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How to make sustainable CO₂ conversion to Methanol: thermocatalytic versus electrocatalytic technology

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Abstract

Electrocatalytic (EC) and thermocatalytic (TC) conversion of CO₂ to methanol are promising carbon capture and utilization technologies. Herein, these CO₂-to-methanol conversion processes are analysed in terms of technical, environmental and economic feasibility. To this purpose, the catalytic performance of the same catalyst (CuO/ZnO/Al₂O₃) was evaluated in both EC and TC processes. Here is showed for the first time that this catalyst is (apart from TC route) also able to generate methanol through CO₂ EC reduction. This work presents lab scale tests, scaled-up simulations and evaluates the environmental and economic performance of these processes.

The carbon footprint of the TC and EC processes, scaled-up to the same productivity of ~3 kg/h methanol, scored ~8 kgCO₂ eq/kgCH₃OH. Strategies to reduce this impact are presented, such as

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2 improving the current density of the EC cell (i.e. 200 mA/cm² results in a reduction of 68% to 2.72
3 kgCO₂ eq/kgCH₃OH) and the availability of 100% renewable electricity (saving up to 62% carbon
4 footprint of both processes). Considering an effective allocation of the methanol productivity on a
5 real market scenario, both the TC and EC processes would start to be economically competitive at
6 methanol productivities > 19.1 kg/h and 3.3 kg/h, respectively. Moreover, if O₂ valorisation, a low
7 price of the renewable electricity and a carbon tax are considered, the economic profitability will rise;
8 e.g. the minimum levelised cost of product (LCOP of 1.45 €/kg and 1.67 €/kg, respectively) could be
9 reduced by 53%. Finally, our results pointed out that the CO₂ electroreduction process must be
10 optimized (e.g. improving catalysts performance and EC cell design reducing mass transfer
11 limitations) to achieve industrially relevant rates and the maturity of the thermocatalytic technology.
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26 **Keywords**

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29 Life Cycle Assessment (LCA), CO₂ hydrogenation, Electroreduction, Methanol, Ternary oxides,
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31 Synthetic fuels, Power-to-Fuels
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38 **Nomenclature**

39 Acronyms and Abbreviations	
40 LCA	41 Life Cycle Assessment
42 CED	43 Cumulative Energy Demand
44 CC	45 Climate Change
46 WRD	47 Water Resource Depletion
48 CE	49 Counter electrode

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CZA	CuO/ZnO/Al ₂ O ₃ catalyst
CV	Cyclic voltammetry
EC	Electrochemical
FE	Faradaic efficiency
FID	Flame ionization detector
GC	Gas Chromatography
GDE	Gas Diffusion Electrode
GHG	Greenhouse Gas
HC	Hydrocarbons
IPCC	Intergovernmental Panel on Climate Change
MeOH	Methanol
MPS	Medium Pressure Steam
RE	Reference electrode
RWGS	Reverse Water Gas Shift
SEM	Scanning Electrode Microscope
TCD	Thermal conductivity detector
TC	Thermochemical
TRL	Technology Readiness Level
WE	Working electrode

1 Introduction

The reduction of Greenhouse Gas (GHG) emissions has become of central importance for the overall sustainability. Currently, around 85% of the energy matrix is dependent on fossil fuels[1]. Burning fossil fuels provokes environmental pollutants such as CO₂, SO_x, NO_x, particulate matters, etc. being CO₂ the most representative GHG, its concentration has increased in the atmosphere from 278 ppm at the beginning of the industrial revolution to >410 ppm in 2019. This fact is causing global temperature raising with critical consequences [1]. Therefore, synthesize high added-value products *e.g.* methanol (MeOH) by CO₂ conversion is a promising approach to tackle the Global Warming. In this regard, carbon can be reused and introduced into a circular economy loop, thus reducing both CO₂ emissions and the dependence of external energy suppliers[2,3].

The conversion of CO₂ has many challenges. molecule.CO₂ free Gibbs energy is very high ($\Delta G^0 = -400$ kJ/mol) and, therefore, requires big amount of energy, optimized reaction conditions and catalysts with high stability [4]. There are several processes (*i.e.* reactions) to produce added-value products from CO₂ conversion; (i) stoichiometric (also called neutralization reactions), (ii) biochemical, (iii) photocatalytic, (iv) photoelectrochemical, (v) electrochemical (EC) and (vi) thermochemical (TC). This research work is focused on EC and TC routes.

Nowadays, the Sabatier and Fisher-Tropsch TC routes are still being investigated to produce fuels or chemicals owing to the fact that it is easy to integrate these processes at an industrial scale[5–9]. A considerable amount of literature has been published on thermocatalytic CO₂ conversion. Most of these studies have been focused on the MeOH production. MeOH provides an excellent means to store energy, it is a vital intermediate for several bulk chemicals and it can be used as a convenient fuel since it has a high-octane rating (almost half of the kWh/L relative to gasoline or diesel)[10]. Since 2009, MeOH installed production capacity is rising around 10% annually[11]. Around of 2 million tons of methanol are produced annually utilizing CO₂ as feedstock[12]. Nonetheless, the

1 results are not yet satisfactory because the traditional TC processes has some weaknesses, such as
2 poor stability of support in the presence of steam, it is less thermodynamically favourable than the
3 existing syngas route, and it requires a high energy demand[13]. On the other hand, the hydrogen
4 required by the process is still mainly produced from steam methane reforming (SMR), which is not
5 a cost-effective and sustainable process.[14] In terms of maturity, In 2016, Pérez-Fortes et al.[15]
6 cited a TRL of 6–7 for methanol synthesis from CO₂, which implies that this technology has been
7 demonstrated at prototypal scale in an operational environment. Hence, this TRL suggests that the
8 thermochemical conversion of CO₂ to produce methanol may be early industrialized [16].
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20 On the other hand, the EC conversion of CO₂ to methanol have advantages with respect to current
21 TC processes, such as (i) the direct use of renewable energy source, (ii) the use of water for the in-
22 situ protons (H⁺) generation and (iii) mild reaction conditions to convert the CO₂ into fuels or
23 chemicals, which are conventionally derived from petroleum. However, large overpotentials are
24 required to electrochemically reduce CO₂ (> 3.0 V) and to get reasonable amounts of fuels. Other
25 issues of the EC CO₂ reduction to methanol (or other liquid fuels) are the low productivity and the
26 low selectivity of state-of-the-art EC processes [17–25]. Moreover, the practical application of this
27 technology is delayed not only by fundamental developments (i.e. of new catalysts materials) but also
28 by the few efforts focussed on process engineering optimization and scale-up [26]. Nonetheless, the
29 future for electrosynthetic processes is promising. Compared with 10 years ago, there is now a
30 growing awareness of EC routes and the practical targets that might be achieved by electrochemical
31 processes. Also, with the increasing availability of a great diversity of EC cells and an increasing
32 experience of integrating electrolytic cells for H₂ production into complete industrial
33 processes[14,26–29], there are now lower obstacles to their scale-up. The EC CO₂ reduction
34 technology has been demonstrated at a broad range of TRLs from 3 to 6.[30–32] The lower TRL of
35 this technology with respect to the TC one demonstrates the lower level of current progress for its
36 commercialisation. It is still required additional engineering work on both novel electrocatalyst
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integrating smart catalyst and EC reactors, properly optimized to avoid mass transfer, selectivity and kinetics limitations. However, despite its relative immaturity, the current and continuous investments for the development of this technology may allow it to progress to higher TRLs, so that their positive attributes, such as CO₂ utilisation with renewable energy, may be exploited sooner[16].

Chemical industry is on track to achieve the emissions reductions required by 2050 (as defined during the Paris Agreement). The International Energy Agency recommends research in chemistry and engineering projects that will lower the energy use and the GHG footprint[11]. In this regard, some research has been carried out about different catalytic routes for the conversion of CO₂ into MeOH[7,25,33]. However, there is still very little scientific understanding of their environmental challenges[34]. Other than the efficiency of the process, it is also of main importance to evaluate its sustainability (in the overall life cycle analysis of exploited materials and energy sources). Perez-Fortes et al. [27] carried out an exhaustive work about the MeOH synthesis by TC processes using captured CO₂. They assessed the techno-economic aspects and the environmental issues by means of CO₂ metrics, however they did not conduct a Life Cycle Assessment (LCA) but pointed out that a complete LCA study should be done in the future. Furthermore, CO₂ hydrogenation is highly dependent on an efficient catalyst[35,36]. Consequently, research[37] recognises the necessity of exploring the environmental impact of the catalyst in the CO₂ conversion technologies as well as of integrated water electrolysis systems[38].

The aim of this work is to analyse the potential of scaling-up the TC and EC CO₂-to-methanol conversion processes. Therefore, the catalytic CO₂-to-methanol conversion was firstly evaluated at laboratory-scale by means of the electrocatalytic and thermocatalytic pathways, whose performance was compared. A low-cost catalyst composed of three oxides: copper oxide (CuO), zinc oxide (ZnO) and aluminium oxide (Al₂O₃), with a state-of-the-art performance for the TC process, was synthesised by the co-precipitation method and tested for this purpose. Herein, this kind of catalyst was tested for the first time in an EC CO₂ reduction process and its ability to produce methanol by this low

1 temperature process is demonstrated. In this way, the performances of these two CO₂-to methanol
2 conversion processes were simulated in a scaled-up configuration. To this purpose, considering the
3 different lab-scale productivities of the two processes, certain assumptions have been made based on
4 literature and our experimental data, to find feasible target in operative conditions that can bring to
5 their practical implementation. Another standpoint of this work is to consider the entire process,
6 including downstream separation and purification steps to obtain a commercial product (99.9
7 %mol_{methanol}). For the TC case, both the lab-scale reactor performance and a scaled-up process able
8 to reach an industrial methanol productivity of 3 kg/h were analyzed. Instead, a step by step and more
9 detailed study was performed for the scale-up of the EC CO₂ reduction process, because it has poorly
10 been studied in literature. Starting from the lab-scale case, another six EC cases were analysed to
11 subsequently consider the influence of: recycling of unreacted CO₂; increase of the electrode area up
12 to 100 cm²; increase of the inlet gas flow rate; increase of the current density up to 100 mA/cm² and
13 increase of the Faradaic efficiency up to ~90%, in order to reach the same final productivity of the
14 scaled-up TC process, for comparison purposes. A complete analyses of energy requirements of all
15 these process conditions was made. Moreover, the economic assessment (comprising a estimation of
16 operative and capital costs) and climate impacts (determined by a full LCA) of the most promising
17 cases of study are also presented, focusing then into the strategies to be implemented to attain techno-
18 economic and environmental benefits from these two TC and EC technologies with respect to an
19 industrial fossil-fuel-based process for methanol production.
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2 Methodology

2.1 *Process description of laboratory-scale processes*

A ternary CuO/ZnO/Al₂O₃ (CZA) catalyst was prepared via the coprecipitation route according to a method modified from literature[39]. The detailed description of the CZA catalyst preparation, and the experimental description of the thermocatalytic and electrocatalytic CO₂ reduction laboratory tests is given in the Supplementary Material (SM, Sections S1 to S3).

