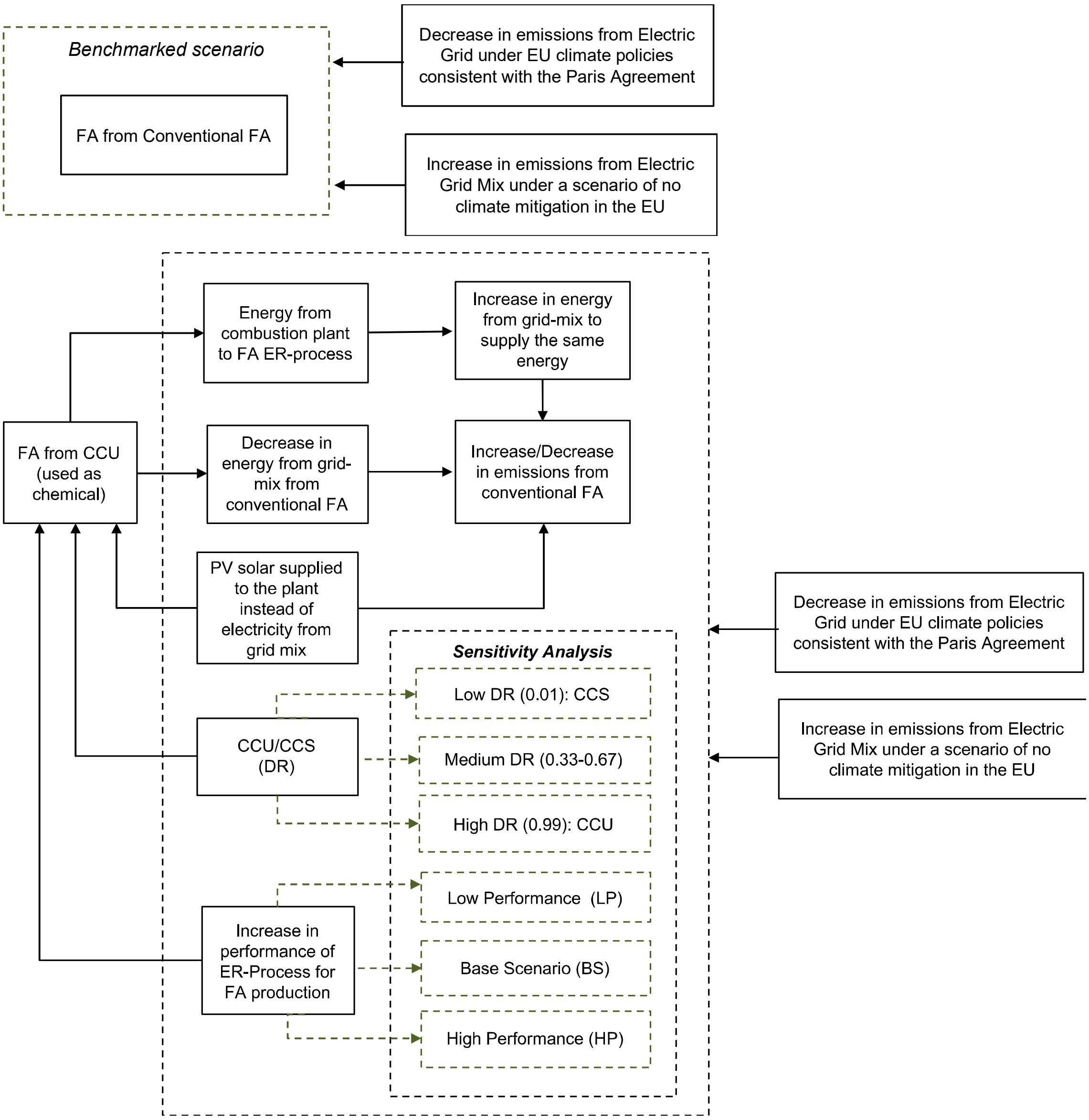


Figure 3. Overview of the marginal and alternative processes included in the scenarios described in Table 1.

Figure 3 provides an overview of the marginal processes and emission sources/sinks included in each scenario. These relate to (i) the production and consumption of energy (either from the coal combustion plant for ER FA production, or from the grid mix for FA production by the conventional process), (ii) the deployment of CCS technologies and consequently the availability of CO_2 to produce FA from ER process, (iii) the performance of the ER process (which has been included as an implicit sensitivity analysis conducted on key process parameters to explore the system's operational ranges and to assess the impact of process conditions on the technical performance of the system), as well as to (iv) the use of PV electricity instead of electricity from the production mix. According to this overview, Table 1 contains the description of the proposed scenarios.

Table 1. Details of the proposed scenarios. Limitations of these scenarios are shown in Appendix A.

Scenario	**Description**	**Sub-scenario**	**Description**
1. Benchmarked System (CONV FA + gELC)	The combustion plant supplies energy to the grid (subsystem 1). Production of FA using the conventional process using energy from the Grid (gELC, subsystem 2).	1.1. Energy (2DS)	Electric Grid Mix under EU climate policies consistent with the Paris Agreement.
		1.2. Energy (BAU)	Electric Grid Mix under a scenario of no climate mitigation in the EU.
2. ER FA System (ER FA + gELC)	The combustion plant supplies energy to the grid (subsystem 1). CO_2 to FA from ER process using energy from the combustion plants and additionally from the grid to compensate energy (subsystem 2).	2.1. Energy (2DS)	Electric Grid Mix under EU climate policies consistent with the Paris Agreement.
		2.2. Energy (BAU)	Electric Grid Mix under a scenario of no climate mitigation in the EU.
3. Performance Technology (ER FA (LP-BS-HP) + gELC)	The combustion plant supplies energy to the grid (subsystem 1). Considers the maturity of the ER FA process (Subsystem 2).	3.1. Low Performance (LP)	Pessimist scenario including FA outlet at 2% wt; 5 V; current density 70 $mA \cdot cm^{-2}$. Electric Grid Mix under 2DS, or BAU.
		3.2. Base Scenario (BS)	Medium scenario including FA outlet at 10% wt; 3.7 V; current density 140 $mA \cdot cm^{-2}$. Electric Grid Mix under 2DS, or BAU.
		3.3. High Performance (HP)	Optimist scenario including, FA outlet at 30% wt; 2.6 V; current density 1,125 $mA \cdot cm^{-2}$. Electric Grid Mix under 2DS, or BAU.
4. CCU/CCS ratio ER FA (HP), DR + gELC)	The combustion plant supplies energy to the grid (subsystem 1). Considers the ratio of CO_2 to use (CCU) vs storage (CCS). CO_2 to FA from ER process using energy from the combustion plants and additionally from the grid to compensate energy (subsystem 2). Total FA	4.1. ER (DR=0.99)	CCU (DR=0.99). Electric Grid Mix under 2DS, or BAU. All captured CO_2 is used for making FA.
		4.2. ER (DR=0.67)	CCU (DR=0.67) in combination with CCS. Electric Grid Mix under 2DS, or BAU.
		4.3. ER (DR=0.33)	CCU (DR=0.33) in combination with CCS. Electric Grid Mix under 2DS, or BAU.
		4.4. ER (DR=0.01)	CCS (DR=0.01). Electric Grid Mix

	production is the same, either by CONV FA (CO_2 storage) or by ER FA (CO_2 use).		under 2DS, or BAU. All captured CO_2 is sent to geological storage.
5. PV solar energy (ER FA (HP), DR + PV ELC)	The combustion plant supplies energy to the grid (subsystem 1). CCU/CCS ratios. CO_2 to FA from ER process using energy from the combustion plants and additionally from PV energy for the ER cell (Subsystem 1). (subsystem 2). Total FA production is the same, either by CONV FA (CO_2 storage) or by ER FA (CO_2 use).	5.1. (PV) (DR=0.99)	CCU (DR=0.99). Electric Grid Mix under 2DS, or BAU. All captured CO_2 is used for making FA.
		5.2. (PV) (DR=0.67)	CCU (DR=0.67) in combination with CCS. Electric Grid Mix under 2DS, or BAU.
		5.3. (PV) (DR=0.33)	CCU (DR=0.33) in combination with CCS. Electric Grid Mix under 2DS, or BAU.
		5.4. (PV) (DR=0.01)	CCS (DR=0.01). Electric Grid Mix under 2DS, or BAU. All captured CO_2 is sent to geological storage.

2.4. Dynamic Life Cycle Assessment (d-LCA)

Life Cycle Assessment (LCA) is a powerful tool to assess the environmental performance of processes and products on a life cycle basis, providing a holistic view of the environmental sustainability of the selected scope. One of the recognized limitations of the LCA method is the lack of a time dimension in the definition of both the Life Cycle Inventory (LCI) and Life Cycle Impact Assessment (LCIA) steps (Finnveden et al. 2009). Including the temporal dimension in LCA is a relatively recent research subject. Currently there are several methodological frameworks available offering guidance on how to perform dynamic Life Cycle Inventory (d-LCI) and dynamic Life Cycle Impact Assessment (d-LCIA) (e.g. Beloin-Saint-Pierre et al. 2017, Hayato Shimako et al. 2018, Cardellini et al. 2018). Essentially, all these methods start with collecting temporally explicit data for the inventory, compute the inventory in a form which preserves the temporal specification, and finally use time-dependant characterisation factors for calculating overall life-cycle impacts. All these authors acknowledge challenges related to (i) gathering temporally-specific inventory data (which would also be specific to a given study), (ii) linking it to the existing “static” LCA databases, and (iii) computing the inventory. To reduce the time needed to compile dynamic inventory data, Collet et al, 2014 suggest a selection method based on sensitivity analysis to temporal specification. Given the nature of the system studied in this study, i.e. a set of energy intensive technologies yet to be demonstrated at scale, for developing a dynamic LCI we used TIAM-UCL for deriving dynamic information on the European electricity mix, which we identified as the flow which needs temporal specification. The model developed in this work is based on soft-linking input-output matrices collecting data from GaBi Professional software v8 (GaBi, 2018) and Ecoinvent 3.3 (Ecoinvent Centre, 2017), and the TIAM-UCL energy system model.

TIAM-UCL is a global energy system model integrated with a climate module, which allow for setting global temperature targets under different socio-economic trajectories. In TIAM-UCL the EU is modelled in three regions: Western EU, Easter EU and the UK. Each region has its own energy system producing and trading energy commodities with the other 15 regions in the model under different regional and global climate targets.

For this case study we assumed a global SSP2 (Shared Socioeconomic Pathways) development trajectory (Riahi et al., 2017), and we constrained the model to find the most cost effective global energy system which delivers an increase of global temperature to 2100 less than 2ºC.

