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Innovative alternatives to methanol manufacture: carbon footprint assessment

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

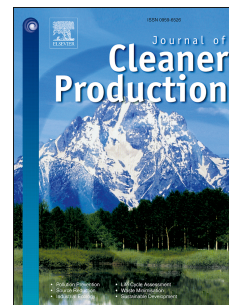University of Cantabria, Department of Chemical and Biomolecular Engineering, Av. Los

Castros s/n, Santander, Spain

* Corresponding author: Marta Rumayor

University of Cantabria, Department of Chemical and Biomolecular Engineering

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

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

Tlf: (+34) 942 20 67 49

Abstract

Finding and implementing more sustainable alternatives to the fossil-dependence routes for methanol (MeOH) manufacturing is undoubtedly one of the challenges of our model of society. Some approaches can be used to convert CO_2 into MeOH as direct hydrogenation or electrochemical reduction (ER). These alternatives lead to lower natural resources consumption respect the conventional routes, but they are still found at different technological readiness levels (TRLs) and some remaining challenges need to be overtaken to achieve a carbon neutral cycle respect the conventional route, especially in the case of ER, which is currently found at its infancy. That would indicate their final industrial competitiveness in a sustainable mode. This study uses Life Cycle Assessment as the main tool in order to compare these two CO_2-based manufacture alternatives (found at different TRLs) with the fossil-route. The results allow for evaluating the potential challenges inherited to the alternative based on ER. Utilization of renewable energy is one of the most important key issues to achieve a carbon neutral product using these options. However, its benefit is neglected due to the high requirement of steam in the purification step, particularly in ER. It was demonstrated that a future scenario using ER

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leads to a lower natural resources consumption (mainly natural gas) compared to the conventional fabrication, which represents an important step towards more green and efficient MeOH synthesis.

Keywords: Methanol; carbon footprint; electrochemical reduction; carbon dioxide utilization

1. Introduction

Methanol (MeOH) is one of the most important building block molecules used in the synthesis of commodities such as formaldehyde, aromatics, ethylene, methyl tertiary butyl ether (MTBE) and acetic acid. In the last years, MeOH has been also proposed as energy storage for fuel cell applications even as a clean fuel or fuel additive in gasoline (Olah, 2005) and certainly, a growing interest will be observed into this field in the coming years. MeOH worldwide production has increased by 50% since 2009, to 72 Mt/y, and is expected to almost triple by 2050 (Philibert, 2017). This chemical can be produced from different sources being the use of traditional fossil fuels (mainly natural gas) the most prominent at industrial scale (Olah, 2005). The conventional route is considered a well-established technology found at the highest level (TRL 9) within the European Commission classification for TRLs (European Commission, 2015). It is a thermal process with a working temperature range of 200-270 ℃ and operating pressure between 50-100 bar (Swiss Centre for Life Cycle Inventories, 2016). From an environmental point of view, it has two main drawbacks: (i) it contributes to the depletion of fossil fuels (consumption of natural resources) and (ii) it involves the emission of carbon dioxide (CO_2) into the atmosphere due to the production process. These associated CO_2 emissions are determined to be about 1 tonne of CO_2 per tonne of MeOH when it is produced from natural gas and most of these CO_2 emissions come directly from the steam methane reforming (SMR) step involved in the process (Philibert, 2017). Under the current global threat derived from Climate Change, research community pursues new production alternatives in an attempt to shift from the fossil-dependence processes to other alternatives coherent with global efforts to pursue a feasible solution. So that, in a favourable transition toward a more sustainable

and prosperous society, the overall goal would be a dramatic curbing of the CO_2 emissions on a planetary scale thus keeping global temperatures changes under safety limits. According to the 21st Conference of Parties (COP21), known as the Paris Agreement, and the 2050 global climate change objectives the goal is to keep a global temperature rise below 2 ºC above pre-industrial levels during this century and to pursue efforts to limit the temperature increase even further to 1.5 ºC (United Nations Framework Convention on Climate Change (UNFCCC), 2016). In this context, Carbon Capture Utilization (CCU) technologies are a growing field of research trying to meet both targets within the EU Framework (Bui et al., 2017). CCU could be a convincing profitable opportunity since the surpluses of CO_2 can be used as a carbon-neutral feedstock in different innovative CCU options for CO_2 conversion to fuels (like methane) and chemicals (such as MeOH and formic acid, among others) (Kondratenko et al., 2013; Ritter, 2007). These technologies involve a clear reduction of greenhouse emissions, but also, they can mitigate the dependency on fossil carbon sources of the conventional chemical industry.