2.2 *Process scale-up and simulation*

The thermocatalytic and electrocatalytic processes were compared first at a laboratory scale for verifying their feasibility and obtaining raw data, which are suitable for their scale up, in order to be able to evaluate their environmental impacts and economic competitiveness. The scale-up of these processes, which is the main aim of this work, was simulated and the hypotheses used are described in the further paragraphs.

2.2.1 *Thermocatalytic process*

The simulated thermocatalytic process consists of four sections: a hydrogen production unit, a carbon dioxide compression chain, a reactor and a separation and purification section, as illustrated in the conceptual scheme in Figure 1.

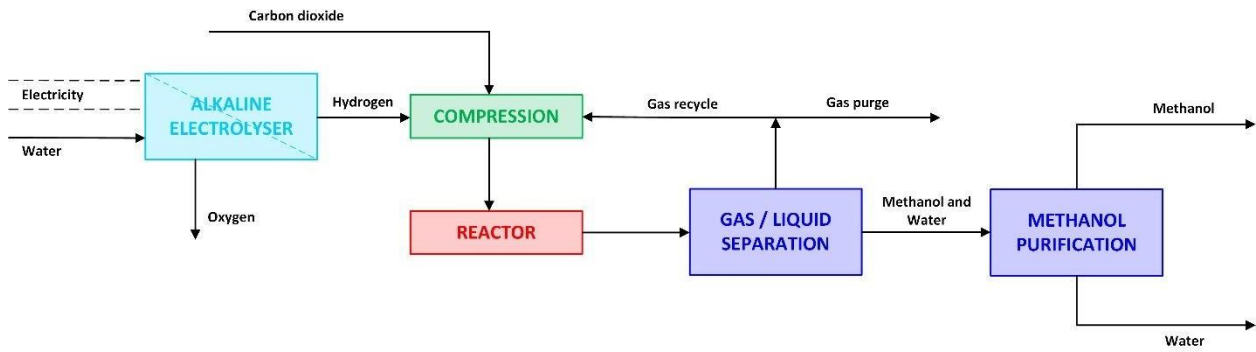
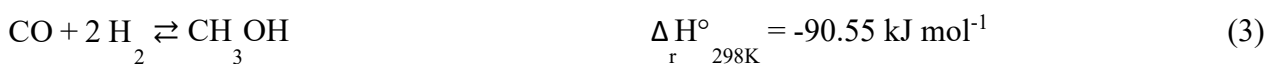


Figure 1. Conceptual design of the scaled-up thermocatalytic process.

Firstly, renewable hydrogen could be produced by using a low-temperature electrolyser (e.g. alkaline electrolyser)[40–43]. This strategy was exploited to render comparable the electrocatalytic and the thermocatalytic processes. Hence, water is pumped to 20 bar (suitable pressure for electrolysis) and it is fed to an alkaline electrolyser, which is powered by renewable electric energy. According to the open literature, the electrolysis has an efficiency of $\sim 70\%$ (LHV basis)[42,43]; even if water splitting is an endothermic reaction, the process requires heat removal due to its low efficiency. In addition, this heat could be used for heating the inlet water stream. The cathodic outlet stream (hydrogen) is cooled down ($40\text{ }^{\circ}\text{C}$) for condensing water vapour; and then it is mixed with fresh CO_2 and the gaseous recycle.

Secondly, CO_2 could be recovered from a process that emits large quantities of CO_2 by using carbon capture and utilization (CCU) technologies [42,44–49]. More specifically, the most common technologies are scrubbing with liquid solvents [50–53], adsorption on solids [48,52–54] and separation with membranes [55–57]. In order to make conservative hypotheses, a biogas-to-biomethane upgrading plant was assumed as the source of CO_2 ; hence, an impurity of 1.5% mol of methane (inert) was considered. The CO_2 stream has to be compressed up to 20 bar (process pressure) by using multistage compression (a maximum discharge/inlet pressure ratio equal to 3 was assumed) for optimizing the specific energy consumption. Subsequently, CO_2 and H_2 are mixed in

stoichiometric ratio (H_2/CO_2 molar ratio equal to 3) with the gas recycle stream. This gaseous stream is pre-heated through an economiser and then heated to 250 °C by using an electric heater. The reactor is kept at 250 °C by using cooling water for removing the excess of heat produced during the reaction. More in detail, the process involves three reactions: CO_2 hydrogenation to methanol and reverse water gas shift (RWGS) reaction, that are linearly independent, and CO hydrogenation to methanol (linearly dependent on the other two reactions), as reported in equations (1), (3) and (2), respectively[58,59].



According to the open literature, a Langmuir-Hinshelwood-Hougen-Watson kinetic model of the CO_2 hydrogenation to methanol on a CuZnAl-based catalyst was used[58]. Finally, the gaseous products are cooled to 30 °C and separated from the condensed water and methanol. On the one hand, the gaseous stream is recycled back to the reactor, but a small portion of these gases is purged to avoid inert gas accumulation. On the other hand, the liquid stream is fed to a stripper column for removing dissolved gases (mainly CO_2) that are recirculated. Lastly, the liquid bottom stream is fed to a distillation column for purifying the methanol at 99.9 %mol in the distillate and limiting the loss of methanol in the bottom wastewater stream at 10 ppm. For the sake of clarity, all the operative conditions of the simulated thermocatalytic process are summarised in Table 1 and a detailed process flow diagram is reported in Supplementary Figure S3.

Table 1. Operative parameters of the simulated thermocatalytic process.

Alkaline electrolyser efficiency	% (LHV basis)	70 %
Average reactor temperature	°C	250

Weight hourly space velocity in the reactor	$\text{Nm}^3 \text{kg}_{\text{cat}}^{-1} \text{h}^{-1}$	30.0
H_2/CO_2 inlet molar ratio	-	3
CO_2 molar fraction in the bottom of the stripper column	ppb	≤ 1
Methanol purity in the distillate	% mol	≥ 99.9
Methanol molar fraction in the bottom	ppm	≤ 10
Purged gas fraction	%	1.0

2.2.2 Electrocatalytic process

The simulated electrocatalytic process consists of two main sections: an electrocatalytic module and a separation and purification section, as schematised in Figure 2.

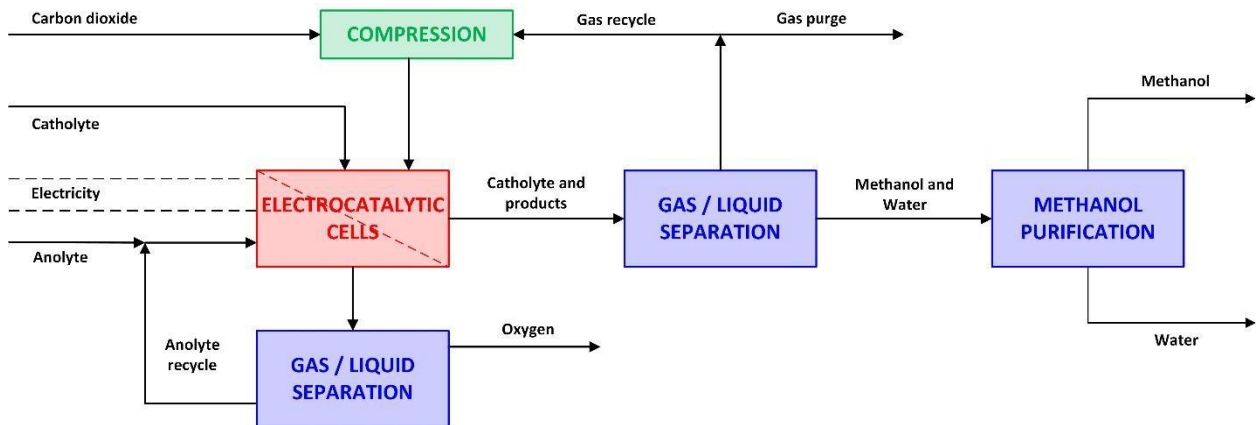
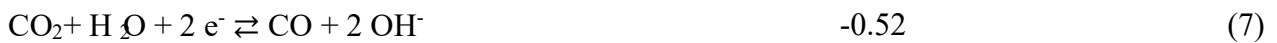


Figure 2. Conceptual design of the scaled-up electrocatalytic process.

First of all, the electrocatalytic module consists in several parallelised stacks of cells, that are composed by an anode, a cathode and an electrolyte. In the present work, the electrolyte is a 0.1 M aqueous solution of KHCO_3 , while the two chambers are separated by a semi-permeable membrane that allows the permeation of OH^- . On the one side, the anode could be made of noble metals (for

instance, Pt and Ir), on which the oxidation of OH⁻ occurs, as reported in equation (4). On the other side, the cathode is made of a CuZnAl-based catalyst which is deposited on a porous carbon paper. The reduction of both CO₂ and water occurs on the catalytic surface. More in detail, the cathodic reaction system is very complex; in fact, the water is reduced to H₂ and OH⁻, as detailed in equation (5). Nevertheless, at the same time, CO₂ and water reacts to produce methanol (6), CO (7) and by-products (for instance, formate in equation (8)). Furthermore, CO₂ is fed to the cathode and it partially dissolves into the catholyte, producing CO₃²⁻ and HCO₃⁻ species that could be part of the complex reaction system. For the sake of clarity and simplicity, the reaction mechanisms were not investigated and implemented in the simulation of the EC process.



Products dilute the electrolyte solution; therefore, the residence time of the electrolyte was defined for achieving a maximum reduction of 5 % of its initial concentration and maintaining conditions similar to the laboratory-scale batch process. The anolyte is recovered and recycled in order to reduce operative costs.

The outlet catholyte stream is fed to the second section of the process for separating gases and purifying the methanol. H₂, CO and CO₂ are mainly separated from water and liquid products in a biphasic vessel. On the one side, the liquid stream is fed to a stripping column to remove dissolved

gases and then it is fed to a distillation column to purify the methanol in the distillate, similarly to the TC process. On the other side, the gaseous stream is partially purged, then mixed with fresh CO₂ and recycled to the cathode of the electrocatalytic module. The operating pressure of the electrocatalytic cells is not atmospheric as the laboratory-scale cell due to dilution of the CO₂ in the recycle. For the purpose of operating in condition near the laboratory-scale test unit, a maximum operative pressure of 5 bar was assumed. The gaseous purged fraction was selected in order to guarantee a CO₂ partial pressure within the cathode equal to 1 bar, which is the operative value of the laboratory-scale cell. The main operative parameters of the electrocatalytic process are summarised in Table 2 and a detailed process flow diagram is illustrated in Supplementary Figure S4.