Depending on assumptions regarding the technology base potentially available over time in the energy system, the availability of resources, especially biomass for energy, the emissions of non-energy related processes, the pathways indicated by TIAM, and subsequently the EU electricity mix can vary. For this study we used temporal data from TIAM-UCL related to the potential evolution of the energy system under two climate mitigation scenarios, no climate mitigation (Business as Usual, BAU) vs climate policies consistent with the Paris Agreement (2DS). Specifically, we took the composition of the electricity mix every 5 years from 2015 to 2040 and compiled time-dependent datasets for European electricity production. While the share of different technologies supplying electricity to the grid is computed by TIAM-UCL as the most cost optimal solution for the given climate constraints, the average resource consumption and emissions related to the electricity produced every 5 years were calculated based on the Ecoinvent dataset.

Based on d-LCA nomenclature developed by Beloin-Saint-Pierre et al. (2017), the assessment requires two matrices describing the d-LCI: matrix G, where different elementary flows (row) are separated by their period of emission (column); and matrix E describing the time dependent energy and emissions for each period where elementary flows (row) are occurring. As a result, matrix H describes the impact generated by elementary flows (row) at every time step (column).

$$\begin{pmatrix} H_1 t_0 & \cdots & H_1 t_n \\ \vdots & \ddots & \vdots \\ H_n t_0 & \cdots & H_n t_n \end{pmatrix} = \begin{pmatrix} G_1 \\ \vdots \\ G_n \end{pmatrix} \cdot \begin{pmatrix} E_1 t_0 & \cdots & E_1 t_n \\ \vdots & \ddots & \vdots \\ E_n t_0 & \cdots & E_n t_n \end{pmatrix} \qquad (1)$$

In this work, each row of the matrix G is linked to a specific process where energy and materials are consumed or avoided for the considered systems, while each column correspond to the specific period of time. On the other hand, for the matrix E, each row is linked to the emissions scenarios and the columns to the periods of time.

The dynamic parameters of the conventional process (CONV FA) and ER process (ER FA) for the dynamic LCA related to the potential evolution of the energy system under BAU and 2DS scenarios are shown in Tables S1-4 of the SI.

2.5. Life Cycle Inventory

The LCI data for the coal combustion plant and the conventional process of formic acid manufacture are taken from the commercially available Ecoinvent database v3.3 (Ecoinvent Centre, 2017). For the combustion section, it is assumed that hard coal is used as feedstock. The quality of the data that is available from the Ecoinvent database can be considered high for the power plant, i.e. the coal combustion and flue gas treatment processes. Data for the upstream processes in the coal supply chain have not been considered in this work.

For compiling the LCI of electrochemical reduction of CO_2 to FA connected to a coal combustion plant we considered that all the CO_2 emissions from the coal combustion plant are sent to the capture section. For the capture section, it is assumed that 89 % of the CO_2 is captured, and 11% is released to the atmosphere. For the ER FA process we considered data from three different alternatives of ER FA that were found in the literature (Spurgeon and Kumar, 2018; Yang et al. 2017; Martín et al. 2015). The alternatives were selected because of their demonstrated capability of producing FA concentrations between 2.0% wt. and 30.0% wt., the later coming to the concentration of commercial FA supplied currently. All the alternatives studied present the same mode of operation, being single pass (see Table 2). The main differences are the electrolyte flow rate used. Additionally, there are differences in the electrode and membrane materials, and the faradaic current efficiency (FE). For the "central" d-LCA we consider the data from Yang et al. (2017), and we use the other two references for the sensitivity analyses.

Table 2. Technical conditions of the ER process: performance influence.

	Low performance (LP)	**Base Scenario (BS)**	**High performance (HP)**
Cell Voltage, V	5	3.7 [a]	2.58 [c]
Current density, $mA \cdot cm^{-2}$	70	140 [a]	1,125 [b]
FE, %	50	94 [a]	98[a]
HCOOH outlet, ER, % wt.	2	10 [a]	30 (generic 50% improvement from 20% wt.)
Durability, h	2,500	2,500	5,000 [d]

[a] Single pass case of experiment in Yang et al. (2017).

[b] Martín et al. (2015).

[c] Minimum cell voltage from Spurgeon and Kumar, (2018).

[d] Overpotential from Martín et al. (2015).

The detailed LCIs for required materials and energy corresponding to each set of experimental data were calculated by means of a sequence of energy and mass balances. Mass balances were performed in each unit, ensuring that there were no mass losses for any element. This methodology ensures that each ER alternative is treated equally; thus, the results are directly comparable although they come from different references using different methods for LCI. For the energy balance, it was assumed that the direct current for the ER process could be obtained from the generator, ignoring conversion losses. The electricity consumption for the other demanding processes, namely CO_2/H_2 compression and H_2 liquefaction, O_2 compression and liquefaction, catholyte and anolyte water pumping and cathode recovery, also assumed as supplied by the generator. Heat as steam and cold water are the utilities used in the distillation step. The data for these was also obtained from Ecoinvent data. Tables 3 and 4 shows an overview of the LCI both for benchmarked scenario and the alternatives scenarios.

The electricity needed in the process, such as the electricity demanded in the reduction of CO_2 to FA, the electricity for the pumps within the reactor cell, and the electricity needed for liquefying both O_2 and H_2 was assumed to come from the power plant. Heat, as steam, is a utility used in the distillation unit

Table 3. LCI for the benchmarked scenario (CONV FA), per kg of FA produced by the conventional process.

	Unit	Values
ENERGY		
Total Electricity	kWh	1.04
Heat, from natural gas	MJ	14.6
Heat, other than natural gas	MJ	8.17
RAW MATERIALS	kg	
Methanol	kg	4.00E-02
Carbon monoxide	kg	6.14E-01
Water	kg	5.99E-01
PRODUCTS		
Formic acid	kg	1.00
EMISIONS (CO_2 eq)	kg	
WEU: electricity production from grid	kg	*as a function of the energy profile computed by TIAM-UCL*(1)
Water	kg	7.00E-04
Chemical factory	kg	6.10E-02
Methanol production	kg	1.00E-03
Carbon monoxide production	kg	9.37E-01
Heat, district or industrial, natural gas	kg	4.85E-01
Heat, district or industrial, other than natural gas	kg	5.32E-01

(1) Detailed information of the energy profile can be found in the Supplementary Materials.

Table 4. LCI for the alternative ER FA alternatives, reported per kg of FA produced by the ER process.

	Unit	Low performance (LP)	Base Scenario (BS)	High Performance (HP)
ENERGY				
Total electricity	kWh	11.79	4.63	3.10
ER cell	kWh	11.65	4.59	3.07
Pumping & compression	kWh	1.26E-01	4.10E-02	3.6E-02
Separation of CO_2/H_2	kWh	1.03E-02	1.11E-03	3.58E-04
Steam	MJ	337.80	62.20	14.90
RAW MATERIALS				

CO_2	kg	9.57E-01	9.57E-01	9.57E-01
H_2O	kg	1.127	5.93E-01	5.76E-01
PRODUCTS				
HCOOH	Kg	1.00	1.00	1.00
H_2O	kg	1.8E-01	1.8E-01	1.8E-01
H_2	kg	4.3E-02	3.00E-03	1.00E-03
O_2	kg	6.96E-01	3.70E-01	3.55E-01
EMISIONS (CO_2 eq.)				
ES: electricity production, photovoltaic, 570 kWp open ground installation, multi-Si	kg	7.90E-01	3.10E-01	2.08E-01
EU: electricity production from grid	kg	*as a function of the energy profile computed by TIAM-UCL*(1)		
Water	kg	7.00E-04	7.00E-04	7.00E-04
RER: steam production in chemical industry	kg	23.30	4.29	1.02
Avoided (H_2 production)	kg	-3.38E-01	-2.20E-02	-7.00E-03
Avoided (O_2 production)	kg	-3.50E-02	-1.90E-02	-1.80E-02

(1) Detailed information of the energy profile can be found in the Supplementary Materials.

Table 5 summarizes the LCI developed as a data source for the study of the influence of CCU technology versus CCS technology. As it can be seen in table CO_2 emission data from electricity production from the grid is a function of the energy profile over time, and more information can be found in the Supplementary Materials (Tables S1 and S3).

Table 5. LCI for the combination of partial CO_2 utilisation (CCU) with partial CO_2 storage (CCS), reported 1 kg of FA produced by the ER process. Scenario: HP technology and 2DS energy profile.

	Unit	**Derivation Ratio**			
		0.99	**0.01**	**0.33**	**0.67**
ENERGY					
Total electricity	kWh	3.10	3.10	3.10	3.10
ER cell	kWh	3.07	3.07	3.07	3.07

Pumping & compresion	kWh	3.60E-02	3.60E-02	3.60E-02	3.60E-02
Separation of CO_2/H_2	kWh (x10^{-4})	3.60	3.60	3.60	3.60
Steam	MJ	14.90	14.90	14.90	14.90
RAW MATERIALS					
CO_2	kg	1.09	107.40	3.26	1.60
H_2O	kg	5.76E-01	5.76E-01	5.76E-01	5.76E-01
CO_2 to storage	Kg	1.00E-02	94.70	1.94	5.00E-01
CO_2 to ER	kg	9.56E-01	9.56E-01	9.56E-01	9.56E-01
PRODUCTS					
HCOOH	Kg	1.00	1.00	1.00	1.00
H_2O	kg	1.76E0-1	1.76E0-1	1.76E0-1	1.76E0-1
H_2	kg	1.00E-03	1.00E-03	1.00E-03	1.00E-03
O_2	kg	3.55E-01	3.55E-01	3.55E-01	3.55E-01
EMISIONS (CO_2 eq.)					
Direct Capture	kg	1.19E-01	11.82	3.58E-01	1.76E-01
EU: electricity production from grid	kg	*as a function of the energy profile computed by TIAM-UCL* [(1)]			
ES: electricity production, photovoltaic, 570 kWp open ground installation, multi-Si	kg	2.08E-01	2.08E-01	2.08E-01	2.08E-01
Water	kg	1.00E-03	1.00E-03	1.00E-03	1.00E-03
RER: steam production in chemical industry	kg	1.02	1.02	1.02	1.02
Avoided (H_2 production)	kg	-7.00E-03	-7.00E-03	-7.00E-03	-7.00E-03
Avoided (O_2 production)	kg	-1.80E-02	-1.80E-02	-1.80E-02	-1.80E-02

[(1)] Detailed information of the energy profile can be found in the Supplementary Materials.

To undertake the d-LCA we needed to make a series of additional assumptions: (i) a CO_2 valorisation plant is in the same site of the CO_2 source (no transport is required); (ii) the feed of CO_2 to the plant is assumed to be pure and with a suitable pressure for the ER process; (iii) the feed of CO_2 to the plant is assumed to be free of environmental burdens, i.e. 100% of the burdens are allocated to the electricity produced by the coal-fired power plant; (iv) the vapour steam needed for FA purification is at dry saturated conditions; and (v) the electrolytes used in the ER process can be perfectly separated.