Regarding the production of methanol from CO_2, Olah and Goeppert suggested the so-called 'methanol economy' as a sustainable alternative energy model to the current carbon-based (Olah, 2005). The concept will not eliminate the use of fossil fuels but will result in a carbon-neutral loop. Producing methanol in a more sustainable way could be achieved by a variety of methods, which are currently found at various levels of maturity in terms of TRLs. Some of these techniques are based on homogeneous catalysis (Kar et al., 2018), heterogeneous catalysis (Álvarez et al., 2017), photocatalytic reduction (Lais et al., 2018) or electrochemical reduction (Alper and Yuksel Orhan, 2017) sharing a substantial input of energy per unit of reduced CO_2. In terms of maturity, the most developed CO_2 utilization alternative for producing MeOH is the direct hydrogenation (DH) of CO_2 (Kar et al., 2018), which can be potentially classified at TRL 6-7 (Pérez-Fortes et al., 2016). It is considered to be the most economic option, after fossil fuels usage (Olah, 2005). Its main challenge is producing and utilising the required hydrogen (H_2) in a cost-effective and sustainable manner as the alternative almost always relies on the production of H_2 from water electrolysis (which in turn should be supplied with renewable electricity),

followed by the hydrogenation of CO_2 (captured) (see Table 1 for reference). The process is currently being utilised by the company Carbon Recycling International (Iceland), which has a carbon-neutral capacity per year of 4,000 t (Philibert, 2017).

Electrochemical Reduction (ER) of CO_2 has been proposed as a promising option. This technology has some advantages (Ganesh, 2016; Kauffman et al., 2015) that eventually would lead to more environmentally friendly options: (i) it can be fully developed at atmospheric temperature and pressure; (ii) its conditions are moderate and controllable; (iii) the products of ER can be adjusted by some reaction parameters, such as redox potential, temperature, electrolyte, etc.; (iv) a proper optimization of electrocatalysts can minimize the by-products obtained; (v) the electrical power can be supplied by renewable energy sources (such as photovoltaics or wind power) minimizing any indirect CO_2 emissions (Dominguez-Ramos et al., 2015). This option is developed at laboratory scale and it assigned to a TRL in the range of 3-5 in the light of current developments (see Table 2 for reference). Its TRL reflects that some limitations still remain challenging, from product concentration or catalyst lifetime to the high overpotentials required (Albo et al., 2015). The increased number of published research articles and their citations during the last five years reflect an accelerated progress in this alternative (Endrödi et al., 2017). The vast majority of these studies are focused on the development of new catalysts (Qiao et al., 2014) and the enhancement of product selectivity (Jhong et al., 2013) which is expected to lead to efficient CO_2 electrolyzers on a practical scale [16].

Table 1. Technical features of the DH of CO_2 alternative for MeOH production

Scale	Approach	Thermal and pressure operation conditions		Energy demands		Hydrogenation features		
		Typical operating T	Typical operating P	Electricity	Heat	H_2 supply	Catalyst	Data source
		(ºC)	(bar)					
Industrial	Real	225	50	Integrated (partially)		Electrolysis		(Olah, 2005)
	Simulated	210	78			Thermal (pipeline network)	$Cu/ZnO/Al_2O_3$	(Pérez-Fortes et al., 2016)
		250	50				Cu/Zn/Al/Zr	(Kiss et al., 2016)
		220	50			Electrolysis	$Cu/ZnO/Al_2O_3$	(Van-Dal and Bouallou, 2013)
		210	76				$Cu/ZnO/Al_2O_3$	(Pérez-Fortes and Tzimas, 2016)
		240	80	Grid/Renewable			$CuO/ZnO/Al_2O_3$	(Bellotti et al., 2017)
		240	50	Hydro power plant	Integrated		$Cu/ZnO/Al_2O_3$	(Asif et al., 2018)
		234	30	Integrated (partially)				(Rivera-Tinoco et al., 2016)
				Grid/Renewable			$Cu/ZnO/ZrO_2$	(Kourkoumpas et al., 2016)
		220	50	Renewable/Integrated			$Cu/ZnO/Al_2O_3$	(Biernacki et al., 2018)
Laboratory	Experimental	180–220	30				$Pd/ZnO/Al_2O_3$	(Xu et al., 2016)
		210	50				PdIn-based	(García-Trenco et al., 2018)
		270	30	-			$Pd–Cu/CeO_2$	(Choi et al., 2017)
		200–260	10-60				Au/Cu–Zn–Al	(Pasupulety et al., 2015)
		260	331				$Cu/ZnO/Al_2O_3$	(Gaikwad et al., 2016)