Table 2. Operative parameters of the electrocatalytic process.

Operative total pressure of the electrocatalytic cells	bar	≤ 5
CO ₂ partial pressure at the cathode inlet	bar	1
Concentration of KHCO ₃ in the inlet electrolyte	mol dm ⁻³	0.1
CO ₂ molar fraction in the bottom of of the stripper column	ppb	≤ 1
Methanol purity in the distillate	% mol	≥ 99.9
Methanol molar fraction in the bottom of the distillation column	ppm	≤ 10

2.2.3 Definition of the cases of study

First of all, two laboratory-scale cases were defined for the thermocatalytic and the electrocatalytic processes, namely TC-lab and EC-lab, respectively. These two cases were defined to compare the laboratory-scale processes and to obtain raw data for the Life Cycle Inventory. It is worth noting that experimental test benches do not include gas-liquid separation, product purification and heat integration. Hence, as described before, a scaled-up concept for each process was proposed in order

1
2 to study the technical, economic and environmental assessment of these two different technologies,
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4 considering also the separation and purification steps required to obtain a commercial product.

5 Since the scale-up of an EC CO₂ reduction process has been poorly studied in literature, a step by
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7 step and more detailed study was here performed. Some electrochemical raw data are strictly related
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9 to the laboratory-scale test benches, and different operative conditions can be implemented at a higher
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11 scale. For these reasons, six EC cases were analysed: EC-1, EC-2, EC-3, EC-4, EC-5 and EC-6;
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13 whereas, only one scaled-up TC case was considered (TC-1). All the operative parameters concerning
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15 the case studies are summarised in
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20 Table 3.

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26 Table 3. Parameters of the electrocatalytic case studies.

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Parameter	Unit	EC-lab	EC-1	EC-2	EC-3	EC-4	EC-5	EC-6
Inlet gaseous molar flow rate in the cathode (stream 3)	mol h ⁻¹	2.44	2.44	2436	2436	2436	2436	2436
Active cell area	cm ²	3	3	3	100	100	100	100
Inlet gaseous volumetric flow rate in a single cell	NI h ⁻¹	2.44	2.44	2.44	2.44	14.07	14.07	14.07
Current density	mA cm ⁻²	2.4	2.4	2.4	2.4	2.4	100	100
CO faradaic efficiency	%	14.49	14.49	14.49	14.49	14.49	14.49	2.541
CH ₃ OH faradaic efficiency	%	32.70	32.70	32.70	32.70	32.70	32.70	89.30
HCOOH faradaic efficiency	%	0.54	0.54	0.54	0.54	0.54	0.54	0.068
H ₂ faradaic efficiency	%	52.16	52.16	52.16	52.16	52.16	52.16	8.091

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59 The characteristics of the EC cases of study are as follows:

- 1 • **EC-1:** the process involves lab-scale EC cells and it includes a recycle of the gases. The purge
2 fraction was optimized for keeping the CO₂ partial pressure at 1 bar at the cathode inlet. In
3 addition, by-products (H₂ and CO) were considered as inert species (although it is known that CO
4 electroreduction could also occur).
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- 7 • **EC-2:** the overall inlet CO₂ stream was increased by 1000 times.
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- 9 • **EC-3:** the active cell area was increased from 3 cm² to 100 cm², which is a state-of-the-art scale
10 for TRL5 CO₂ electrochemical reduction demonstration technologies[30] and for fuel cells
11 [42,43,60]. It is worth noting that this variation causes changes in the fluid-dynamic regime and
12 in the current and potential distribution[61].
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- 15 • **EC-4:** the gaseous flow rate in a single cell was increased in order to maintain the lab-scale fluid-
16 dynamic regime. More in detail, the Reynolds number was kept constant[61] assuming a
17 negligible thickness of the cell with respect to its sides; therefore, equation (9) was derived under
18 these assumption. $A_{c,n}$ (m²) represents the active cell area of the n-th case of study and V_n is the
19 gaseous flow rate at the inlet of the cell of the n-th case of study.
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$$V_4 \approx \dot{V}_1 \cdot \sqrt{\frac{A_{c,4}}{A_{c,1}}} \quad (9)$$

- 22 • **EC-5:** the current density was increased from 2.4 mA/cm² to 100 mA/cm², which has already
23 been achieved for some CO₂ electroreduction process [62]. The potential and current distribution
24 undeniably depends on many characteristics of the EC cell (e.g., geometry, catalyst, electrodes,
25 electrolyte, etc.)[61].
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- 28 • **EC-6:** the electrocatalytic performances (faradaic efficiencies) were selected in order to achieve
29 TC-1 methanol productivity.
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2.2 Economic assessment procedure

An economic assessment of a process is crucial for establishing its feasibility and the competitiveness of a product on the market. The estimation of the capital and operating costs is described in the further paragraphs.

2.3.1 Levelised cost of product

The levelised cost of product (LCOP, €/kg) represents the average cost of product over the time horizon considering the inflation rate (IR), which was assumed equal to 2 %, while the time horizon (TH, y) was defined as 20 years[42,63]. The most important assumption for calculating the LCOP is the zeroing of the net present value (NPV, €) at the end of the time horizon. According to equation (10), the NPV is defined as the difference between the sum of the discounted cash flows over the time horizon and the total plant investment (TPI, €). The cash flow (CF_t, €/y) is defined as the difference between revenues and expenditures; while the discount rate was reasonably assumed equal to 10 %[42,64–67].

$$NPV = -TPI + \sum_{t=1}^{TH} \frac{P_{MeOH,t} \cdot LCOP - O\&M}{(1 + DR)^t} \quad (10)$$

Where $P_{MeOH,t}$ (kg/y) represents the annual productivity of methanol and O&M (€/y) is the operating and maintenance cost.

2.3.2 Operating and maintenance cost estimation

The operating and maintenance cost (O&M, €/y) represents the overall costs related to maintenance, operating labour, replacement, raw materials, utilities, gaseous pollutant treatment, wastewater treatment and waste disposal[42,63–65,68]. For the sake of brevity, the operating and maintenance cost estimation procedure and the economic data for its calculation are detailed in the Section S6 of the SM.

2.3.3 *Capital cost estimation*

The total plant investment (TPI, €) could be estimated as the sum of the total module costs (TMC, €) of all the pieces of equipment[42,63–65,68]. For the sake of brevity, the detailed estimation of the TPI is reported in the Section S7 of the SM.

2.4 *Life Cycle Assessment procedure*

A comparative LCA of the previously mentioned TC and EC processes was conducted. LCA is an objective method to evaluate the environmental impacts of a product or a process and a suitable tool to assess the environmental impacts of chemical reactions[69]. LCA methodology is standardized[70,71] and this research work was carried out following the ISO standards.

The phases of an LCA are four: i. Goal and scope definition. ii. Life Cycle Inventory (LCI). iii. Impact assessment and iv. Interpretation.

2.4.1 *Goal and scope*

The comparative LCA aims to determine the environmental impacts of methanol production by means of thermocatalytic and electrocatalytic processes by using the same CO₂ conversion catalyst, which allows a more direct comparison of the influence of the different process conditions and required downstream processing of the stream generated by these two technologies.

This LCA is based on experimental data (primary) from laboratory experiments. Insights from lab scale are interesting for research in the early stage. However, there is a disparity between the productivities of these two processes, being the TC route more productive than EC. Thus, this study also explores the environmental impacts of the scaled-up versions of both technologies, considering that the EC technology theoretically reaches the TC productivity, being the latter more mature for industrialization. Hence, the here reported LCA compares first the MeOH production in lab scale. Subsequently, a comparative LCA of the cases of study: TC-1, EC-5 and EC-6 reported in the section

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2 2.2 was performed to explain the differences on environmental impacts of these scaled-up cases (at
3 industrially relevant productions rates), including also the downstream and purification processing
4 steps.
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7 System boundaries of this LCA study encompass those elements necessary to carry out the CO₂
8 reduction into MeOH: Cell materials, catalyst, gas flows (inlet and outlet) and the energy of the
9 reaction. The results will be showed per 1g MeOH production. The approach followed in this research
10 work covers all stages from cradle-to-gate. This is where the system boundary is drawn since it is
11 assumed that the final product (MeOH) could be distributed to be consumed and its end-of-life is
12 outside of the considered system, which is more focused in the production process.
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24 2.4.2 *Life Cycle Inventory (LCI)*

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26 Life Cycle Inventory is the phase in which all the inputs and outputs are gathered. For the sake of
27 briefness, the LCI of all cases of study is showed and explained in Section S9 of the SM.
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30 31 32 33 2.4.3 *Impact assessment*

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35 The third LCA phase is the Impact assessment. This phase involves the calculation of the potential
36 environmental impacts of the system. In the present paper, Climate Change (CC), Water Resource
37 Depletion (WRD) and Cumulative Energy Demand (CED) have been calculated[72–74]:
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- 42 • CC is an environmental impact developed by the Intergovernmental Panel on Climate Change
43 (IPCC)[75]. It contains the climate change factors of IPCC with a timeframe of 100 years and the
44 results are expressed in kg CO₂ eq.
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- 47 • WRD represents the freshwater scarcity [76].
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- 50 • CED represents the primary energy consumption [77] of the system.
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56 Finally, the fourth phase of an LCA is the Interpretation phase and it will be analysed in the following
57 section.
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3 Results and Discussion

3.1 Laboratory-scale methanol production

The detailed description of the CZA catalyst performances of the thermocatalytic and electrocatalytic CO₂ reduction laboratory tests is given in the Supplementary Material (SM, Section S5). This investigation revealed that this catalyst working under high temperature and pressure conditions in a thermocatalytic process has the significant potential to produce the same product (MeOH) under milder electrochemical conditions. For a brief comparison, the best MeOH yields and productivities over the here synthesised CZA catalyst at the tested TC and EC lab-scale conditions are presented in Figure 3. What is striking about the result is that the electrochemical reduction of CO₂ can approach the methanol yield of a thermocatalytic process (*i.e.* ~20.5 g MeOH/kg_{cat} gCO_{2,INLET}). However, the best methanol productivity that was reached by means of the lab-scale EC reactor was 4-fold lower than such of the lab-scale TC reactor due to the significant difference in scale of the two test benches.

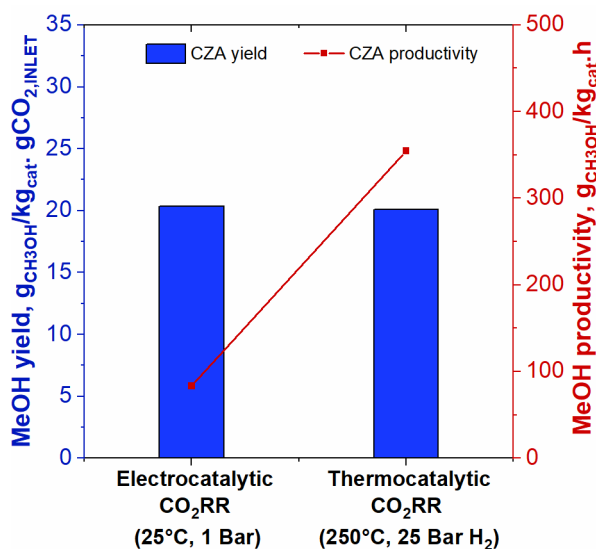


Figure 3. Comparison of methanol yield and productivity for TC and EC reduction CO₂ over the synthesized CZA catalyst.