2.6. Environmental assessment

As some LCA studies found, CCS systems increase the emission of toxic substances such as NH_3, MEA, formaldehyde, and acetaldehyde leading to the corresponding increase in the toxicity impact categories (e.g. Singh et al., 2011). Assumed the complexity of the systems and the explorative approach of this research, including more impact categories at this stage might not be meaningful, as we would be looking at generic pollutants emitted in a generic EU space, which we would then use for deriving a potential local impact, again based on generic factors. Therefore, we limit this study to estimating the carbon footprint (CF) and the fossil resource consumption (FRC) following a cradle to gate d-LCA perspective.

Ecoinvent 3.3 database (Ecoinvent Centre, 2017) and GaBi Professional software (GaBi, 2018) were used in the background process. The CML 2016 method (Guinée et al. 2001) was used with a hierarchic perspective.

We have considered the FRC index as a measure of resources included in both system and alternatives since fuel savings could be a relevant benefit of CCU options (Pérez-Fortes et al. 2016a). In addition to this, we consider that using results on both fossil resources and CO_2 emissions, we can test this relationship over time, introducing a direct link between fossil fuels and raw materials from energy and chemical product subsystems respectively.

2.7. Economic assessment

In parallel with the environmental evaluation, we also estimated the economic costs of representative scenarios, which is the capital and operating costs. Based on the equipment size and mass and energy balances from the process models (Dominguez-Ramos et al. 2015 and 2019), capital and operational costs were calculated for each of the systems investigated. Capital costs and operational costs were used to determine the total systems costs and the net present value (NPV) as a metric to evaluate the profitability of CCU vs. CCS plants from a private investor perspective. Finally, FA cost was calculated for each scenario to evaluate how the introduction of CO_2 capture units would affect the final product cost. A detailed description of the economic assessment methodology, including the economic overall key performance indicators (KPIs), as well as the FA ER plant cost parameter are presented in the SM.

In the context of the FA market, Perez-Fortes et al. (2016) present market penetration pathways based on the legislation in Europe and state of art technologies. According to this, under an optimistic scenario in which FA is used as hydrogen carrier, the current demand could increase up to fourteen times, reaching 24,000 t/year, which implies a CO_2 provision over 21,000 t/year. However, because the use of FA falls outside of the system boundaries in this work, we have only considered the current production of FA in Europe to carry out the economic assessment.

3. Results

3.1. Influence of the technology performance

Figure 4 shows the results from the d-LCA for FA production from the conventional process (CONV FA) and ER process (ER FA) under the 2DS scenario (below 2 ^{0}C by the end of the century), including the energy system to supply grid electricity (gELC). The CO_2 emissions of the two FA production systems vary as a function of the technology performance and the energy system supplying the electricity to the FA system. The CO_2 emissions associated to the CONV FA + gELC (2DS) scenario were estimated at 4.3 Mt CO_2 per functional unit, decreasing to 3.3 Mt CO_2 per functional unit by 2040 due to the decarbonisation of the energy system under climate policies consistent with the Paris Agreement.

The CO_2 emissions of ER FA technologies range from 11.2 to 8.5 Mt CO_2 per functional unit for the high performance (HP) technology in 2016 and 2040 respectively; and from 53.8 to 38.1 Mt CO_2 per functional unit for the low performance (LP) in 2016 and 2040 respectively. According to this, the technological development has a leading influence on the CO_2 emissions, which could be up to five times less in a high performance scenario. On the other hand, note that if we only consider the FA production technologies (source of energy not included), the CO_2 emissions for the conventional FA production are significantly lower than for the ER FA process, between 4 and 50 times for HP and respectively LP technologies. In this case (without considering the energy supply), our results fit with previously published studies, 2-5 kg CO_2/kg FA for the convectional FA, and respectively 14-20 kg CO_2/kg for ER FA (Dominguez-Ramos et al. 2015; Rumayor et al. 2018; Cuellar-Franca and Azapagic, 2015; Cuellar-Franca et al. 2015). However, in the following we argue that it is critical to include the energy supply in the evaluation of the FA environmental profile.

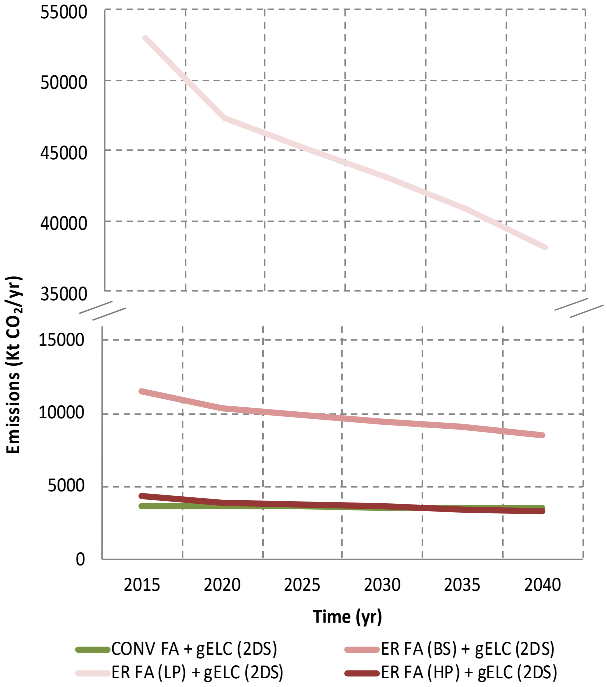


Figure 4. Dynamic carbon footprint for the benchmark and the CCU using alternative FA production technologies for the whole system (FA production and energy supply).

According to Table 4, the electricity consumption by the ER FA process ranges between 3.1 kWh/kg per mass unit of FA (HP technology) and 11.8 kWh/kg per mass unit of FA (LP technology). This is mainly driven by the consumption of steam, 14.9 to 337.8 MJ/kg per mass unit of FA in the HP and respectively LP technologies, highlighting the significance of the purification step. As expected, the higher the FA concentration is at the outlet of the ER cell, the lower is the steam consumption (HP scenario). As consequence of the energy and steam consumption for CO_2 capture and separation and the ER FA process itself, power plant's electricity output to the grid is reduced by 120 kWh per ton CO_2 captured, or 21.8 kWh per kg FA produced. If the demand for electricity is assumed unaltered by the FA production, this implies that the electricity producers have to compensate for the reduced output with more electricity production. In this work, we have modelled the compensated electricity based on grid characteristics in Europe from 2015 to 2040 according to the TIAM-UCL model results under a 2DS climate mitigation scenario, estimating that the CO_2 emissions embedded in the electricity from the grid amounts between 200 and 500 kt CO_2 per functional unit (40 to 500 gCO_2/kWh supplied electricity). At the same time, the avoided emissions from the recovery of CO_2 from the coal combustion plants to the ER FA process are 340 kt CO_2 per functional unit. All these result into that in the more optimistic scenario, i.e. high performance (HP), the ER FA process system is competitive in terms of global warming with the conventional process. As we have previously referred, the analysis differs substantially when we do not include the energy supply in addition to the chemical process, the CONV FA looking much less emission intensive than all ER FA alternatives. However, not including the energy generation into the system boundaries might lead to misleading conclusions.

3.2. Energy assessment

Figure 5 shows the main sources of CO_2 emissions for the alternative ER FA (HP) + gELC (2DS), selected as an optimistic scenario under an energetic point of view, including emissions from (i) the energy for the CO_2 capture; (ii) the energy consumed by the ER FA process; (iii) the energy from the grid to compensate the energy consumed from the coal combustion plant for ER FA production; and (iv) the avoided emissions of CO_2 used as raw material in the ER FA production. The ER FA is energy intensive and the energy related emissions dominate its carbon footprint, i.e. blue columns in Figure 5. Moreover, although the energy consumption is the same over time, the CO_2 emissions from the grid are diminished over time, contributing from 22% in 2015 to 5% in 2040 to the total FA footprint, consistent with the dynamic energy profile considered under a 2DS decarbonisation scenario.

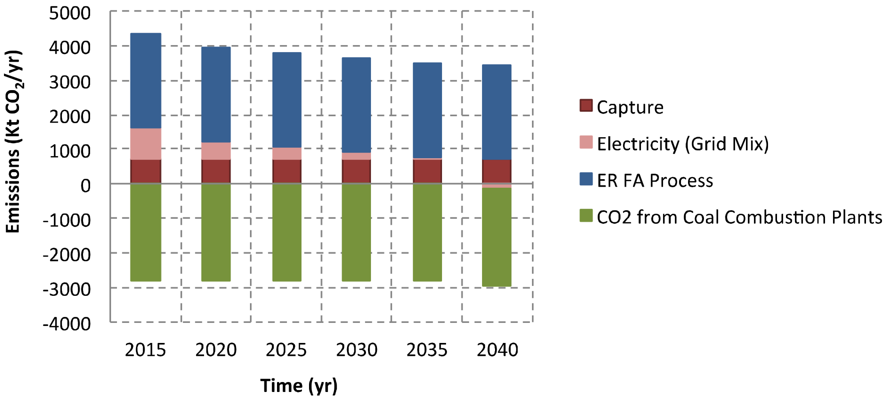


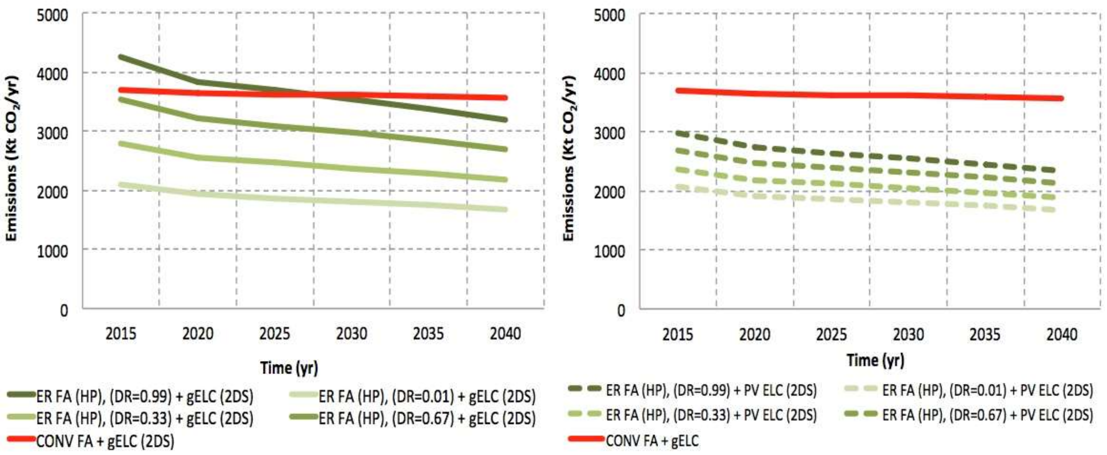
Figure 5. Main source of CO_2 emissions for the alternative system under the ER FA (HP) + gELC(2DS) scenario.