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Table 2. Technical features of the ER of CO_2 alternative for MeOH production

Scale	Approach	Thermal and pressure operation conditions		Electrochemical features				
		Typical operating T	Typical operating P	Cathode material	Faraday Efficiency, FE	Current density, j	Cathodic potential, E	Data source
		(ºC)	(bar)		(%)	(mA·cm^{-2})	(V)	
Industrial	Simulated	Room		-	100	40-400	-1.21	(Verma et al., 2016)*
				-	90	200-300	-2	(Jouny et al., 2018)*
Laboratory	Experimental			FeS$_2$/NiS	64	3.1	-0.6	(Zhao et al., 2017)
				Cu$_2$O	45.7	6.93	-1.3	(Albo et al., 2015)
				Cu$_2$O	38	4	-0.8	(Malik et al., 2016)
				[PYD]Cu-Pd	26			(Yang et al., 2016)

*Production of CO and HCOOH with coproduction of CH_3OH, among others.

It is evident that these promising alternatives can offer many environmental advantages in the near future (i.e. recycling CO_2 or avoiding fossil fuel) but there is a lack of update studies reviewing the whole picture of how to convert CO_2 into MeOH using ER, thus making the venture worthwhile at an industrial scale. In this context, the next step would be to decrease the energy demands and the emissions targets taking as a benchmark the conventional route.

The present study aims to provide a comparison, in terms of carbon footprint (CF), as the selected environmental metric, of two CO_2 utilization options (shown in Table 1) using the conventional route as a benchmark. The CO_2 utilization alternatives were selected due to their different TRLs and they consist of: i) ER of CO_2 (TRL 3-5) powered by Photovoltaic Solar energy and ii) DH of recycled CO_2 (TRL 6-7). For the purpose of this study, a Life Cycle Assessment (LCA) was the key tool used to understand and address the environmental impact in Climate Change (Artz et al., 2018; Gunniya Hariyanandam et al., 2016; International Organization for Standardization, 2006). This tool has been applied in other environmental assessments related with methanol production by means of different routes (Biernacki et al., 2018; Li et al., 2018) however, there is still a lack of environmental assessments concerning the ER technology. Therefore, the main goal of the present study is to assess the requested MeOH concentration at the output of the ER reactor for its industrial competitiveness to even its CF against the values from the valorisation option at higher TRL (DH) and to the conventional route. The results obtained by LCA allow for evaluating the raw materials and fossil fuels consumption as well as the total amount of CO_2 avoided from additional products such as hydrogen and oxygen. The results obtained so far represent important steps toward a low-CF methanol synthesis.

2. Methodology

Three alternatives for the production of MeOH were analysed and compared in terms of the CFs. The alternatives consist of two CO_2 valorisation routes that are based on PV solar powered