Electrocatalysis would be a promising opportunity to reduce CO₂ to methanol, as long as its performance will be industrially attractive. Therefore, this work shows through simulations that,

1 scaling up both EC and TC processes under realistic assumptions for increasing the overall CO₂
2 conversion and the methanol productivity, they can have an industrial appeal. Further research is
3
4 needed to overcome these transition scenarios from the laboratory to the large scale, as it will be
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6 better explained in the following paragraphs.
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10 **3.2 Technical assessment of both TC and EC processes**

11 All the investigated scenarios shown in

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14 Table 3 were modelled under realistic assumptions to simulate the transition from laboratory-scale to
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16 a large scale. Figure 4 sum up relevant results attained for the two technologies at the laboratory scale
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18 and in the best simulated scenarios. It can be seen from the Figure 4 that the difference in terms of
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20 CO₂ conversion between the two lab-scale processes is extremely significative; however, this aspect
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22 is counterbalanced by the specific electric consumption. Concerning the integrated TC case (TC-1),
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24 it achieves a CO₂ conversion of 91.4 % and the specific electric consumption of the overall process
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26 is 10.5 Wh/g_{CH₃OH}. Regarding the EC process, the best industrial scenarios are EC-5 and EC-6, in
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28 which the CO₂ conversion reaches 74.9 % and 95.8 %, respectively. Nonetheless, their specific
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30 electric consumption is slightly higher than the one of the TC-1 case. Figure S11 shows the results
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32 for all the other simulated EC cases, whose performances are far away to reach that of TC scaled-up
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34 version. These results prove how the here considered assumptions had a significant contribution to
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36 the performance of a hypothetical industrial version of the electrocatalytic process.
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47 It is worth mentioning that considering the recycling of the unreacted CO₂ gas, among others
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49 operative conditions, the current densities that would have to be reached to get the same productivity
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51 of the TC-1 process (100 mA/cm²) are not far from the state-of-the-art values reached up to now for
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53 the EC CO₂ reduction to methanol (Figure S10). On the contrary, Figure S12 (SM) shows the worst
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55 scenario, which indicates that current densities >1000 mA/cm² would have to be reached if the
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57 simulated scenario had not considered the recycling of the unreacted CO₂ gas. This demonstrates that
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by tuning the operative conditions of the process, electrocatalysis would be a promising opportunity to reduce CO₂.

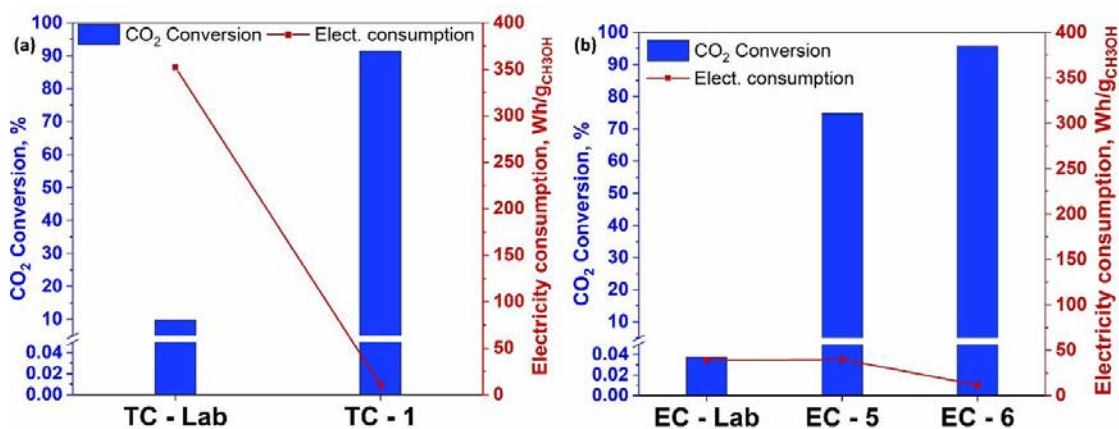


Figure 4. CO₂ conversion and specific electricity consumption of: (a) lab-scale (TC-Lab) and scaled-up thermocatalytic (TC-1) processes, (b) lab-scale (EC-Lab) and scaled-up electrocatalytic (EC-5 and EC-6) processes.

As seen in the Figure 4, both thermocatalysis and electrocatalysis could provide promising CO₂ reducing scenarios to produce methanol. It should be noted that the TC process is a path more viable than the EC process, since the first is a well-established technology nowadays[14]. Nevertheless, after analysing the scientific works done so far, it is possible to realize that the actually achieved current densities in EC CO₂R reactors with methanol production (~ 90 mA/cm², see Figure S10, SM) are only 10 % lower than the here proposed target value (i.e. 100 mA/cm², for EC-5 and EC-6 cases). Moreover, the transformation of CO₂ to other high-octane alcohols (C₂₊) like ethanol has already achieved a current density of around 300 mA/cm². [78] Therefore, further efforts to optimize process conditions and cell designs, in order to decrease mass transfer limitation issues and pursuing high methanol production rates (high current densities) and selectivity are still envisaged. Indeed, the here reported CZA electrocatalyst is able to produce high current densities when there are no mass transfer limitations, as it can be seen in the Linear Sweep Voltammetry recorded on this electrocatalyst in a Rotating Disk Electrode (RDE) System (see Figure S13, SM). On the other hand, nowadays, the

production of CO or/and syngas in EC CO₂R systems is valuable and have reached >100 mA/cm² on existing catalyst[2,26]. Therefore, a hybrid co-electrolysis of CO₂ to syngas, afterwards used for converting CO₂ to MeOH through a thermocatalytic process, could also be a promising alternative to the direct EC conversion in a one-step process[14,26–29].

In following, detailed results (see Table 4) and a deeper discussion on both TC and EC case studies are reported.

Table 4. Results on the simulated TC and EC case studies.

Parameter	Unit	TC-1	EC-1	EC-2	EC-3	EC-4	EC-5	EC-6
Number of cells	-	-	1804	1804207	55402	54311	1651	1745
Catholyte residence time	h	-	120	120	24	10	0.5	0.5
Anolyte residence time	h	-	670	670	20	20	0.5	0.5
Pressure	bar	20	4.89	4.88	4.85	4.98	4.99	5.0
Purge fraction	%	1.00	0.11	0.11	3.61	0.64	21.1	3.89
Catalyst amount	g	3995	7.9	7939	8126	7966	242	256
CH ₃ OH productivity	g h ⁻¹	3009	0.663	663	672	663	835	3012
Overall CO ₂ conversion	%	91.43	58.54	58.44	60.30	59.14	74.86	95.76
Electric consumption	Wh _{el} g ⁻¹	10.52	54.65	54.99	40.35	42.29	39.86	11.68
Chilled water consumption	Wh _{th} g ⁻¹	1.02	53.55	53.31	1.66	9.28	0.26	0.07
Cooling water consumption	Wh _{th} g ⁻¹	5.67	108.9	106.8	21.44	44.24	15.09	4.63
MP steam consumption	Wh _{th} g ⁻¹	1.91	113.6	111.3	22.11	45.82	15.83	4.86

Regarding the thermocatalytic process (TC-1), the overall pressure in the reactor is 20 bar, the reaction temperature is 250 °C, the space velocity is 30 Nm³ kg_{cat}⁻¹ h⁻¹ and the gaseous purged fraction is 1.0 % of the recycled gases. As reported in

1 , the overall CO₂ conversion is greater than 91.4 %, although the CO₂ conversion per pass is 9.64 %,
2 because a CH₃OH selectivity of around 96.1 % can be reached due to the separation of water and
3 methanol from the gases. Moreover, the kinetic model[58] includes the CO hydrogenation to
4 methanol and the reverse water gas shift reaction; hence, the methanol productivity is 0.878
5 mol_{CH₃OH}/mol_{CO₂} (0.639 g_{CH₃OH}/g_{CO₂}). As far as the specific consumptions are concerned, the electric
6 consumption is high (10.52 Wh_{el}/g_{CH₃OH}) due to the electrochemical production of renewable H₂. In
7 detail, the electricity demand is divided as follows: 96.7 % for electrolysis, 1.7 % for CO₂
8 compression and water pumping and 1.6 % for heating the gases at the reactor inlet. The chilled water
9 consumption is 1.02 Wh_{th}/g_{CH₃OH} in the condenser of the stripping column, whereas, the cooling water
10 consumption in all coolers is 5.67 Wh_{th}/g_{CH₃OH}. The two reboilers require 1.91 Wh_{th}/g_{CH₃OH}: 14 % for
11 the stripper (165 °C) and 86 % for the distillation column (120 °C). In this case of study, a heat duty
12 equal to 3.43 Wh_{th}/g_{CH₃OH} was thermally integrated in the head-tail economizer.
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29 Concerning the electrocatalytic cases of study, there are many considerations that have great
30 importance for the scale-up of the electrocatalytic device. Firstly, EC-1 involves a separation and
31 purification section and a gas recycle (that is of fundamental importance to enhance the CO₂
32 conversion and CH₃OH productivity with respect to the lab-scale, see Figure 4 and Figure S11, SM).
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34 To keep the CO₂ partial pressure at 1 bar, the total pressure was increases up to 5 bar (arbitrary limit
35 to have a low-pressure process and maintain the conditions close to the laboratory-scale cell, that is
36 a CO₂ partial pressure of 1 bar). It is worth mentioning that H₂ and CO were considered as inert
37 species within the electrocatalytic cell due to the lack of a detailed reaction pathway; therefore, these
38 aspects should be further investigated and can be a course of improvement of the EC reactor
39 performance. The gas recycle increases the flow rate of gaseous reactants and, for keeping constant
40 the fluid-dynamic within a cell, the system was parallelised in 1804 cells. These features result in an
41 increase of the overall CO₂ conversion (~ 58.5 %). In this case study (EC-1), the methanol
42 productivity is 0.663 g_{CH₃OH}/h, which corresponds to a specific productivity of 0.193
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1 mol_{CH₃OH}/mol_{CO₂} (0.141 g_{CH₃OH}/g_{CO₂}). However, the specific consumptions are extremely high due
2 to a low CH₃OH faradaic efficiency and a low concentration of the products in the liquid outlet stream
3 (0.246 % mol methanol). The electric specific consumption is 54.65 Wh_{el}/g_{CH₃OH} (71.7 % for the
4 electrocatalytic reactions and 28.3 % for compression and pumping). The chilled water consumption
5 is 53.55 Wh_{th}/g_{CH₃OH}, the cooling water requirement is 108.9 Wh_{th}/g_{CH₃OH} and MP steam consumption
6 is 113.6 Wh_{th}/g_{CH₃OH}.