Under these overall conditions, the proposed CCU system, could be favourable in terms of global warming, despite the high-energy consumption. This highlights the importance of considering the system as a whole, since the decision-making must be linked to both the production of chemical products and the supply of energy.

3.3. CO_2 emissions under a CCU versus CCS scenario

In order to assess the alternative CCS, in addition to a combination of CCU and CCS systems (Scenario 4), we varied the CO_2 fraction (DR) sent to compression, transport and storage (Figure 2). It is important to point out that only restricted values of CO_2 fractions (low DR values) are currently found to be technically plausible for the conversion to FA (Dominguez-Ramos et al. 2015). The current envision deals with relatively small modular facilities that can valorise a fraction of all the CO_2 captured rather than a facility fully oriented to the production of high volumes of FA. Note that high DR values imply the CO_2 as a resource for producing FA, while low values of DR suggest higher CO_2 storage.

In order to take into account the most comparable scenarios in CO_2 terms to the conventional FA process and the most optimistic energetic scenario, Figure 6 displays the CO_2 emissions for the CCU and CCS systems for ER FA (HP) + Energy (2DS), both for grid electricity and for PV electricity. Figure 6(a) shows the dynamic reduction in CO_2 emissions from 4.2 to 3.3 Mt CO_2 per functional unit for a DR of 0.99 (CCU), vs 2.1 to 1.7 Mt CO_2 per functional unit for DR of 0.01 (CCS), which is associated with the dynamic energetic profile under a considered progressive decarbonisation. When we compare these emissions with those corresponding to the conventional scenario, we find that, independently of the DR fraction, the ER FA systems are less emission intensive than the CONV FA system from 2030 onwards, assuming a decarbonisation of the energy system consistent with the Paris Agreement. Note that using PV electricity for the ER FA (HP) process makes it less emission intensive from the first use.



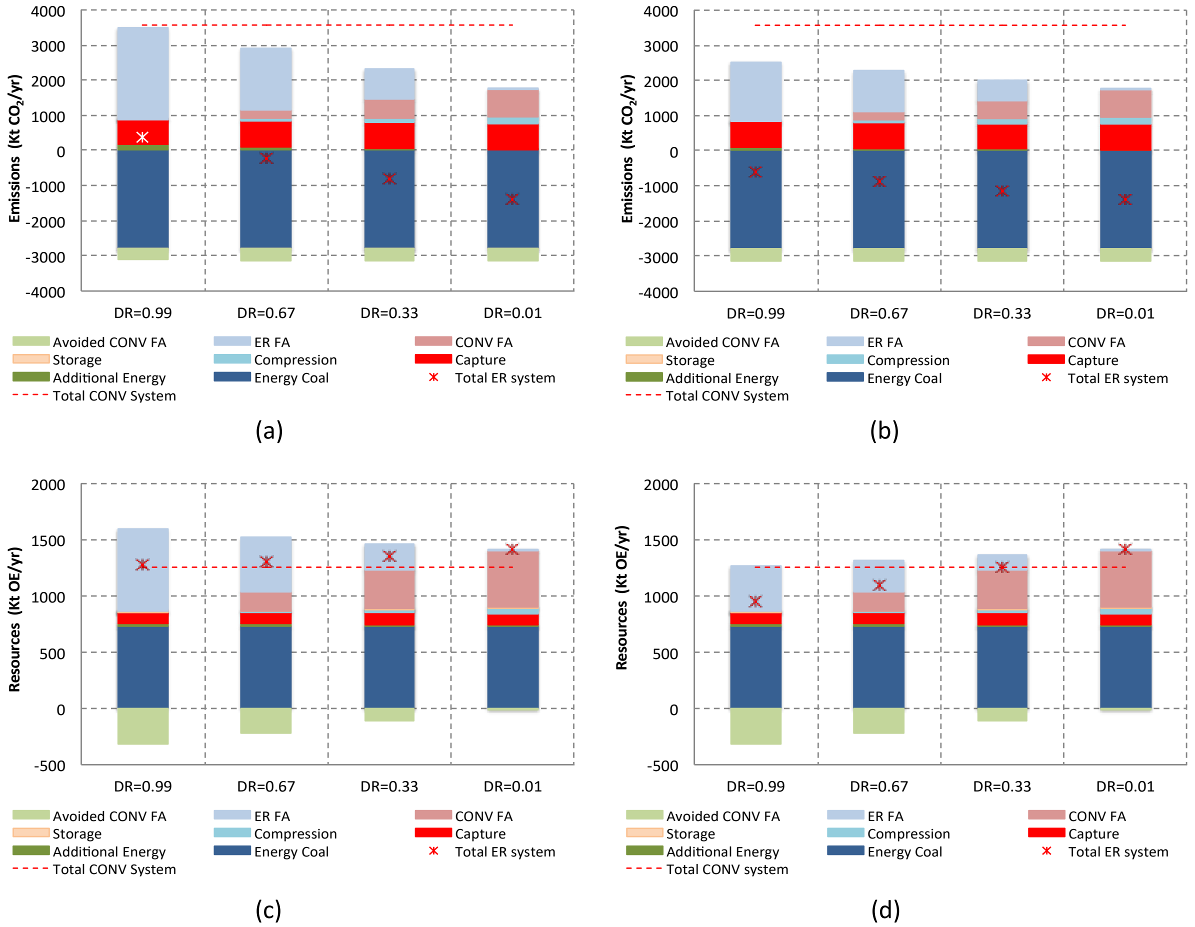
(a) (b)

Figure 6. CO_2 emissions for the CCU and CCS systems for the ER FA (HP) + Energy (2DS) alternative: (a) CO_2 emissions under a grid energy scenario (gELC); (b) CO_2 emissions under a PV solar energy scenario (PV ELC).

According to these results, even under high efficiency (HP) assumption, the CCU technology needs a decarbonised electricity input (i.e. similar to those under a 2DS future) to yield similar or less emissions as compared to the conventional technology. If the energy system doesn't decarbonise (see SI), ER FA yields to increased CO_2 emissions when grid electricity is used for the ER. In the latter case, only using PV electricity would make ER FA less emission intensive than CONV FA.

We have investigated the use of surplus of renewable energy from PV solar energy for supplying energy to ER FA manufacture. In this scenario, the additional energy required in the ER FA process is obtained from a PV solar source integrated into the chemical plant instead of taking it from the grid. Following results in Figure 6(b), in this particular case, the CO_2 emissions could decrease to 2.3 Mt per functional unit, a decrease of 35% as compared to 3.6 Mt CO_2 per functional unit when a grid energy scenario is considered. The demand of steam for the purification stage is the main consumer of energy, and therefore the highest contribution to GHG of ER FA. Reducing the energy requirements of purification, in other words increasing the efficiency of the separation process, could be done through: i) increasing the efficiency of the ER process leading to higher concentrations of FA in the output stream; and ii) intensifying the FA production process through reactive distillation processes (Sharma et al. 2018). Other options could include sourcing steam from a renewable source, as well as considering different concentration of FA for commercial purposes, reducing the need for steam. It is remarkable that the integration of solar PV energy would allow reducing CO_2 emissions below the benchmarked scenario, even in a non-decarbonisation scenario (BAU scenario), achieving in this case a reduction in emissions of up to 30%. The practical design of the integration of ER for the production of FA has not been proposed yet. FA can be handled and safely stored so it is likely to be conceived a storage tank for the produced FA. The ER section would be operating under conditions of high irradiation so it can be flexible regarding the incoming electrons from the PV solar source. However, the intermittency of solar power generation might be an important bottleneck in implementing this option in practice.

Figures 7a and 7b show the composition of CO_2 emitted under CCU vs. CCS scenarios. They display the CO_2 emissions in 2040 in each of the variants analysed in Figure 6, and considering the following contributions: (i) ER FA CO_2 emissions; (ii) avoided CO_2 emissions from the ER FA by-products H_2 and O_2; (iii) CO_2 emissions from capture; (iv) CO_2 emissions from compression; (v) CO_2 emissions from storage; (vi) CO_2 emissions from energy from coal; (vii) CO_2 emissions from energy from the grid to compensate the reduced electricity to the grid mix; and, (viii) avoided CO_2 emissions related to the consumption of and CO in the conventional process. Results in Figure 7 show that both in the grid energy scenarios (Figure 7a) and PV solar energy scenarios (Figure 7b) the avoided CO_2 emissions from the energy coal combustion plants and from the ER FA by-products (H_2 and O_2) compensate the emissions from the ER FA process. Both CCU and CCS scenarios result into less CO_2 emissions than the conventional FA system (dotted line). The difference is more noticeable in the CCS scenarios (DR=0.01). Note that the conventional FA is less intense in emissions under a 2040 decarbonization simulated scenario. The PV solar energy scenarios have the lowest emissions, as the ER FA emissions are the lowest.



(a) (b)

(c) (d)

Figure 7. Fossil resources consumption and CO_2 emissions for the CCU and CCS systems for the ER FA (HP) + Energy (2DS) alternative in 2040: (a) CO_2 emissions under a a grid energy scenario (gELC); (b) COs emissions under a PV solar energy scenario (PV ELC); (c) fossil resources under a grid energy scenario (gELC); (d) fossil resources under a PV solar energy scenario (PV ELC).

3.4. Fossil resources consumption under a CCU versus CCS scenario

Figures 7c and 7d display the fossil resource consumption in 2040 in each of the variants analysed in Figure 6. It is conspicuous that there is a redistribution of fossil resources consumption for the FA production, either from the conventional FA system as from the alternative ER FA system regardless of whether the option is CCU, CCS or a combination of both. The magnitude of fossil resources consumed in the ER FA system under a CCS scenario (DR = 0.01) is similar to the resources consumed in the ER FA process CCU plus the resources avoided from the conventional production of FA. Note that in a full CCU scenario, the avoided resources from the conventional system do not compensate the resources required to generate the additional energy needed in the ER FA process. This holds true although under the decarbonised scenario considered in this work the grid energy is less intensive in fossil resources, and the increase in fossil resources consumption associated to the energy is only 2%.

An overall overview of the obtained results reveals, once again, the important influence of energy consumption in the studied scenarios, underlying the need to include energy when evaluating technical strategies to reduce emissions and fossil resources consumption in the chemical industry.