ER of CO_2 (labelled as A_{ER}) and on DH of CO_2 (labelled as A_{DH}); and a third route as the conventional process of MeOH, labelled as A_{CONV} (Figure 1). CFs were determined by means of the LCA tool (cradle-to-gate approach). The analysis was conducted through four phases: goal and scope definition, life inventory analysis (LCI), life cycle impact assessment (CF as the relevant metric) and interpretation of the results obtained. The alternative A_{ER} is derived from the current best performance of ER of CO_2 within the research group of the authors (Albo et al., 2015; Albo and Irabien, 2016) modified by a set of hypotheses that are described in the 2.3 section. An assessment of the alternative A_{DH} was found in the literature and it is supported by a series of hypothesis (Pérez-Fortes et al., 2016; Pérez-Fortes and Tzimas, 2016). Both options differ mainly in their TRLs, which is higher in A_{DH} (6-7) than in A_{ER} (3-5). Alternatives A_{ER} and A_{DH} were compared with the conventional process, A_{CONV}, which is used as a benchmark. On one hand, the results obtained displays the different stages of development of the two potential options for CO_2 valorisation. On the other hand, the comparison of the results between the novel A_{ER} and both the traditional A_{CONV} and the alternative A_{DH} were performed in order to provide an overview of the main remaining challenges inherited to this novel technology to achieve at least a carbon-even loop compared to them. The comparison shows a pathway to pursue its potential industrial competitiveness mainly based on the concentration of MeOH at the outlet of the ER reactor. Additionally, an assessment of the amount of raw materials required in each route was carried out demonstrating mainly the amount of fossil fuel savings. The production of 1 kg of MeOH at a commercial concentration of 99.7% wt. was used as the functional unit. The scope of the study covers the generation of utilities (electricity, heat and water) for the production of the already mentioned MeOH at commercial purity. Neither the distribution nor the utilization of the MeOH are considered here. Ecoinvent 3.3 database (Swiss Centre for Life Cycle Inventories, 2016) and GaBi Professional software (Thinkstep AG., 1991) were used in the background process.
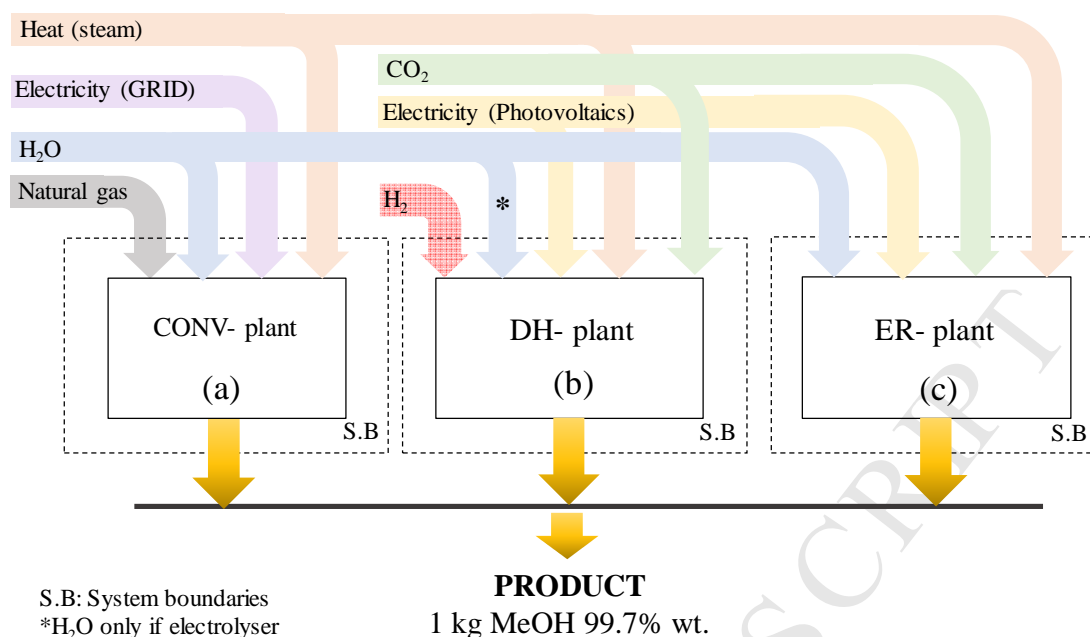
Figure 1. System frameworks: (a) conventional A_{CONV} (b) alternative A_{DH}; (c) alternative A_{ER}

2.1. MeOH conventional synthesis (A_{CONV})

The conventional route (Figure 1(a)) for the production of 1 kg of MeOH was assumed as steam reforming involving three main steps: i) steam reforming of natural gas for the production of required synthesis gas; ii) the synthesis of MeOH; and iii) the processing of crude methanol (distillation) to the desired purity. The chemical reactions involved in the steam-reforming are displayed in Table 3.

Table 3. Main reactions in the conventional MeOH manufacture (Ott et al., 2012)

Steam reforming of natural gas	Synthesis of Methanol
$CH_4 + H_2O \rightarrow CO + 3H_2$; ($\Delta H = 206$ kJ mol^{-1})	$CO + 2H_2 \rightarrow CH_3OH$; ($\Delta H = -98$ kJ mol^{-1})
$CO + H_2O \rightarrow CO_2 + H_2$; ($\Delta H = -41$ kJ mol^{-1})	$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$; ($\Delta H = -58$ kJ mol^{-1})

In the process, natural gas acts as both feedstock and fuel. It is known that this type of plants has a thermal energy (LHV) consumption per unit of mass of MeOH typically around 29 MJ·kg^{-1} -37 MJ·kg^{-1} (LHV) (Althaus et al., 2007). Part of the syngas is used as feedstock (20 MJ·kg^{-1}

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(LHV)), and another part is used as fuel for the utilities. From the converted feed, 1 kg MeOH and 0.06 kg H_2 are yielded. No use of CO_2 and H_2 production is considered (as H_2 is assumed to be burned in the furnace) (Althaus et al., 2007). The CF of MeOH resulting from the conventional process, as unit of mass per unit of mass of MeOH produced, is 0.525 $kg \cdot kg^{-1}$ (Swiss Centre for Life Cycle Inventories, 2016). This value is reasonably low due to the fact that the requested energy demand is sourced from the natural gas.