7 In the second electrocatalytic case of study (EC-2), the variation in the CO₂ inlet flow rate drastically
8 increases the total number of electrocatalytic cells due to the low performances of the cells and their
9 small active area. All the other operative parameters were not affected by a change in the flow rate;
10 hence, the specific energy consumptions are roughly the same of the previous case of study.

11 A realistic value of the active area (100 cm²) was assumed in the third case of study (EC-3) for
12 reducing the number of electrocatalytic cells. It is worth pointing out that the current and potential
13 distribution between the electrodes changes due to a variation of the polarization, which strictly
14 depends on the geometry of the EC cell[61]. This aspect was not modelled due to the lack of
15 information about the distribution of the current on the surface of the electrode; nevertheless, it will
16 have to be coped in future researches. The variation in the cell area results in an increase of the
17 concentration of the products in the liquid stream; therefore, the specific energy consumptions are
18 drastically reduced: 40.35 Wh_{el}/g_{CH₃OH} of electricity, 1.66 Wh_{th}/g_{CH₃OH} of chilled water, 21.44
19 Wh_{th}/g_{CH₃OH} of cooling water and 22.11 Wh_{th}/g_{CH₃OH} of MP steam.

20 Regarding the fourth case of study (EC-4), the volumetric flow rate within a cell was increased to
21 keep constant the Reynolds number. This variation results in a decrease of the methanol concentration
22 in the liquid stream (due to the constant faradaic efficiency) and, consequently, an increase in the
23 specific energy consumptions. In addition, the size of the electrocatalytic stacks do not change with
24 respect to the previous case.

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2 In the fifth case of study (EC-5), to approach industrially relevant conditions, the current density was
3 increased from 2.4 mA/cm² to 100 mA/cm². This parameter is affected by several features (e.g.
4 geometry, overpotentials, polarization, etc.); however, it has to be considered as a target value, that
5 should be achieved to obtain performances similar to other electrochemical processes that involves
6 the electrochemical reduction of CO₂ (e.g. CO₂ reduction to CO). The variation in the current density
7 affects all the operative parameters and the size of the electrocatalytic module. More in detail, the
8 number of the electrocatalytic cells decreases drastically and, at the same time, both the anolyte and
9 catholyte residence time is reduced. Moreover, an increase in the methanol specific productivity
10 (0.244 mol_{CH₃OH}/mol_{CO₂}) is followed by a reduction in specific energy consumptions.
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22 Lastly, in the sixth electrocatalytic case of study (EC-6), the methanol faradaic efficiency was
23 increased from 26.4 % to 89.3 %, by proportionally reducing the other faradaic efficiencies. This
24 value of the CH₃OH faradaic efficiency was selected in order to achieve a target CH₃OH productivity
25 equal to the thermocatalytic case of study (TC-1), that is highly relevant for an industrial application.
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32 More specifically, the overall CO₂ conversion reaches 95.76 % with a specific methanol productivity
33 equal to 0.879 mol_{CH₃OH}/mol_{CO₂} (0.639 g_{CH₃OH}/g_{CO₂}). Hence, the specific electric consumption is
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37 11.68 Wh_{el}/g_{CH₃OH} (99.23 % for electrolysis and CO₂ reduction and 0.77 % for compression and
38 pumping); while thermal specific consumptions are: 0.07 Wh_{th}/g_{CH₃OH} of chilled water, 4.63
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42 Wh_{th}/g_{CH₃OH} of cooling water and 4.86 Wh_{th}/g_{CH₃OH} of MP steam. These values are comparable with
43 the results obtained for the thermocatalytic process; more in detail, the MP steam demand in the TC-
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47 1 case is 2.5 times lower than in the EC-6 case study due to the high methanol concentration in the
48 liquid stream which is fed to the purification section. Hence, it comes out that the EC conversion of
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3.3 Economic assessment on the scaled-up processes

3.3.1 Levelized cost of product

At this stage, the feasibility (technical viability and economic profitability) requires an economic assessment of the most energetically competitive cases of study. Therefore, three of them were selected for the economic assessment: TC-1, EC-5 and EC-6. Figure 5(a) illustrates the levelised cost of product at the variation of the methanol productivity of the plant. According to a market estimation, the methanol industrial price ranges between 0.2 €/kg and 0.9 €/kg[79,80], although for laboratory use it can be one order of magnitude higher. As expected, the LCOP decreases as the productivity rises for all the three cases and it exhibits a minimum. Regarding the TC-1 case of study, the LCOP of methanol decreases from 27.13 €/kg at 1 kg/h to 1.45 €/kg at $5 \cdot 10^5$ kg/h. More specifically, in the optimal economic condition, the LCOP (1.45 €/kg) is constituted by operative costs (70.2 %) and capital costs (29.8 %). In detail, the operative costs are distributed as follows: maintenance (10.9%), labour (0.6%), utilities (76.3%), replacement (3.8%), raw materials (7.2%) and waste treatment and disposal (1.2%). As expected, the most significant contribution is related to utilities and, in more detail, they are distributed as follows: electric consumption of the electrolyser (68.7 %), heating energy (24.8 %) and cooling energy (6.6 %). Considering raw materials cost, they are related to CO₂ (86.3 %) and water (13.7 %). Whereas, the capital costs are constituted by heat exchangers (41.2 %), alkaline electrolyser (10.2 %), pumps and compressors (2.5 %), columns, vessels and reactors (46.1 %). The highest investment cost of the TC-1 case is related to the heat exchangers due to the low heat transfer coefficient of gases [65,81], which increases the heat exchange area. Those findings are consistent with data reported in the literature [59,80,82–84]; however, they are strictly related to techno-economic assumptions. What stands out from Figure 5(a) is that the TC-1 process does not seem to be economically more competitive than the traditional production of methanol, but could be introduced in some specific application fields like laboratory uses.

Regarding the two electrocatalytic case studies (EC-5 and EC-6), the results of the economic assessment are completely different between them. On the one hand, the LCOP in the EC-5 case reaches a minimum (6.86 €/kg) at $2 \cdot 10^4$ kg/h, and it is divided as follows: 18 % of capital costs and 82 % of operative costs. More in detail, the LCOP is high because of the low efficiency of the electrocatalytic cells; moreover, the operative costs reflect the considerable specific energy consumptions.

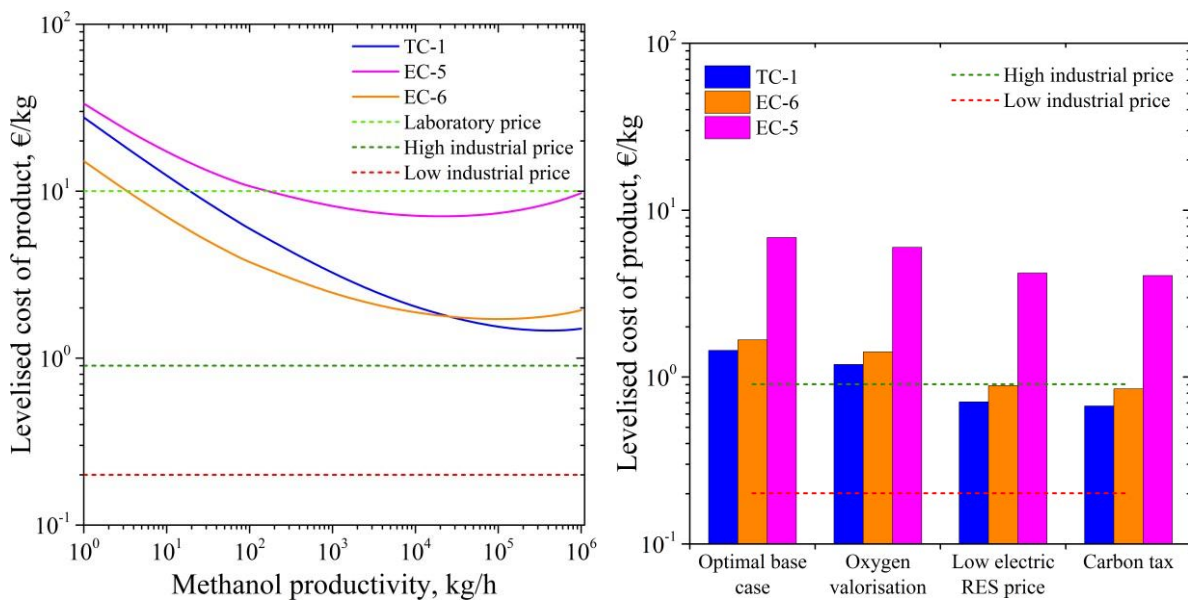


Figure 5. (a) Levelised cost of product (€/kg_{MeOH}) at the variation of the CH₃OH productivity in the three selected case studies: TC-1, EC-5 and EC-6. (b) Levelised cost of product (€/kg_{MeOH}) subsequently considering O₂ valorisation (0.15 €/kg_{O2}), a lower price of the renewable electricity (0.005 €/kWh_{el}) and a carbon tax (0.025 €/kg_{CO2}). For the sake of clarity, the economic estimation refers to the cost in December 2019 (CEPCI index equal to 592).

On the other hand, the LCOP of the EC-6 case of study ranges between 15.16 €/kg and 1.67 €/kg by varying the methanol productivity from 1 kg/h to 10⁶ kg/h. In the optimal condition, operative costs (78.6 %) are greater than the capital costs (21.4 %). More specifically, capital costs are constituted by the total module costs of heat exchangers (35.8 %), electrocatalytic cells (26.0 %), columns and

vessels (37.4 %) and pumps and compressors (0.8 %). The cost of heat exchangers is one of the most important items of the TPI in both cases of study (i.e. TC-1 and EC-6). In more detail, the overall heat transfer coefficient of liquids is much greater than that of gases. Hence, the size of the heat exchangers is smaller in the case of study EC-6. Consequently, if the same methanol productivity is considered, their cost in the case of study EC-6 will be 59% lower than in the case of study TC-1. Similar to the TC-1 case, operative costs are distributed as follows: labour (1.1 %), maintenance (6.9 %), utilities (79.8 %), raw materials (8.2 %), replacement (3.1 %) and waste treatment and disposal (0.9 %). These results are consistent with techno-economic analyses of other electrocatalytic processes [85]; however, the distribution of each cost depends strictly on technical and economic assumptions and on the plant size and design.