3.5. Techno-economic evaluation

The feasibility of producing FA by ER of CO_2 at industrial scale depends not only on the operational and environmental performance of the process, but also on its economic viability. Data from several commercial plants (Perez-Fortes et al. 2016a) indicate that the current FA manufacture price is about 0.65 €/kg FA. This implies a gross profit of 0.175 €/kg FA, which we take as economic reference value in this study. To analyse the economic performance of the ER FA process as a function of the technology characteristics (HP, BS and LP cases, as described in Table 2), we show in Table 6 the economic assessment results at ER FA manufacture level. The complete economic results for the CCU plants is included in the SM (Table S7).

The results in Table 6 show that the investment costs (from the Capital Expenditure, CAPEX), are strongly influenced by the performance of the process, the low performance ER FA process (LP) being the most expensive of all alternatives. As both the LP and BS technology scenarios are not economically feasible, in continuation we only use the high performance (HP) scenario to study the influence of the derivation ratio in the CO_2 emissions (DR) on the economic profile of ER FA (ER FA (HP), (DR=0.99-0.01) + gELC (2DS)). In this scenario, the biggest contributor (90%) to the total investment cost is the electrolyser cost. This fact highlights the need of further development of the electrolyser components (cathode, anode and membrane) to drive down the cost of the electrolyser.

Table 6. Economic assessment results as a function of the performance technology (HP vs LP and the BS case) and the derivation ratio (ER FA (HP), (DR=0.99-0.01) + gELC (2DS)).

	Unit	Low Performance (LP)	Base Scenario (BS)	High Performance (HP)			
				DR=0.01	**DR=0.33**	**DR=0.67**	**DR=0.99**
INVESTMENT COSTS (from CAPEX)	**M€/plant**	**10,080**	**1,440**	**392**	**121**	**116**	**105**
NPV	**M€/plant**	**-10,600**	**-1,320**	**-1,082**	**-97.4**	**-81.7**	**-76.8**
OPERATIONAL COST							
Fixed costs	€/kg	20.17	2.86	4.94	0.52	0.45	0.43
Variable costs	€/kg	14.09	1.96	4.34	0.27	0.24	0.18
Total Cost of Production FA	**€/kg**	**78.97**	**10.71**	**7.08**	**1.18**	**1.08**	**1.05**
Revenues (FA+H_2+O_2)	€/kg	1.11	0.69	0.67	0.67	0.67	0.67
Market price FA	€/kg	0.65	0.65	0.65	0.65	0.65	0.65
Gross Profit	**€/kg**	**-77.86**	**-10.02**	**-6.41**	**-0.51**	**-0.41**	**-0.38**

Indicatively, the level of CAPEX from capture has been estimated at 18.1 €/t CO_2 captured. The operational costs from capture and storage arise to 25.1 €/t CO_2 captured vs. 18.9 €/t CO_2 used. These values should be interpreted with caution, as many other factors should be considered for calculating them; e.g. the heat and electricity for the capture and compression are always withdrawn from the power plant so they are not considered here, although in reality it means a relevant energy penalty for the power plant. Only the cost of the capture and the compression are considered. The CO_2 emissions which are not captured are considered as an environmental burden.

The extra operational costs due to the energy and material requirements for the CO_2 capture are partly compensated in the CCU case (DR=0.99) and in the combined CCU-CCS alternatives (DR>0.33) by the revenues from selling FA. Additionally these scenarios benefit from avoided consumption of feedstock (methanol and CO), which adds to the operational costs in the conventional and CCS cases. The total system costs follow the same trends, from 1.05 €/kg FA for DR=0.99 (CCU alternative) to 7.08 €/kg FA DR=0.01 (CCS alternative). Fernández-Dacosta et al. (2017) found similar results for the capture and storage of CO_2 in an oil refinery. Note that no CO_2 price (tax) has been considered in the estimation of the total costs. From a coal power plant perspective, taking into account a CO_2 allowance price from the emissions trading system will further motivate the introduction of CO_2 capture units.

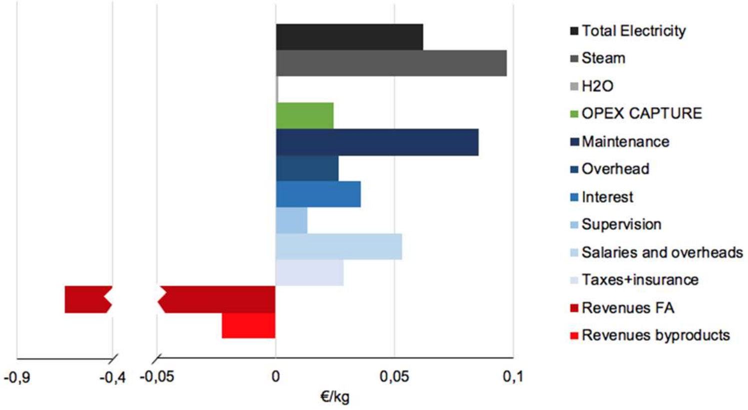
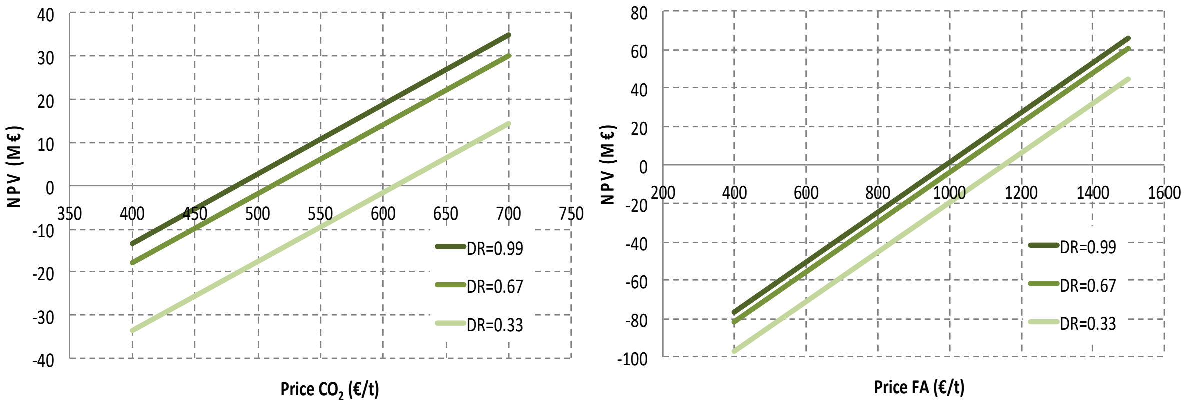


Figure 8. Distribution of the operating costs in the case ER FA (HP) + Energy (2DS), DR=0.99.

Figure 8 displays the breakdown of the operating cost considering both fixed and variable costs of production and the revenues from FA and the by-products (revenues are depicted towards the negative direction of the X-axis).

As expected, the cost of electricity for the ER process and the steam consumption in the distillation unit are important contributors to the variable production costs, underlining the strong influence of the market energy prices of these utilities in the CCU plant. This influence might be even higher under deep decarbonisation scenarios as it has been previously widely studied by Perez-Fortes et al. (2016a), concluding that the prices needed to make the plants profitable are far from market conditions.

The revenues from FA and the by-products from ER FA are critical for the operating costs, so the market prices of these products are decisive variables to consider in the decision making process. In order to understand better the influence of CO_2 prices could have on the revenues from the ER FA process, we run a sensitivity analysis. We aim at shedding light on the sufficiency of the FA and CO_2 market prices to compensate the chemical industry for the potentially higher cost of electricity.



(a) (b)

Figure 9. NPV variation as function of prices and the breakeven price that make NPV equal to zero: a) NVP for variation of CO_2 price; b) NVP for variation of FA price.

Figure 9 shows the NPV variation as function of prices and the breakeven price that makes NPV equal to zero. Under our simulated conditions, positive NPV requires a price of FA higher than 1,000 €/t for DR=0.99, and 1,300 €/t for DR=0.33 (reference price, 650 €/t), or an income from the CO_2 utilization higher than 460 €/tCO_2 for DR=0.99, and 610 €/t CO_2 for DR=0.33. As a reference, we have simulated scenario of NPV being zero. In this case, we found FA prices higher than 850 €/t and an revenue from the CO_2 utilization higher than 290 €/t CO_2, which could be possible under a future scenario of decarbonisation and new markets for the FA, i.e. when FA is used as H_2 carrier in the production of fuel cells (Perez-Fortes et al. 2016a).

4. Discussion

CCU technologies are expected to have an important contribution to the ambitious goals of reducing CO_2 emissions in the chemical industry (Ecofys-Cefic, 2013). We argue that the discussion around CCU versus CCS should include technical, environmental and economic considerations. This paper discusses CCU vs CCS from the three perspectives, aiming at contributing to growing scientific evidence around using CCS and/or CCU for specific applications in the chemical industry. However, keeping in mind the specific CCU and CCS settings in this work, our results and findings should be considered as particular case study, rather than the ultimate evidence to support CCU or CCS.

The CO_2 emission intensities shown in this work embed not only the CCUS ability to reduce CO_2 emissions, but also the influence of the energy mix under a decarbonization scenario. According to this, the CCU scenarios could be competitive with CCS only when using renewable energy (further detail on the CO_2 emission intensities (kt CO_2/yr FU) of all sub-scenarios mentioned in Table 1 is presented in Table S6 of the SM). However, CO_2 emission and sequestration by CCUS technologies show only a part of the story. To complete this picture, resource consumption and the cost of decarbonisation should be considered. Accordingly, Figure 10 summarizes the main results in terms of climate change contribution and fossil resources consumption, which, complemented with the economic results shown in Table 6, present a general overview of the technological and operational options for the production of FA in Europe as an inconspicuous contribution to climate change mitigation.

Following Figure 10, in terms of comparing the CO_2 balance between sending the captured CO_2 to storage vs using it for FA, the results show that geological storage (CCS under the assumptions on the transport and storage of liquid CO_2) yields more emissions reduction in all cases, even when compared to the most efficient ER FA method. Moreover, the use of an LCA approach is key in order to avoid that the additional energy or materials needed for CCU induce higher emissions than those of the conventional process. In order to accomplish the highest emission reduction, integration of renewable energy is needed.