2.2. Alternative based on direct hydrogenation of CO_2 (A_{DH})

The process involved in A_{DH} (Figure 1(b)) is governed by two reactions: a direct reaction of the recycled CO_2 with hydrogen ($CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O$) and an undesirable reaction that may consume the feed meant for MeOH formation ($CO_2 + H_2 \leftrightarrow CO + H_2O$). The data used in this study was found in the literature (Pérez-Fortes et al., 2016; Pérez-Fortes and Tzimas, 2016; Van-Dal and Bouallou, 2013). This alternative displays a CF per unit mass of MeOH as low as 0.23 $kg \cdot kg^{-1}$. The CF value is supported by a set of hypothesis (Pérez-Fortes and Tzimas, 2016): (i) hydrogen needed by the A_{DH} plant is supplied by H_2O electrolysis; (ii) the CO_2 utilization and the capture plants are at the same site (no transport is needed); and (iii) the compression of CO_2 from atmospheric pressure to the pressure of the synthesis process is allocated to the utilisation plant.

2.3. Alternative based on electrochemical reduction of CO_2 (A_{ER})

In order to estimate the CF of the novel ER- alternative (A_{ER}), the LCA system framework was set as in the Figure 1(c). The methodology involves mainly three steps: the ER of CO_2 in the reactor, the distillation of the mixture MeOH/water to the desired purity (99.7 %wt.) and the compression of subproducts H_2 and O_2 to the liquid forms that are ready to transport. Energy consumption is considered in the form of PV solar electricity for the reduction step and heat (steam) for the separation step according to the nature of each individual process.

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Mass balances are in agreement with the reaction shown in Table 4, assuming neutral to acid conditions. CO_2 and H_2O are injected in the cathode. As the solubility of CO_2 is assumed to be very high, the solubilized CO_2 reaches the cathode surface without mass transfer limitations. Then, CO_2 is reduced to MeOH, in the presence of the corresponding electrolyte in the cathodic compartment of the ER cell. Concurrently, the formation of O_2 is considered as the only reaction that takes place in the anodic compartment. It is well known that an ideal electrocatalyst would lead to a value of 100% of its faradaic current efficiency (FE). This would correspond with the formation of pure MeOH in the cathode and pure O_2 in the anode. However, some of the applied current density is intrinsically deviated to other parallel reactions, reducing the FE. In this study, the H_2 evolution reaction (HER) is considered as the only parallel reaction. It is assumed that H_2O 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 that takes place in the anode.

Table 4. Main and side reactions

Cathodic reaction	Anodic reaction
$CO_2 + 6H^+ + 6e^- \rightleftarrows CH_3OH + H_2O$ $2H^+ + 2e^- \rightleftarrows H_2$	$3H_2O \rightleftarrows 1.5O_2 + 6H^+ + 6e^-$
Overall reaction	
$CO_2 + 2H_2O \rightleftarrows CH_3OH + 1.5O_2$	

A purification process using distillation is required to increase the MeOH concentration at the outlet of the ER up to the accepted commercial concentration value at 99.7% wt. Therefore, cooling and heating are needed. The distillation process was simulated and optimized using the software ASPEN PLUS v9 (Aspen Technology Inc., n.d.) and it was based on the modification of a study found in the literature (Chlang and Luyben, 1983). The optimization of the distillation is out of the scope of this study. Briefly, it consists of two distillation columns in series with 64 trays and fed on the 17th tray. The operating pressure is fixed at 17 psia. The simulation of the

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distillation considers only the presence of H_2O (obtained as a head product) and MeOH at the required concentration (obtained as the bottom product). Distilled water is recirculated and reinjected to the inlet freshwater stream to the cathode. Then, net water consumption is the difference between H_2O in the inlet stream and H_2O 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 also as a pure liquefied product. A summary of additional hypotheses that were taken into account in this work are listed next:

i.   A CO_2 valorisation plant is in the same site as 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. The feedstock CO_2 sourced to the plant is for free, so 100% of the burdens are allocated to the product which directly releases the CO_2 e.g.: electricity from a coal-fired power plant.

iv.   The vapour steam needed for MeOH purification is at dry saturated conditions.

v.   Electrolytes used in the ER process can be perfectly separated. Therefore, there is no net consumption.

vi.   The lifetimes of the electrocatalytic materials are long enough to neglect their carbon footprint.