Oxygen is the main by-product of the electrochemical production of H₂ from water and it could be economically valorised. Its price ranges between 0.07 €/kg[43,86] and 0.15 €/kg[83,87] and the impact on the LCOP of the TC-1 and EC-6 cases could reach 18%, reducing it by approximately 0.25 €/kg, as reported in Figure 5(b). Another scenario in which both TC and EC processes can become even more economically attractive is when renewable electricity prices are reduced (0.004 – 0.010 €/kWh_{el})[42,63]. Indeed, an additional reduction of about 33% could be added to the previous mentioned case (O₂ valorisation). Hence, the two optimal cases of study (TC-1 and EC-6) start to be economically competitive with the traditional methanol production. Lastly, CO₂ taxation could rise due to more severe environmental restrictions[83,87]. Therefore, if a carbon tax of 0.025 €/kgCO₂ is considered, an additional reduction of roughly 3 % of the LCOP should be reached.

3.3.2 Allocation of the product on the market

The analysis of the LCOP provided the first indication of an economic viability of both processes. However, this study lack of some more precise information that could be useful for assessing a reliable economic viability. Hence, the allocation of the product on the market for NPV zeroing

1 should add a worthwhile contribution to the economic assessment of each process. For the sake of
2 brevity, the equations used for this estimation are detailed in the Section S8 of the SM.
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5 In the SM, Figure S8 illustrates the allocation of the methanol production for NPV zeroing at the
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7 variation of the plant productivity in the three cases of study (i.e. TC-1, EC-6 and EC-5). As a result
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9 of this assessment, if the real market scenario lay on the straight line, the NPV would be zero, the
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11 payback period (PBP) would be equal to the time horizon (i.e. 20 y) and the rate of return on
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13 investment (ROROI) would be 11.75 %. In addition, if the real market scenario lay below the straight
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15 line, the process would be economically profitable (i.e. $NPV > 0$, $PBP < TH$ and $ROROI > 11.75\%$);
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17 otherwise, it would not be cost-effective (i.e. $NPV < 0$, $PBP > TH$ and $ROROI < 11.75\%$). Moreover,
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19 cases of study TC-1, EC-6 and EC-5 start to be economically viable for methanol productivities
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21 greater than 19.1 kg/h, 3.3 kg/h and 150 kg/h, respectively.
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27 In conclusion, the economic assessment revealed that both small- and large-scale renewable methanol
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29 production facilities would be economically profitable if the product could be distributed successfully
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31 on the real market scenario. The EC processes requires evidently great research and development
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33 efforts to achieve the performance assumed in this work. However, even small pilot plants could be
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35 economically sustainable if the target performances are reached.
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40 41 **3.4 Life cycle assessment on the EC and TC processes**

42 43 44 45 **3.4.1 Comparative LCA on laboratory-scale EC and TC processes**

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47 A comparative LCA was conducted to investigate the environmental impacts of MeOH production
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49 by means of the two technical routes (TC and EC). LCI management was performed by using Simapro
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51 8 software. The first set of analyses examine the impact of producing 1g MeOH by means of TC or
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53 EC technology, both using the same catalyst in the laboratory-scale (Lab).
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1 The results for CC, WRD and CED impact categories suggest that the highest impacts are obtained
2 when the MeOH is produced by the TC-Lab route. Regarding CC, the EC-Lab case study has the
3 potential effect of producing $1.95 \cdot 10^{-2}$ kgCO₂ eq/g_{MeOH} while the TC-Lab case reaches around than 10
4 times higher values ($1.94 \cdot 10^{-5}$ kgCO₂ eq/g_{MeOH}). Furthermore, there is a significant difference between
5 the two assessed technologies in terms of WRD. Results revealed that WRD is 0.014 m³ in the EC-
6 Lab case and 0.680 m³ in the TC-Lab one. Therefore, water saving could be 0.67 m³ if 1g MeOH is
7 produced by means of EC-Lab instead of the TC-Lab technology. The CED was quantified as 0.104
8 MJ when 1g of MeOH is produced by EC-Lab route and ~37.2 times higher (3.87 MJ/g) when is
9 produced by the TC route.
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22 Notwithstanding the foregoing, both lab scale cases of study were deeper analysed in order to detect
23 the source of the effects and how they contribute to the final impact. Figure 6(a) shows the impact
24 contributions of every material used in the EC-Lab case study. The CO₂ consumption in the gas
25 diffusion process provokes a negative contribution in CC, which is considered as an environmental
26 benefit. Clearly, the catalyst components (CuO, ZnO, and Al₂O₃) and the carbon cloth, electrode
27 substrate, have not significant contributions to the final impacts (< 1 %). It is possible to notice that
28 the Nafion membrane gets the highest contribution (89.4%) in CC. Nevertheless, its impact was lower
29 in WRD (36.8 %) and 41.9 % in CED. These results reflect those of Evangelisti et al (2017),[88] who
30 also found a strong relationship between the CC impact and the membrane in a fuel cell stack. Also,
31 the Nafion 5% solution used to prepare the electrode has some impacts, that are 4.9 % in CC, 0.5 %
32 in WRD and in 1.1 % CED. Furthermore, the here reported results revealed that the environmental
33 impacts of the KHCO₃ based electrolyte regarding CC were negligible, but KHCO₃ influenced by
34 27.2 % and 27.0 % in CED and WRD, respectively. Therefore, KHCO₃ is one of the main contributors
35 to the impacts in WRD and CED and this is cannot be ignored. A recent study [89] examined the
36 trend in capture, storage and use of CO₂ by means of a dynamic LCA for formic acid production.
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57 Despite the catholyte in that study was an aqueous solution of KHCO₃, it was not taken into
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1 consideration in the inventory stage. Hence, if the present research work had followed the Aldaco et
2 al. (2019) [89] assumption about do not include the KHCO_3 in the inventory, the EC-Lab
3 environmental impacts would have been lower. Nevertheless, herein, it was preferred to include all
4 the elements that are mandatories for conducting the MeOH synthesis reaction in our experimental
5 setup. At this respect, KHCO_3 is essential and cannot be excluded from the system boundaries.
6
7 Considered the contribution of the Pt/Ir wire to the impacts, it is important to bear in mind the higher
8 environmental impacts of Pt with respect to Ir. Pt can reach values up to 3.4 % of the total CED
9 impact. The energy contribution in this EC-Lab case barely affects CC (2.6%), but in WRD it
10 represents 15.3% and 11.4 % in CED. Similarly, the use of deionized water hardly affects the CC (4.7
11 %), but it gets higher values in WRD (17.2 %) and CED (13.9 %).
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24 Figure 6(b) shows the breakdown of the environmental impacts of the TC-Lab case of study. The
25 most striking result is that energy contributes to more than 96% in the three assessed impact categories
26 for this case. Thus, materials and flow gases contributions are almost negligible. Due to this huge
27 contribution of the energy, CO_2 consumption in the TC-Lab process is only able to reach 1.7 % of
28 environmental benefits (negative value in CC).
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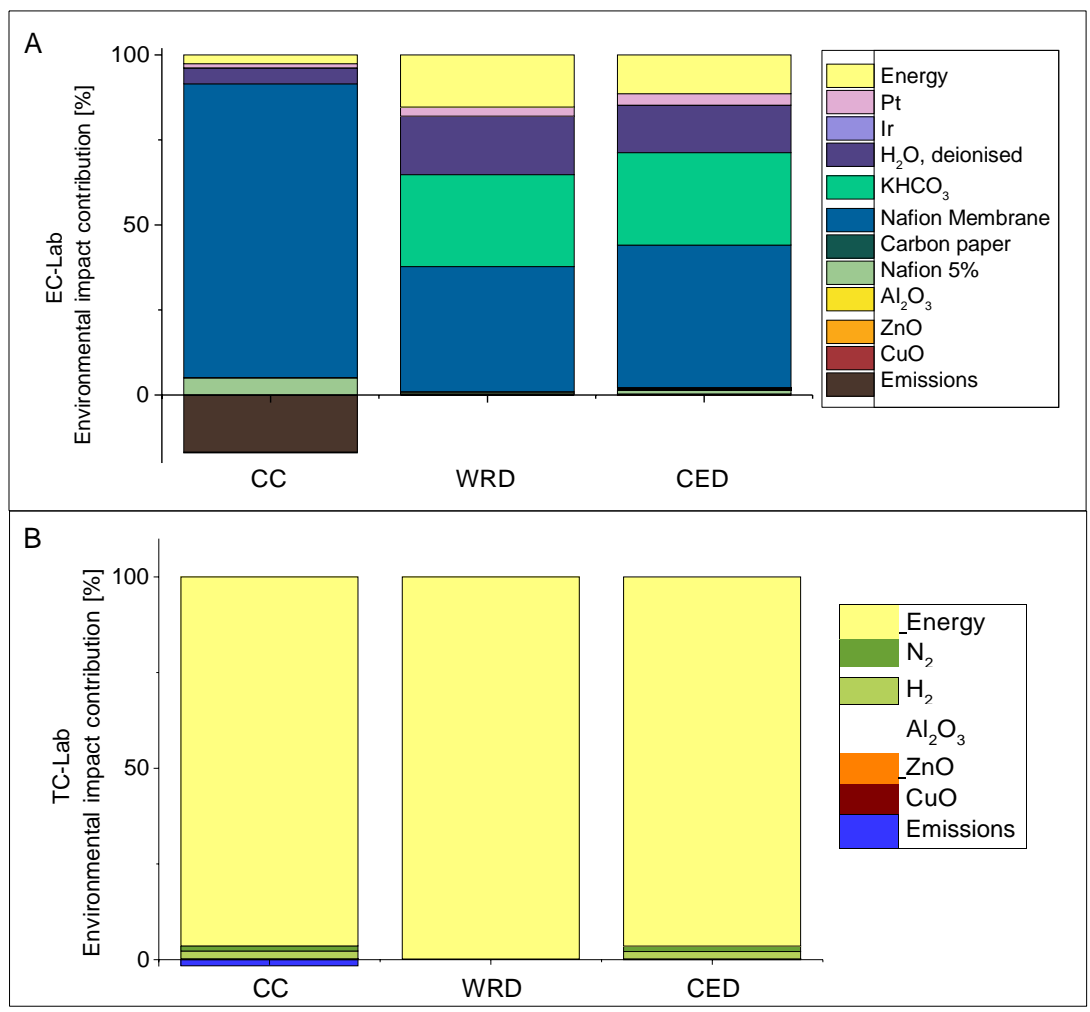


Figure 6. Laboratory-scale case studies Impact Contribution Results: (a) EC technology, (b) TC technology.

It is worth noting that either the energy or the H₂ did not come from a renewable source in the TC-Lab technology. There are several environmental enhances at this respect. If power supply runs with renewable energy, TC environmental impacts will be significantly decreased. In this research work, the country energy mix network powers the power supply. A sensitive assessment just changing the origin in the power supply energy item revealed a reduction in the environmental impacts. When it is assumed renewable energy origin, (i.e. open ground photovoltaic installation) reduction in the impacts was 87 % in CC, 86 % in WRD and 91 % in CED. Nevertheless, even

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2 with this assumption, impacts from the EC-Lab case are still being lower than those from TC-
3 Lab.