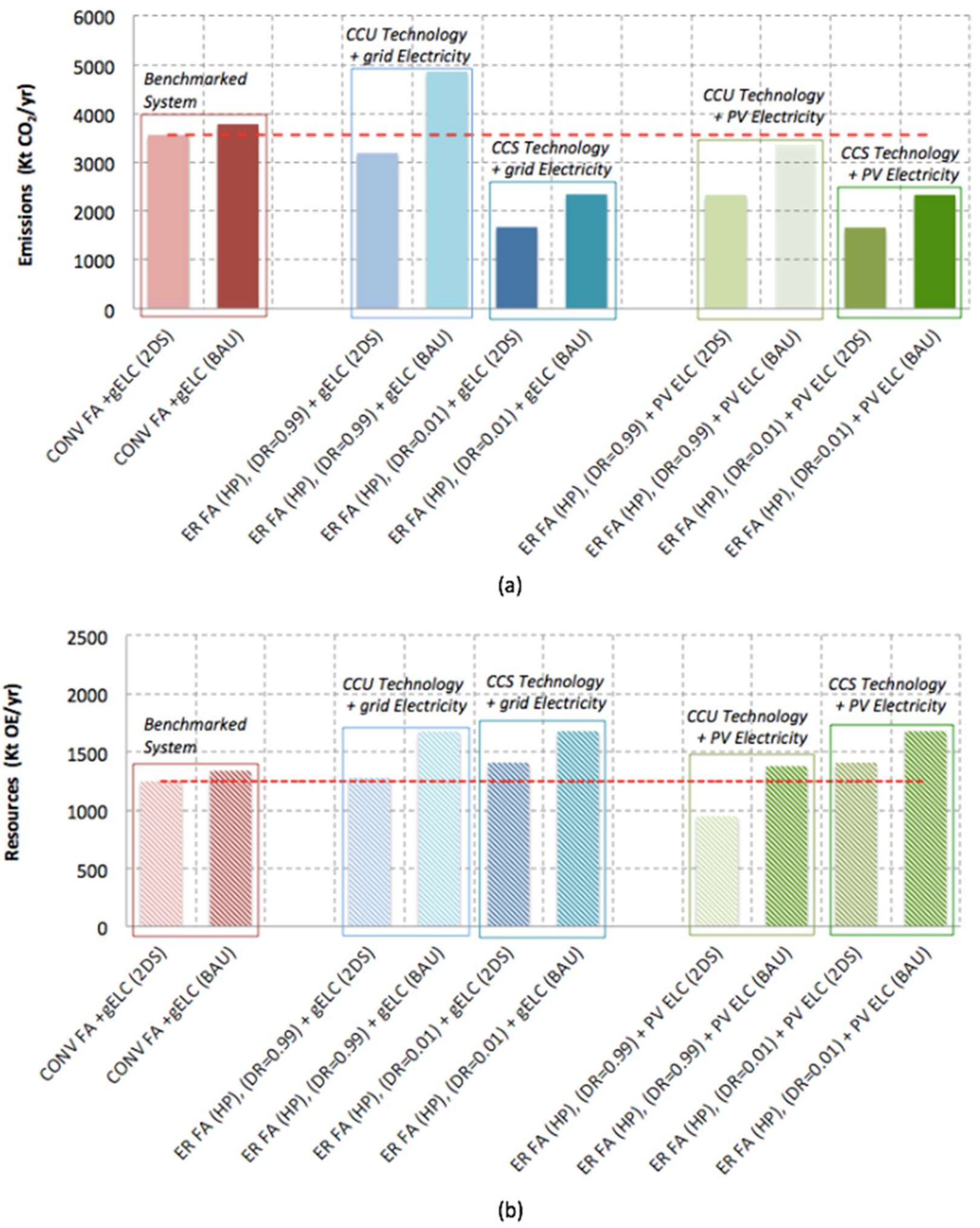


Figure 10. Results overview of CO_2 emissions (a) and fossil resources consumption (b) for the main considered scenarios for 2DS and BAU in 2040.

Reductions of up to 50% as compared to the current FA technology are possible in a scenario of future decarbonisation consistent with the Paris Agreement. Additional to CO_2 emissions reduction, the CCS technology allows for a permanent storage of CO_2, i.e. the carbon is permanently removed from the global carbon cycle over a time-scale meaningful to global warming, i.e. potentially thousands of years. However, the success of CCS for mitigating climate change depends both on its technological development and the CO_2 sequestration rates in permanent geological storage sites (Mac Dowell et al.

2017). Furthermore, CCS raised risk and security concerns (Li and Liu, 2017). Whilst these concerns are outside of scope here, they should be taken into consideration and balanced against CCS advantages found in this study.

Owing to the scale and rate of CO_2 production compared to that of utilization allowing for long-term sequestration, some studies argue that it is highly improbable that the chemical conversion of CO_2 (i.e. CCU) will contribute significantly to the mitigation challenge (Mac Dowell et al. 2017). Indeed, our results show that using captured CO_2 from fossil power plants for FA production reduces very little the emissions of the combined chemical and energy system (ER FA (HP), (DR=0.99) + gELC (2DS)), or could even increase overall chemical + energy system emissions under a global BAU scenario, i.e. ER FA (HP), (DR=0.99) + gELC (BAU). ER FA alternatives are environmentally better than the CONV FA process only when the energy driving the conversion is low carbon, i.e. in the scenario ER FA (HP), (DR=0.99) + PV ELC (2DS) the reduction in CO_2 emissions as compared to CONV FA + gELC (2DS) is 35%. This suggests that clean power sources such as wind and solar would be needed to drive the electrolysis. However, using renewable power for operating ER FA-processes means running the ER under a volatile energy supply. Trade-offs between CO_2 emission reduction and continuous operation of the ER FA plant dependant on the availability of intermittent power were not subject of investigation here, but might raise questions over the utilization of renewable energy within the chemical industry.

The main advantage of capturing CO_2 emissions from coal combustion plants and using them for chemical production resides in the possibility of replacing fossil resources used in the chemical industry by waste CO_2 emissions and decarbonising power at the same time, i.e. synergic decarbonisation of both chemical and power sectors. The ER FA manufacture should mainly aim to replace fossil resources, thus supporting a transformation of the chemical manufacture towards renewables. The same thinking could be extended to all chemical industries, especially the energy intensive ones. This is intimately related to the aforementioned opportunity to integrate energy systems and production systems, especially in the chemical sector. According to the Figure 9b, the ER FA process from captured CO_2 allows for reducing fossil resource consumption. The use of CO_2 as a resource offers an additional opportunity for resource management and recycling, as proposed by the vision of a circular economy (Naims, 2016). In this sense, the ER FA from captured CO_2 could be integrated into the security strategies of political resources and resource efficiency instruments, as proposed by Bruhn et al. (2015).

The techno-economic feasibility results indicate that when capture costs are included, the costs of FA production through ER FA process and CCU is higher than the benchmarked process. Indeed, based on the results of this work, with FA production costs that double the costs of the CONV FA, the deployment of the ER FA is largely determined by the extent to which costs can be reduced over time in comparison with other CCU applications, as well as favourable scenarios of FA and CO_2 market prices. Currently, the price of CO_2 in the EU ETS is not the adequate price that can foster the change towards production systems that generate less or virtually no emissions. Some important efforts should be made in the field of research and innovation: (i) to drive down the high capital costs mainly driven by the capital expense of the electrolyser units (in this work estimated to be about 46% of the total fixed capital cost); innovation to reduce the cost per electrode area could have an important effect on the adoption of ER FA (Perez-Fortes et al. 2016a); (ii) to reduce the huge energy requirements (which account for 70 to 85% of the operating costs); a potential option is to use surplus renewable energy; (iii) to reduce other costs related to materials and chemicals including electrodes or capture solvents (Rumayor et al., 2018). The need to achieve cost reductions is therefore underlying their successful deployment. If their costs cannot be abridged to comparable levels, their potential deployment should be stimulated through additional benefits that can create added value and that are directly related to possible avoided costs of CO_2 emissions, i.e. avoiding use of fossil resource for chemical production. Accordingly, other drivers (e.g. support through emissions reduction policies) would clearly be required for them to move beyond the pre-commercial stage and attract investment from business and industry.

The present study has some limitations, which should be covered by further research. In this work, FA has only been treated as a chemical product, taking into account FA production, demand and the current market rules, neglecting its potential use as a hydrogen carrier or hydrogen source in emergent energy applications (Perez-Fortes et al. 2016a). We have not analysed secondary trade-offs, which can lead to reduction and/or increase in CO_2 emissions outside the immediate scope of the activity, sometimes referred to as "leakage effects", e.g. the decrease in consumption of CO and methanol from the conventional FA production could increase their availability to produce fuels displacing gasoline and diesel consumption. These trade-offs call for a consequential LCA approach in order to reflect the consequences of choosing one or the other system, reflecting physical and monetary causalities and introducing more consistency in the decision making process.

Finally, it is imperative that any sustainability evaluation of a decarbonisation technological solution is site-dependent. In the particular case of using CO_2 for FA, future research will need to particularise the suggested d-LCA framework to real site locations, taking into account the location of FA producers, potential new PV installations, and particular coal combustion plants.

Conclusions

This work provides an assessment of the commonalities and differences between the use and/or storage of CO_2 from coal combustion plants and their relationship with the chemical process industry, in order to contribute to the decision making process on the decarbonisation of the chemical industry. On the whole, the CCU and CCS technologies reviewed in this paper are good candidates for the decarbonisation of current FA production, although in some cases further research is needed to clarify the relative impacts compared to more conventional process pathways.

Our assessment highlights interesting trade-offs between resources security, economic and environmental performance in the CCU and CCS systems. As expected, the considered CCS system leads to greater reductions in CO_2 emissions than CCU, and therefore has a higher climate change mitigation potential among all the systems studied. However, compared to CCS systems, CCU has a better economic potential and lower fossil consumption. CCU options are cheaper than CCS because of FA revenues compensate for the high cost of capture, but they are still far more expensive than the conventional FA process. In the CCU system the intensive fossil resource consumption by the conventional FA process is displaced by the use of the CO_2 captured, contributing to the double decarbonisation of the power system and chemical production. Accordingly, the FA manufacture by an electro-reduction process seems a promising alternative for climate change mitigation, especially when renewable energy is integrated in the CCU process. In this case the challenge will be to adapt the operation of the process to an intermittent energy supply, which needs further research to demonstrate the full challenges and benefits of the utilization of renewably generated energy within the chemical process industry.

In particular, any consideration of CCU and CCS in climate policy should take into account not only the product system, but also the energy system associated to the product manufacture. Consequently, new legislation and public and industrial policies for CCU and CCS should consider this integrated approach. Although this work contributes to the development of a methodology that allows a comprehensive accounting of emissions, fossil consumption and economic assessment, a consequential life cycle approach seems a crucial task for the future, in order to considerer other physical and economic causalities that are related to a product or/and technology-specific life cycle assessment.

Furthermore, since the CO_2 capture is a post-combustion system, some air pollutants could to increase their emission levels compared with systems without CCU and CCS, and therefore, other impact categories associated with this type of technologies should be taken into account in order to fill this research gap starting from spatially explicit LCA studies.