LCI (cradle-to-gate) was performed and supported by the experimental conditions obtained within the research group of the authors (Albo and Irabien, 2016). MeOH is synthesised in the electrolytic cell with a FE of 45.7%. Current density (j) and overall cell voltage (E) have values of 6.93 mA·cm^{-2} and 2.335 V, respectively. The concentration of MeOH at the outlet stream of ER and the reaction rate were subsequently estimated in order to even the CF of this process to the CF of A_{CONV} and additionally to A_{DH}. These recalculations were considered useful for this study, as the current lab results are still not industrially competitive. Then, two scenarios were created, labelled as $A_{ER-CONV}$ and A_{ER-DH}. $A_{ER-CONV}$ shows the results corresponding with an ideal

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situation of carbon-even cycle compared with the conventional A_{CONV} (CF around 0.525. kg $CO_2 \cdot kg^{-1}$ MeOH produced). The second scenario, A_{ER-DH} shows the results corresponding with an ideal situation of carbon-even cycle compared with the alternative A_{DH} (high TRL) (CF around 0.23 kg $CO_2 \cdot kg^{-1}$ MeOH produced). Therefore, $A_{ER-CONV}$ and A_{ER-DH} come from an adaptation of the original data and in fact, they display the target values needed for the future competitive developments, which in any case, they would be necessary to achieve a carbon neutral cycle. Finally, the maximum CO_2 reduction value that could be reached by ER method was calculated using the hypothesis of perfect/ideal conditions in the ER cell. In this context, three additional hypothetical scenarios were created, labelled as $A_{ER-ideal}$, $A_{ER-CONV-1}$ and $A_{ER-DH-1}$. $A_{ER-ideal}$ shows the ideal situation in which FE is maximum (100%), the cell potential (E) has its intrinsic minimum value (1.214 V) and the MeOH concentration is at its maximum value (100% wt.). This case would indicate the minimum possible energy consumption (in the ER cell) and no steam requirement (for distillation) so it would represent the maximum CO_2 that could be saved by ER of CO_2 to MeOH option. $A_{ER-CONV-1}$ and $A_{ER-DH-1}$ come from $A_{ER-CONV}$ (using the corresponding estimated MeOH concentrations) but now, ideal conditions of E_{cell} and FE were considered. Then, these scenarios display the maximum reduction of CO_2 emissions whether the best ER conditions were achieved. $A_{ER-ideal}$, $A_{ER-CONV-1}$ and $A_{ER-DH-1}$ are taking into account the avoided amount of CO_2 and they are dismissing any by-products generated (i.e. O_2 and H_2) for a better demonstration of the ER influence in the CF.

3. Results and discussion

3.1. Assessment of MeOH concentrations to even the carbon footprint of the selected alternatives

Table 5 shows the requested utilities demand as electricity and heat (as steam) of the chosen alternatives. These values were obtained from their corresponding LCIs for manufacturing 1 kg of MeOH at 99.7% wt. at the bottom of the corresponding distillation columns (Supplementary

material). It can be observed the results of the additional two scenarios that complement A_{ER} ($A_{ER-CONV}$ and A_{ER-DH}). In this context, it was estimated a minimum value of 40% wt. of MeOH concentration at the outlet stream of ER and a reaction rate around 3.80 mol·m^{-2}·s^{-1} (keeping the rest of the variables fixed) in $A_{ER-CONV}$. A value of 67% wt. and 6.03 mol·m^{-2}·s^{-1} in A_{ER-DH} was obtained. These hypothetical scenarios would indicate the final industrial competitiveness when compared to the conventional process (A_{CONV}) and the additional alternative at high TRL (A_{DH}).