4 5 6 7 8 *3.4.2 Comparative LCA on the scaled-up EC and TC routes*

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10 For the sake of completeness, this research work aimed to evaluate not only the environmental
11 impacts of these two lab scale cases, but also of the scaled-up EC and TC technologies, for which the
12 EC technology gets an industrially relevant productivity that equals that of the TC route. In this
13 context, the EC cases of study (EC-5 and EC-6) were evaluated by varying the EC experimental
14 conditions in the LCA inventory. The LCI of the three scaled-up cases of study is reported in the
15 section S9 of the SM. In these scaled-up scenarios, CH₃OH is produced with the same catalyst as in
16 the laboratory-scale cases, but considering the assumptions previously explained in section 2.2.
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29 Section 2.2 indicates that important changes should be conducted from lab-scale to the scaled-up
30 versions of both EC and TC processes. This fact will be mirrored in their environmental impacts. The
31 thermocatalytic process proposes recycling gas streams, pre-heat some gas streams integrating all
32 steps in a MeOH production plant. As it will be seen, these actions will reduce the environmental
33 burden of energy consumption that the TC technology had in the lab scale. Regarding the
34 electrocatalytic process, it will get more productivity in its scaled-up version. Hence, the energy
35 efficiency will be better in the scale-up than in the lab-scale. Moreover, there are recycled CO₂ gas
36 streams, which improve the environmental behaviour with respect to a plant without this kind of
37 recycled loops. In the following paragraphs these changes will be explained in terms of environmental
38 impacts.
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53 Figure 7 provides the LCA results of the three environmental categories assessed in for the TC-1, EC-
54 5 and EC-6 cases per 1 g of MeOH production. TC-1 represents the scaled-up scenario for MeOH
55 production by means of the thermocatalytic approach, while EC-5 and EC-6 represents the
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1 electrocatalytic routes reaching a current density of 100 mA/cm². The main difference between EC-
2 5 and EC-6 is an increase of selectivity. Selectivity to MeOH is 26% in EC-5, while it is around 90
3 % in EC-6 to reach a MeOH production of 3011.84 g/h, which is similar to the TC-1 case of 3008.76
4 g/h (see LCI in section S9 of SM, and Table 4).
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10 As shown in Figure 7, the MeOH production by electrocatalysis in the EC-5 scenario reported
11 significantly more impacts than the EC-6 and TC-1 cases. The CC, WRD and CED impact
12 categories obtained better environmental results in the TC-1 case, which is closely followed by EC-
13 6 case of study. Hence, the lower selectivity to MeOH of the EC-5 case is a drawback also from the
14 environmental point of view, since the energy consumption required to separate it from the water is
15 too high, as concluded also in the economic analysis in section 3.3 and better detailed in following.
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20 Figure 7 depicts the contributions to the impacts of the inputs and outputs considered in the LCI, as
21 well as, comparative LCA results between TC-1, EC-5 and EC-6. Among all the items considered in
22 the LCI, steam, cooling energy, chilled water and electricity are the main contributors to all the
23 assessed impact categories (i.e. CC, WD and CED). This are all items related with energy
24 consumption. This means that energy consumption is the main responsible for the environmental
25 impacts in the scaled-up technologies for CH₃OH production. Furthermore, in the CC results, the use
26 of CO₂ emissions has a key role to play. Indeed, CO₂ consumption produces an environmental benefit
27 as showed in Figure 7(a).
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45 Climate Change impact category represents the potential of the system to produce CO₂, which causes
46 changes in the atmosphere and thus to contribute to climate change. In the EC-5 case study, this value
47 is of 29.7 kg_{CO₂ eq}/kg CH₃OH, being the highest carbon footprint of these three scaled-up cases. Even
48 though, EC-5 is the case study with the highest CO₂ consumption, which would be reflected as the
49 highest environmental benefit. However, this fact is not enough to compensate the huge contributions
50 of energy consumption that make EC-5 case as the highest in terms on CC. Instead, the carbon
51 footprints of TC-1 and EC-6 are of 8.1 and 8.59 kg CO₂/ kg CH₃OH, respectively, being about 28%
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1 of that of the EC-5 case. For the EC-6 case the carbon footprint is only 0.480 kg_{CO₂ eq}/kg CH₃OH
2 higher than for the TC-1 scenario.
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5 However, it is important to highlight that both thermocatalysis and electrocatalysis routes (even in
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7 the here reported scaled-up versions) are far to obtain the carbon footprints of other more developed
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9 and already industrialized technologies. For instance, the carbon footprint for a generic methanol
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11 from methane process of Ecoinvent database [90] is 0.6 kg CO₂/ kg CH₃OH. Other study in China
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13 [91] by using coal to methanol (0.6 million tons/year) technology obtained 2.971 t CO_{2,eq}/t methanol
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15 as carbon footprint. It is evident that herein we are comparing totally different production scales but,
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18 to the best of our knowledge, there are no studies of carbon footprint for CH₃OH production via the
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20 use of CuO/ZnO/Al₂O catalyst in TC or EC technologies, which makes hard to do an accurate
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22 comparison. However, these results suggest that further effort need to be conducted to lower the
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24 environmental impact from both TC and EC routes, to make them competitive and sustainable from
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26 the CC point of view. It should be noted that this research work has been conducted with transparency
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28 principles and declaring all of the items used, even if the CC results were not as encouraging as
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30 expected. As it will be shown in the next section, a reduction in CC could be get it by using as much
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32 renewable energy as possible or by using more efficient energy supplies. Also, assuming an even
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34 better performance of the EC cell can improve these results, although it could result unrealistic based
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36 on the current state-of-the-art.
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44 With respect to the WRD question, it was found that the EC-6 case ($2.42 \cdot 10^{-2}$ m³ H₂O/g CH₃OH)
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46 would potentially consume slightly more water than the TC-1 case ($2.29 \cdot 10^{-2}$ m³ H₂O/g CH₃OH).
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48 However, EC-5 suggest that 1 g of CH₃OH will cause 82.4 L of water resource depletion. As shown
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50 in Figure 7(b), the WRD category is mainly influenced by electricity contribution.
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54 The inventory of the lab-scale cases of study (see Table S3, SM) suggested a higher energy
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56 consumption in the TC-Lab case than in the EC-Lab one. However, when the scale-up of these
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58 technologies is performed, energy consumption becomes optimized. In fact, a lower amount of energy
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1 is used in the TC-1 (172 kJ) case than in EC-5 (616 kJ) and EC-6 (183 kJ) per g of MeOH. This is
2 reflected in the CED impact category, which is the indicator of the energy performance of the system,
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4 including downstream processes.
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7 It is encouraging to compare the results for the CED with those found in literature and databases. The
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9 item in the Ecoinvent 3 database [90] describing the MeOH production from natural gas reports a
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11 CED of 33.7 kJ/g CH₃OH. This value seem to be consistent with Patel (2003) [92] which determined
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13 CED as 36.1, 40.1 and 40.8 kJ/g MeOH when it is produced from natural gas, heavy oil or brown
14
15 coal, respectively. This fact means that CED in TC-1 and EC-6 routes of MeOH production are in the
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17 same order of magnitude as the conventional productions.
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22 The comparative scaled-up LCA of the TC vs. EC technologies showed that the TC process is more
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24 environmentally friendly than the simulated EC cases under the here proposed operative conditions
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26 and electrodes scales. These means that the promising results from the experiments in the lab-scale
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28 totally changed their environmental behaviour when the scale-up was conducted. For this reason, it
29
30 is important to point out that to perform more reliable LCA it is preferable to use experimental data
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32 to perform a realistic simulated scale-up, considering all the downstream separation and purification
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34 processes, which then can be then used for the environmental impacts evaluation (as it was proposed
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36 in this work).
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42 The here reported results suggest that there is an effectively association between environmental
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44 impacts and the MeOH production scale, that is the reason of the similar environmental impacts
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46 obtained for the EC-6 and TC-1 cases, in comparison to the better impacts obtained for the EC-Lab
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48 case vs. he TC-Lab one. The rise in energy required in EC-6 technology at the studied scale of CH₃OH
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50 production (vs. the lab scale case) provokes significant increase in the environmental impacts, mainly
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52 because the here studied EC CO₂ reduction process generates MeOH dissolved in the aqueous
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54 electrolyte, with a consequent high energy requirement due to the distillation purification process.
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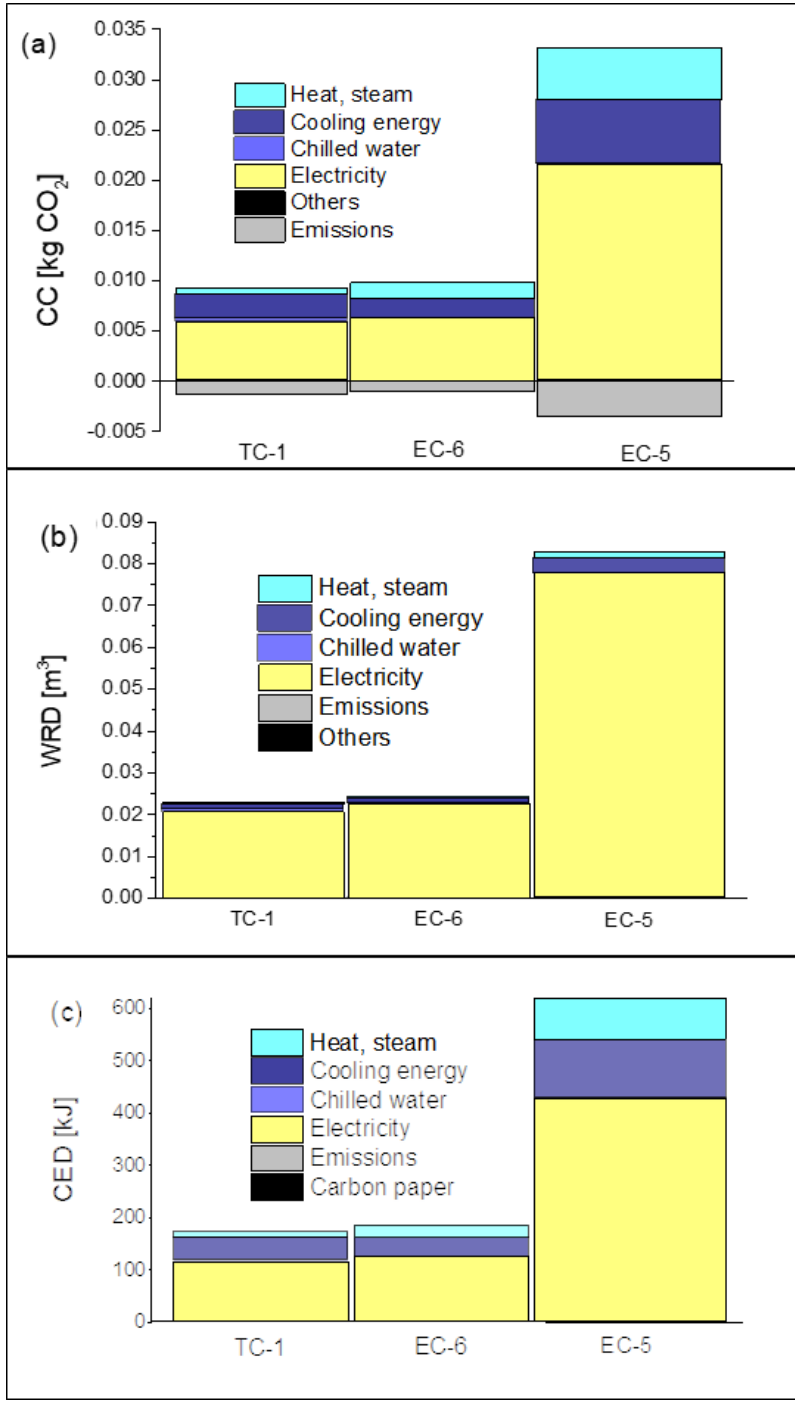