Appendix A

Limitations of the study

The limitations that need to be considered when analysing these scenarios are:

1. The integration of the supply energy system into the chemical processes expands the system boundaries, leading to a more global decision making process than in the case when only the chemical product is considered. However, except for utilising captured CO_2, in this study the chemical process does not influence what happens in the power sector.
2. When the captured CO_2 is used for making products which release the carbon once they are used, the carbon storage in those products is limited or null. The use of CO_2 as a feedstock avoids its emission back to the atmosphere and at the same time it avoids additional fossil fuels to be burned, which in turn prevents more CO_2 to be released. In the particular case of using CO_2 for FA, if the FA is used for materials production, it could potentially store the carbon for as long as the material lasts. In practice, given the multiple uses of FA as a chemical precursor, including its end of life emissions in a LCA would result into a complex exercise

which is also highly uncertain. In this work we have considered that the gate-to-grave emissions will be the same irrespectively of how FA is produced. Therefore we chose to look only at the cradle-to-gate emissions, as that part of the life cycle we would be changing by using captured CO_2.

3. The analysis of the paper is presented in terms of carbon footprint in order to elucidate the potential benefits in terms of CO_2 emissions. We also include fossil resource consumption as this is directly relevant to carbon accounting. Oher impact categories can be potentially included (such as abiotic resource depletion), but the used databases do not provide the necessary LCI data for expanding the impact analysis, e.g. for characterising the catalyst used for the conventional route.
4. In the electrochemical reduction route the impact of electrodes and catalysts can be assumed as negligible as recently stated by Rumayor et al. (2019). In terms of CF, this would be equivalent to a long lifetime thus the impacts can be considered negligible.
5. Although all of the modelled scenarios are considered to be plausible, an assessment of the probability of scenarios has not been performed.
6. Actual change affected by the scenarios could engage combinations of scenarios, and therefore the studied scenarios will be a simplification of a more complex reality. Furthermore, the modelled scenarios are not all-inclusive, and complementary scenarios could be possible.
7. Some scenarios imply the use of a constrained resource that would otherwise be used for an alternative purpose. In this study, the substitute processes used to fulfil that purpose are not included in the life cycle inventory, assuming that the considered scenario does not disturb them.
8. The emission factors for the European grid electricity are expected to be reduced or increased over time, so it have been considered as a dynamic element included in the LCA modelling. In this study we considered both an EU grid mix under no climate action and a grid mix consistent with the Paris Agreement. The profile of the electricity production mix under the two scenarios was taken from TIAM-UCL, a global energy system model. This might be a limitation of the study, as the EU particularities and climate policies implementation are better represented in EU scale energy system models.

9. The location of the FA production could influence the results of the assessment. Also the location of the coal power plant and liquid CO_2 infrastructure and storage will influence the results. However, choosing these locations would be highly subjective, as they will depend on local decarbonisation plans. Instead of choosing a real location, we run this as a prospective study to inform decision makers on the benefits of incorporating a greater share of renewable energy in chemical processes, particularly in the manufacture of FA.
10. As some LCA studies found, CCS systems increase the emission of toxic substances such as NH_3, MEA, formaldehyde, and acetaldehyde leading to the corresponding increase in the toxicity impact categories (e.g. Singh et al., 2011). Assumed the complexity of the systems and the explorative approach of this research, including more impact categories at this stage might not be meaningful, as we would be looking at generic pollutants emitted in a generic EU space, which we would then use for deriving a potential local impact, again based on generic factors. Therefore, we limit this study to estimating the carbon footprint (CF) and the fossil resource consumption (FRC) following a cradle to gate d-LCA perspective.
11. This study does not intend to analyse the substitution of current FA production locations. It is, therefore, a new approach that would need to address specific locations, both in terms of product demand (location of plants with FA demand), CO_2 capture (location of electric power production plants from coal), as well as for the integration of PV energy (location of plants in places with high insolation and land availability).

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SUPPLEMENTARY MATERIAL

Table S1. Energy profile for the European Union computed by TIAM-UCL under a scenario of no climate mitigation in the EU (BAU scenario).

Generation/year (%)	2015	2020	2025	2030	2035	2040
Biomass	1.16	1.10	0.79	0.79	0.75	0.66
Biomass CCS	-	-	-	0	0	0
Coal	28.89	29.32	40.15	5.26	50.75	61.70
Coal CCS	-	-	-	0	0	0
Natural Gas	20.38	21.89	18.40	16.59	16.77	7.82
Natural Gas CCS	-	-	-	0	0	0
Geothermal	0.15	0.12	0.23	0.71	1.54	2.71
Hydro	15.19	15.42	17.49	19.21	20.49	21.99
Nuclear	23.79	20.04	15.30	10.57	7.89	5.20
Oil	0.41	0.32	0.23	0.16	0.11	0.06
Solar PV	3.55	3.55	3.55	1.77	0.38	0
Solar thermal	0.16	0.15	0.14	0.08	0.01	0
Tidal	0.01	0.01	0.01	0.01	0	0
Wind-offshore	1.86	1.46	1.13	0.80	0.55	0.22
Wind-onshore	4.44	4.44	4.44	2.17	0.77	0.00
Total	100.00	100.00	100.00	100.00	100.00	100.00

Table S2. CO_2 intensity of electricity (gCO_2/kWh) for the European Union computed by TIAM-UCL under a scenario of no climate mitigation in the EU (BAU scenario).

gCO_2/kWh	2015	2020	2025	2030	2035	2040
ELC-Centralised	319	335	397	476	488	550
ELC-Total	317	333	397	471	479	534

Table S3. Energy profile for the European Union computed by TIAM-UCL under EU climate policies consistent with the Paris Agreement (2DS scenario).

Generation/year (%)	2015	2020	2025	2030	2035	2040
Biomass	1.17	1.58	1.21	1.04	0.76	0.57
Biomass CCS	-	-	-	2.63	5.64	9.58
Coal	28.98	10.01	5.34	2.55	1.08	0.92
Coal CCS	-	-	-	0	0	0
Natural Gas	20.10	25.56	21.83	19.69	13.74	1.04
Natural Gas CCS	-	-	-	1.96	3.31	5.38
Geothermal	0.15	0.71	1.39	2.35	3.54	5.35
Hydro	11.33	17.07	18.17	20.51	20.75	22.18
Nuclear	23.89	34.35	42.21	44.24	0.10	54.69
Oil	0.41	0.35	0.24	0.16	0.36	0.06
Solar PV	3.57	3.84	3.68	1.79	0.36	0
Solar thermal	0.16	0.16	0.14	0.08	0.01	0
Tidal	0.01	0.01	0.01	0.01	0	0
Wind-offshore	1.86	1.58	1.17	0.81	0.52	0.21
Wind-onshore	4.46	4.80	4.60	2.19	0.74	0.00
Total	100.00	100.00	100.00	100.00	100.00	100.00

Table S4. CO_2 intensity of electricity (gCO_2/kWh) for the European Union computed by TIAM-UCL under EU climate policies consistent with the Paris Agreement (2DS scenario).

gCO_2/kWh	2015	2020	2025	2030	2035	2040
ELC-Centralised	319	175	121	69	13	(56)
ELC-Total	318	174	121	70	14	(55)

ECONOMIC ASSESSMENT OF FORMIC ACID PRODUCTION

The approach used to calculate the fixed capital investment was based on the factorial methodology described by Towler and Sinnott, 2013. The fixed capital investment is made up of: (i) the inside battery limits (ISBL) investment that is the cost of the plant itself; (ii) the modifications and improvements that must be made to the site infrastructure, known as offsite or OSBL investment; (iii) engineering and construction costs; and (iv) contingency charges. Briefly, the equipment cost of the CCU plant was assumed to come from both the ER cell cost and the CO_2 capture cost, as they are the critical units. We scaled-up the ER reactor (currently deployed only at laboratory scale) by including state-of-the-art cathode, anode, membrane and electrodes for an effective mass-transport and high current density based on Spurgeon and Kumar (2018). The cost of these units is calculated using the cost parameters found in literature for the three cases of performance (Spurgeon and Kumar, 2018).

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. Table 6 shows the ER FA plant cost parameters considered in this work.

The following hypotheses for the CCU plant were considered: (i) the geographical location of this analysis is North West Europe; (ii) the temporal scope is 25 years, and the reference year is 2016; (iii) the FA factory capacity is 17,000 t/year, with a production time of 350 days/year; (iv) the capital expenses were assumed to be incurred during the first year, while the operating expenses and product revenue were generated annually for 20 years and were discounted to the year of construction using a standard discount rate (r) of 8.0% (Spurgeon and Kumar, 2018); and, (v) the prices for raw materials, utilities, products and by-products, are estimated for year 2018, and they are considered constant, except for H_2, water, steam and PV electricity that varied among the performances. Cost data was corrected for inflation using the Consumer Price Index (CPI) for the raw materials and the Chemical Engineering Plant Cost Index (CEPCI) for the equipment.

Table S5. CO_2 ER plant cost parameters.

	Units	High Performance (HP)	Base Case (BS)	Low Performance (LP)
Electrolyzer cost (uninstalled)	€/m^2	13,299	26,597	39,896
Electrolyzer single-pass CO_2 conversion	%	25	50	75
Capital cost multiplier, CO_2 capture		5.00E-01	1.0	1.5
H_2, market price	€/kg	5.0	7.0	10
O_2 market price	€/kg	5.00E-02	5.00E-02	5.00E-02
PV electricity	€/MWh	20	55	95
Steam	€/ton	20.	30	45
Carbon dioxide	€/ton	free	Free	free
Methanol	€/ton	380	380	380
Water	€/m^3	1.5	5.0	9.0
HCOOH market price	€/kg	6.50E-01	6.50E-01	6.50E-01

The capital expenditure (CAPEX) was used as indicator of the total fixed capital costs (TFCC) plus the working capital. On the other hand, the net present value (NPV) is the metric used to evaluate the profitability of the CCU plant from a private investor perspective. The TFCC are the initial investment needed to build the plant and the working capital are the additional investment needed to start up the plant. TFCC, NPV and both variable cost of production (VCP) and fixed cost of production (FCP) were estimated as follows.

3.4.1. Fixed cost of production (TFCC)

The fixed cost of production include the following costs:

- *ISBL Plant Costs.* The ISBL plant cost includes the cost of procuring and installing all the process equipment that makes up the new plant. The costs were estimated based on the factorial Lang method:

$$C = F \sum C_e \qquad (2)$$

where C is the total plant ISBL capital cost; $F \sum C_e$ is the total delivered cost of major equipment; and F is the installation factor, known as Lang Factor (F = 4 was used in this study).