Table 5. Electricity and heat demands for each alternative $A_{CONV,}$ A_{DH} and A_{ER} including the two hypothetical scenarios of the alternative A_{ER} ($A_{ER-CONV}$ and A_{ER-DH}).
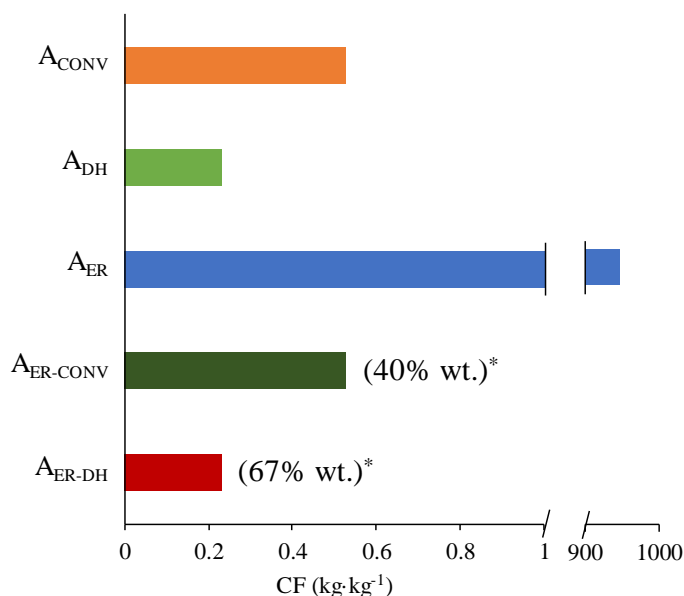
	Units	A_{CONV}	A_{DH}	A_{ER}	$A_{ER-CONV}$	A_{ER-DH}
Electricity	kWh	0.147	11.9*	50.5*	29.3*	29.3*
*Heat***	MJ	6.93	4.62	>10,000	17.6	13.4

*From PV solar; **A*s steam*

The energy consumption as electricity, which is determined by the needed amount of electricity per unit of mass of MeOH produced, is higher in A_{ER} (50.5 kWh·kg^{-1}), $A_{ER-CONV}$ (29.3 kWh·kg^{-1}), A_{ER-DH} (29.3 kWh·kg^{-1}) and A_{DH} (11.9 kWh·kg^{-1}) compared to the conventional process (0.147 kWh·kg^{-1}). Those values come mainly from the required energy by the needed units of electro-reduction (in ER alternatives) and the electrolyser (A_{DH}). On the opposite, the large consumption of steam in the distillation step falls on the ER option. It is not surprising, as the concentration of MeOH reached at the outlet stream of the ER compartment (0.05% wt.) remains low in A_{ER}. The typically achieved concentrations are still far away from those obtained in the ideal cases $A_{ER-CONV}$ (40% wt.) and A_{ER-DH} (67% wt.). The wide range of consumption of steam per mass unit of MeOH (from >10,000 MJ·kg^{-1} to 4.62 MJ·kg^{-1}) highlights the significance of the purification step, particularly in the ER alternative as it is not considering any heat integration. As it was expected, the higher MeOH concentration at the outlet of the ER cell, the lower the steam consumption (A_{ER-DH} scenario). Then, most of the efforts should be directed to increase the efficiency of the electrochemical reaction increasing the concentration of MeOH.

3.2. Distribution of the carbon footprint of the selected alternatives

After the LCI compilations of each alternative were available (Supplementary material), the following step was the description of all contributions to the CFs, defined as the unit of mass of CO_2 equivalent per unit of mass of MeOH produced. Other environmental categories are excluded from the analysis, as the viability of the suggested valorisation options should be firstly fulfilled for the category intended to benefit from the processes. Ecoinvent database was used to provide the CO_2 equivalent emissions for the requested resources such as conventional MeOH manufacture, H_2O, H_2, O_2, heat as steam and the CO_2 equivalent emissions for the requested PV solar energy (Swiss Centre for Life Cycle Inventories, 2016). As it was previously mentioned, the CO_2 used as feedstock was assumed not to contribute to the CF, as all the emissions are allocated to the corresponding main product, which could be electricity in the case of a coal-fired power plant. Figure 2 shows a comparison of CF values corresponding to alternatives A_{CONV}, A_{DH}, A_{ER}, $A_{ER-CONV}$ and A_{ER-DH}. CF values of A_{DH} (0.230 kg·kg^{-1}) and A_{CONV} (0.525 kg·kg^{-1}) were provided by the corresponding references (Pérez-Fortes and Tzimas, 2016; Swiss Centre for Life Cycle Inventories, 2016). To determine the CF of A_{ER}, $A_{ER-CONV}$ and A_{ER-DH}, it was used the LCI data (Supplementary material) using a functional unit of 1 kg of MeOH as the reference and considering that the MeOH is at a concentration of 99.7% wt. The mass of CO_2 used per unit of mass of MeOH was excluded from the use of resources, but in any case, for the three A_{ER} alternatives as well as for A_{DH}, it would represent a value of 1.374 kg·kg^{-1} (stoichiometric ratio). The CF of the electrocatalytic materials were neglected as they are assumed to be lasting enough.