Figure 7. Scaled-up case studies (TC-1, EC-5, EC-6) environmental impacts and their contributions obtained per 1 g of MeOH production. (a) Climate Change impact category comparative results, (b) Water Resource

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Depletion impact category comparative results, (c) Cumulative Energy Demand impact category comparative results.
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3.4.3 *Future sustainability perspectives*

In prospective, there are different operative and boundary conditions that can be pursued in the EC and TC technologies to render them more sustainable than the current MeOH production processes and close to be C-neutral.

To reduce the energy demand of the of the EC process, and the related MeOH purification from water by distillation, new developments should be implemented such as:

- a) the gas-phase EC CO₂ conversion to MeOH that is currently at a proof-of-concept stage[93], which could allow the exploitation of less energy intensive purification technologies, like membrane processes;
- b) the CO₂ partial pressure (here assumed equal to 1 bar) could be increased for improving the CO₂ conversion per passage in the EC cell, so reducing the energetic costs for the CO₂ re-compression for its recirculation;
- c) the electrochemically produced CO (now considered as an inert gas) can be considered as a reagent that contribute to the MeOH production when reliable kinetic data of the CO-to-methanol electroreduction will be available[94];
- d) if the produced amounts of side products like H₂ and formate are important (as in the EC-5 case) they can be exploited and considered as another valuable products of the process (after appropriate purification), so applying the green chemistry concept of atoms economy;
- e) discovering of electrocatalysts with high performances (current density and methanol faradaic efficiency), lessening the formation of by-products;

1 f) optimization of the EC cell geometry by means of experimental data and modelling; and g)
2 engineering of the GDE in order to favour the charge and mass transport within the cell, reducing
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4 ohmic losses and pursuing high current densities ($> 100 \text{ mA/cm}^2$) and industrially relevant
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6 production rates.
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10 Changing some parameters in the LCA model, it is possible to obtain encouraging results for the
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12 future of the EC technology. For instance, in both the EC-5 and EC-6 cases, $100 \text{ mA}\cdot\text{cm}^{-2}$ has been
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14 used as current density. The CH_3OH productivity could be double if this value could be increased to
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16 $200 \text{ mA}\cdot\text{cm}^{-2}$, in line with other CO_2 EC reduction results for ethanol production that already reached
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18 up to 300 mA/cm^2 [95]. Thus, doubling the current density at the same applied potential can halve the
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20 electricity used in the EC process (that is the main drawback for the environmental impacts).
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22 Consequently, the environmental impacts can be reduced of about 68% for the CC, 73% for the WRD
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24 and 67% for the CED in both EC-5 and EC-6 cases, meaning that it is independent of the MeOH FE
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26 (26% or 90%, respectively). Hence, considering for the EC-6 case, with a FE to MeOH of 90% and
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28 200 mA/cm^2 of total current density, the new calculated impacts are $2.72 \text{ kg CO}_2/\text{kg CH}_3\text{OH}$, 6.45
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30 $\text{m}^3 \text{ H}_2\text{O}/\text{kg CH}_3\text{OH}$ and $60.45 \text{ MJ}/\text{kg CH}_3\text{OH}$, which are about 4-times lower than in the previous
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32 conditions. In this way, the carbon footprint became comparable to that of current industrial
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34 technologies for MeOH production at much higher scales and are in-line with previous LCA analyses
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36 of other CCU process using CO_2 and H_2 for methanol production[96].
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42 On the other hand, electricity has a major contribution in the environmental impacts of both EC and
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44 TC scaled-up technologies (see Figure 7); hence, its source can have a huge influence on the carbon
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46 footprint of these processes. The here considered European energy mix is composed of around 30%
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48 of renewable energy. Thus, if this electricity came 100% from renewable energy like photovoltaics
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50 (for example, by taken the Ecoinvent item: photovoltaic electricity of 570 kWp open ground in Italy),
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52 the environmental impacts will get lower values. Evaluating this possibility for the EC-6 and TC-1
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54 processes, a reduction higher than 62% in the carbon footprint is observed in both cases. The CC
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1 passes from the initial values (8.11 kgCO₂ eq/kgCH₃OH in TC-1 and 8.59 kgCO₂ eq/kgCH₃OH in EC-6) to
2 3.09 kgCO₂ eq/ kgCH₃OH in TC-1 and 3.11 kgCO₂ eq/ kg CH₃OH in the EC-6 in this all renewable-
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4 electricity scenario. The WRD and CED are also reduced when electricity came from renewable
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6 energy instead of the generic electric mix. In the 100% renewable energy scenario, the WRD is 5.12
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8 10⁻³ m³H₂O/gCH₃OH in the EC-6 and 4.71 10⁻³ m³H₂O/gCH₃OH in the TC-1, which are reductions close to
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10 80%. Instead, the CED practically does not change because it is independent of the energy source, it
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12 is 68.37 kJ/gCH₃OH with the TC-1 case and changes to 69.2 kJ/gCH₃OH with this 100% renewable
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14 assumption.

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17 Furthermore, a big part of the environmental impacts is also due to the cooling energy. For instance,
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19 its contribution to CC is 1.91 kgCO₂ eq/kgCH₃OH in EC-6, 2.38 kgCO₂ eq/kgCH₃OH in TC-1 and 6.34 kgCO₂
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21 eq/kgCH₃OH in EC-5. Hence, the more we reduce the required cooling energy (used in the compressors
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23 and distillation/separation units), the lower will be the carbon footprint. This behaviour will be similar
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25 for WRD and CED environmental impacts.
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34 **4 Conclusions**

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37 The aim of this work was to compare the CO₂ to MeOH conversion by means of electrocatalytic and
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39 thermocatalytic technologies, starting from primary experimental data obtained with the same catalyst
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41 at laboratory-scale, and then simulating an industrial version of the both processes, including
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43 separation and purification of the final product.
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48 It may be accepted that the electrocatalysis (heterogeneous catalysis of EC reactions) and
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50 thermocatalysis (catalytic hydrogenation) differ from each other only in the means used for the
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52 success of the conversion (molecular hydrogen, operating conditions and/or reactor capacity) and the
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54 intermediates during the reaction. But herein, we demonstrate that a Cu/Zn/Al-based catalyst working
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56 under state-of-the-art conditions in a thermocatalytic process has the potential to also produce the
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1 same product (MeOH) under milder electrochemical conditions. Hence, this work could be an attempt
2 to provide a bridge between the fields of thermocatalysis and electrocatalysis. Further research should
3 certainly be done to better understand the reaction mechanisms on the electrocatalyst, the
4 current/potential distribution within the cell and the behaviour of a three-dimensional electrodes to
5 improve EC cell performances for a future implementation of the electrocatalytic CO₂ reduction
6 technology at a high scale.
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10 Our primary laboratory results reveal that the EC productivity is far to reach that of TC technology,
11 being this latter a more mature process at lab-scale and a well-established technology at industrial level
12 today. Despite this, the environmental impact of EC lab-scale case (CC of 19 kgCO₂ eq/ kgCH₃OH) was
13 lower than the TC lab-scale one. Nevertheless, this tendency changes when a scale up of these
14 technologies is performed, because it is necessary to consider not only the performance of the
15 catalytic reactor but also of all the units of the plant, including separation and purification processes.
16 Hence, the environmental impacts of the TC and EC processes are comparable when scaled-up to the
17 same productivity of ~3 kg/h of methanol. The best environmental scenario was the TC-1 case, which
18 reaches a carbon footprint of 8.11 kgCO₂ eq/kgCH₃OH, and the EC-6 case reached a similar value. It is
19 important to highlight that both these processes were highly influenced by their energy consumption.
20 From the comparison of the lab-scale systems performances, the EC-lab technology has a 9-fold lower
21 energy consumption than the TC-lab (352 Wh/g), but when the best scaled-up scenarios (TC-1 vs
22 EC-6) were compared, they resulted to have similar energy consumptions due to the downstream
23 processing units.
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47 This study suggests that EC and TC technologies can be more sustainable if further efforts are made
48 to reduce their energy demand, for reaching similar or lower environmental impacts than the current
49 benchmark fossil-fuel based technologies for methanol production. For instance, doubling the current
50 density of the EC cell to 200 mA/cm² results in a reduction of 68% of the carbon footprint of this
51 process (reaching up to 2.72 kgCO₂ eq/kgCH₃OH); reducing the cooling energy it is possible to get
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2 considerable savings in CC, WRD and CED. The highest contribution to the impacts in the scaled-up
3 processes is due to the electricity. Hence, the more renewable is the electricity from the country mix,
4 the lower environmental impacts these technologies could reach. In a scenario with a 100% renewable
5 energy such as photovoltaic, it is possible to reach savings in the carbon footprint of up to 62%.
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10 The techno-economic assessments here reported suggest that the EC process results to be
11 economically advantageous over the TC one at low scales ($< 10^4$ kg/h MeOH). Considering an
12 effective allocation of the methanol productivity on a real market scenario and the assumption of
13 zeroing of the net present value in 20 years, both the TC (i.e. TC-1) and EC (i.e. EC-6) processes
14 would start to be economically competitive at methanol productivities greater than 19.1 kg/h and 3.3
15 kg/h, respectively. Moreover, if O₂ valorisation, a low price of the renewable electricity and a carbon
16 tax are considered, the economic profitability will rise. There are still high challenges for the EC CO₂-
17 to-methanol conversion technology to reach a real industrial implementation, while the TC one is
18 closer to this goal.
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34 **5 Conflicts of interest**

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38 There are no conflicts of interest to declare.
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