- *Offsite Costs*. Offsite cost or OSBL investment includes the costs of the additions that must be made to the site infrastructure to accommodate adding a new plant or increasing the capacity of an existing plant. Offsite investments were estimated as 40% of the ISBL as it is the percentage usually used as an initial estimate if no details of the site are known.
- *Engineering Costs.* The engineering costs include the costs of detailed design and other engineering services required to carry out the project. As a rule of thumb for engineering costs is 30% of ISBL plus OSBL cost for smaller projects.
- *Contingency Charges.* Contingency charges are extra costs added into the project budget to allow for variation from the cost estimate. A minimum contingency charge of 10% of ISBL plus OSBL cost was used on the study.
- *Working Capital.* Working capital is the additional money needed, above what it cost to build the plant, to start the plant up and run it until it starts earning income. Working capital was 15% of the fixed capital (ISBL plus OSBL cost).

3.4.2. Variable Costs of Production (VCP)

These include the costs of (i) raw materials consumed by the process; (ii) utilities; and (iii) consumables. These costs were estimated based on mass balances and the material prices as can be seem in Table S7.

3.4.3. Fixed Costs of Production (FCP)

These are incurred regardless of the plant operation rate or output. These costs are estimated as a percentage of the operating labour, ISBL and working capital (labour costs) (Perez-Fortes et al. 2016a). Fixed costs included:

- *Operating labour*. We assumed the plant operated on a shift-work basis. 4 operators, 3 shift positions, and a daily wage and labour cost value of 26.8 € (Eurostat, 2017).
- *Supervision*—taken as 25% of operating labour.
- *Direct salary overhead*—40% of operating labour plus supervision.
- *Maintenance*, which includes both materials and labour, and is typically estimated as 3% of ISBL investment
- *Property taxes and insurance*—typically 1% of ISBL fixed capital.
- *Interest* — 6% of working capital

3.4.4. Net Present Value (NPV)

The net present value (NPV) is the sum of the present values of the future cash flows:

$$NPV = \sum_{n=1}^{n=t} \frac{CF_n}{(1+i)^n} - INV \qquad (3)$$

being CF_n the net cash flow in year n, t the plant life in years and i the interest rate which was assumed as 8%, and INV the initial investment which equals CAPEX. The NPV is always less than the total future worth of the project because of the discounting of future cash flows (Towler and Sinnott, 2013). The net cash inflows were calculated based on the purchase price of the products (FA, H_2 and O_2) and their annual produced amount. A sensitivity analysis has been made in order to study the influence of price of CO_2.

Therefore, the revenues of the plant were calculated as the incomes earned from sales of main products and by-products. The cash cost of production (CCOP) that was determined by the sum of the fixed and variable production costs (minus the by-product revenues). Then, total cost of production (TCP) was calculated as the sum of the CCOP and the annual capital cost (ACC). The ACC can be estimated as a function of the discount rate (d) of 12%, the number of years of the plant (n) and the total fixed capital cost (TFCC) (4).

$$ACC = \frac{d \cdot (1+d)^n}{(1+d)^n - 1} \cdot TFCC \qquad (4)$$

The gross profit of the CCU plant is determined as the main product revenues minus TCP. A sensitivity analysis using an estimation of the evolution of the cost of energy until the year 2040 was carried out.

SUMMARY OF MASS AND ENERGY BALANCE FOR THE SYSTEMS

The model that describes the ER and purification processes has been developed and described in a previous study (Rumayor et al. 2018). Briefly, it is based on the reaction of the CO_2 ER shown in the table, assuming neutral to alkaline conditions. CO_2 and water are injected in the cathode.

Cathodic reaction	**Anodic reaction**
$CO_2 + H_2O + 2e^- \rightarrow HCOO^- + OH^-$ $2H_2O + 2e^- \rightarrow H_2 + 2\ OH^-$	$H_2O \rightarrow 2H^+ + 2e^- + 1/2\ O_2$
Overall reaction $CO_2 + 2H_2O \rightarrow HCOOH + O_2 + H_2$	

CO_2 is reduced to formate ($HCOO^-$) and H_2O to hydroxide ions (OH^-), in the presence of the correspondent electrolyte in the cathodic compartment of the ER cell. At the same time, the formation of oxygen (O_2) and protons (H^+) take place in the anodic compartment. Both the formate ions and hydroxide ions migrate to the centre compartment through the membrane where they balance the protons produced in the anode to form FA (HCOOH) and water (H_2O). In this model, H_2 evolution reaction (HER) is assumed as the unique parallel reaction in the cathode. It is considered that water is the chemical compound that is consumed regardless of the pH in the half-cell being acid or basic. The O_2 evolution reaction (OER) is the only reaction-taking place in the anode.

The distillation process was simulated by Aspen Plus software in a previous study and the details of mass and energy balance can be found in the corresponding supplementary data published (Dominguez-Ramos et al., 2015). Briefly, the simulation considers only presence of water (obtained as a head product) and FA (obtained as the bottom product) at the required concentration. Distilled water is recirculated and reinjected to the inlet freshwater stream to the cathode. Then, net water consumption is the difference between water in the inlet stream and water that is recirculated. The pure O_2 produced as a secondary product, mainly by the anodic reaction, is separated, liquefied and recovered, as well as, H_2, which is produced by the competing reaction and it is assumed to be pure.

Table S6. CO_2 emission intensity (kt CO_2/yr FU) for all referred sub-scenarios in Table 1 of the paper.

Scenario	Year					
	2015	**2020**	**2025**	**2030**	**2035**	**2040**
1.1. CONV FA +gELC (2DS)	3.70E+03	3.65E+03	3.63E+03	3.61E+03	3.59E+03	3.56E+03
1.2. CONV FA +gELC (BAU)	3.70E+03	3.71E+03	3.73E+03	3.76E+03	3.76E+03	3.78E+03
2.1. ER FA +gELC (2DS)	8.93E+03	8.93E+03	8.93E+03	8.93E+03	8.93E+03	8.93E+03
2.2. ER FA +gELC (BAU)	1.15E+04	1.03E+04	9.90E+03	9.49E+03	9.04E+03	8.49E+03
3.1.a. ER FA (LP) + gELC (2DS)	5.30E+04	4.73E+04	4.51E+04	4.31E+04	4.09E+04	3.81E+04
3.1.b. ER FA (LP) + gELC (BAU)	5.21E+04	5.27E+04	5.51E+04	5.79E+04	5.82E+04	6.02E+04
3.2.a. ER FA (BS) + gELC (2DS)	8.93E+03	8.93E+03	8.93E+03	8.93E+03	8.93E+03	8.93E+03
3.2.b. ER FA (BS) + gELC (BAU)	1.15E+04	1.03E+04	9.90E+03	9.49E+03	9.04E+03	8.49E+03
3.3.a. ER FA (HP) + gELC (2DS)	4.34E+03	3.93E+03	3.77E+03	3.63E+03	3.47E+03	3.27E+03
3.3.b. ER FA (HP) + gELC (BAU)	4.33E+03	4.38E+03	4.56E+03	4.78E+03	4.80E+03	4.95E+03
4.1.a. ER FA (HP), (DR=0.99) + gELC (2DS)	4.24E+03	3.84E+03	3.69E+03	3.54E+03	3.38E+03	3.19E+03
4.1.b. ER FA (HP), (DR=0.99) + gELC (BAU)	4.24E+03	4.29E+03	4.47E+03	4.68E+03	4.70E+03	4.86E+03
4.2.a. ER FA (HP), (DR=0.67) + gELC (2DS)	3.54E+03	3.21E+03	3.09E+03	2.98E+03	2.85E+03	2.69E+03
4.2.b. ER FA (HP), (DR=0.67) + gELC (BAU)	3.54E+03	3.58E+03	3.72E+03	3.89E+03	3.91E+03	4.03E+03
4.3.a. ER FA (HP), (DR=0.33) + gELC (2DS)	2.79E+03	2.55E+03	2.46E+03	2.38E+03	2.28E+03	2.17E+03
4.3.b. ER FA (HP), (DR=0.33) + gELC (BAU)	2.79E+03	2.82E+03	2.93E+03	3.05E+03	3.07E+03	3.16E+03
4.4.a. ER FA (HP), (DR=0.01) + gELC (2DS)	2.09E+03	1.93E+03	1.87E+03	1.81E+03	1.75E+03	1.67E+03
4.4.b. ER FA (HP), (DR=0.01) + gELC (BAU)	2.10E+03	2.12E+03	2.19E+03	2.27E+03	2.28E+03	2.34E+03
5.1.a. ER FA (HP), (DR=0.99) + PV ELC (2DS)	2.99E+03	2.73E+03	2.64E+03	2.55E+03	2.45E+03	2.33E+03
5.1.b. ER FA (HP), (DR=0.99) + PV ELC (BAU)	2.99E+03	3.02E+03	3.13E+03	3.26E+03	3.27E+03	3.37E+03
5.2.a. ER FA (HP), (DR=0.67) + PV ELC (2DS)	2.69E+03	2.47E+03	2.38E+03	2.30E+03	2.22E+03	2.11E+03
5.2.b. ER FA (HP), (DR=0.67) + PV ELC (BAU)	2.69E+03	2.71E+03	2.81E+03	2.93E+03	2.94E+03	3.03E+03
5.3.a. ER FA (HP), (DR=0.33) + PV ELC (2DS)	2.38E+03	2.18E+03	2.11E+03	2.05E+03	1.97E+03	1.88E+03
5.3.b. ER FA (HP), (DR=0.33) + PV ELC (BAU)	2.37E+03	2.40E+03	2.48E+03	2.58E+03	2.59E+03	2.66E+03
5.4.a. ER FA (HP), (DR=0.01) + PV ELC (2DS)	2.08E+03	1.92E+03	1.86E+03	1.80E+03	1.74E+03	1.66E+03
5.4.b. ER FA (HP), (DR=0.01) + PV ELC (BAU)	2.09E+03	2.10E+03	2.18E+03	2.26E+03	2.27E+03	2.33E+03

Table S7. Economic KPIs results for the FA ER plant as a function of the performance technology (HP vs LP and the BS case) and the derivation ratio (ER FA (HP), (DR=0.99-

Economic metric	Unit	Low Performance (LP)	Base Scenario (BS)	High Performance (HP)			
				DR=0.01	DR=0.33	DR=0.67	DR=0.99
ISBL	M€	4,520	604	165	50	48	48
OSBL	M€	1,810	242	65	20	19	19
TFCC	M€	9,810	1,310	357	110	106	105
CAPEX	M€	10,800	1,440	392	121	116	104
ACC	M€/yr	1,000	134	36	11	10.8	10.7
FCP	M€/yr	240	33	10.2	4.2	4.15	4.1

ISBL: Inside Battery Limits; OSBL: Offsite Battery Limits; TFCC: Total Fixed Capital Costs; CAPEX: Capital Expenditure; ACC: Annual Capital Cost; FCP: Fixed Cost of Production; CCP: Cash Cost of Production; TCP: Total Cost of Production; NPV: Net Present Value.

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