* Concentration of MeOH at the outlet stream of ER compartment to achieve the CFs values of A_{CONV} and A_{DH}

Figure 2. CF of the selected alternatives A_{CONV}, A_{DH}, A_{ER}, and the scenarios $A_{ER-CONV}$ and A_{ER-DH}

Figure 3 displays the distribution of GHG emissions in each alternative and both hypothetical scenarios $A_{ER-CONV}$ and A_{ER-DH} using their corresponding LCI data (Supplementary material). Eight individual contributors to the CF included are: i) direct emissions in MeOH manufacture (founded in A_{CONV} and A_{DH} according to their references (Pérez-Fortes et al., 2016; Swiss Centre for Life Cycle Inventories, 2016)); ii) natural gas (from A_{CONV}); iii) electricity as renewable (PV solar energy) for the three ER alternatives (ER reactor, pumping, and compression/liquefaction of H_2/O_2) and in A_{DH} (needed for the electrolyser); iv) electricity from the European electric grid that is used in A_{CONV} according to its reference (Swiss Centre for Life Cycle Inventories, 2016) and partly in A_{DH} (only for compression and recirculation) (Pérez-Fortes et al., 2016); v) heat (as steam) for purification; vi) avoided emissions from the byproduct H_2 in A_{ER} alternatives; vii) avoided emissions from the byproduct O_2 (both in A_{ER} scenarios and A_{DH}); and viii) others (i.e. the deionized water as raw material). It should be remarked that the distribution of the CF for A_{DH} was calculated in the present study using the same CO_2 emission factors as those used for the distribution obtained of A_{ER} scenarios

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(Supplementary material) as the CF distribution obtained was not displayed in the original references (Pérez-Fortes et al., 2016; Pérez-Fortes and Tzimas, 2016). The original references displayed values for direct emissions of 0.09 $kg \cdot kg^{-1}$. Regarding the indirect emissions, the reported values were of 0.136 $kg \cdot kg^{-1}$, which are in agreement with the indirect emissions calculated using the carbon footprint of the utilities in the present study (0.143 $kg \cdot kg^{-1}$).

As it was expected, the main contribution to the CF in the case of A_{ER} corresponds to the steam demand for the distillation purposes, which is much lower in A_{CONV} and A_{DH}. In fact, one of the hypotheses of the plants A_{DH} and A_{CONV} is that they cover part of their own heating needs by means of integrating heat among the process streams (Pérez-Fortes et al., 2016; Pérez-Fortes and Tzimas, 2016; Swiss Centre for Life Cycle Inventories, 2016). In the case of A_{DH}, part of the electricity is supposed to be generated by four ad-hoc steam turbines [23] using the recovered heat, so actually, the total CF of this alternative remains the lowest. Therefore, the net contribution of steam utilization to the CFs of the alternatives A_{CONV}, A_{DH}, A_{ER}, $A_{ER-CONV}$ and A_{ER-DH} per unit of mass of MeOH produced are 0.247 $kg \cdot kg^{-1}$, 0.377 $kg \cdot kg^{-1}$, 946 $kg \cdot kg^{-1}$, 1.21 $kg \cdot kg^{-1}$, and 0.919 $kg \cdot kg^{-1}$, respectively. However, the alternative A_{ER} and in its hypothetical scenarios ($A_{ER-CONV}$ and A_{ER-DH}) are showing the worst situation as there is no integration of any heat and electricity (only water is recirculated). Of course, a suitable integration of heat from another nearby chemical plant will definitely decrease the total CF of the ER scenarios. Electricity used in A_{ER}, $A_{ER-CONV}$ and A_{ER-DH}, as well as electricity used in the electrolyser of A_{DH} was assumed to be produced from a renewable energy, in this case PV solar, which has a CF, expressed as mass of equivalent CO_2 per unit of energy as electricity, of 0.068 $kg \cdot kWh^{-1}$ (Swiss Centre for Life Cycle Inventories, 2016). Integration of wind energy could also be explored due to its low CF which has a value of 0.015 $kg \cdot kWh^{-1}$ (Swiss Centre for Life Cycle Inventories, 2016). In the case that this electricity came from the European production mix, the CF value would increase up to 0.495 $kg \cdot kWh^{-1}$ (Swiss Centre for Life Cycle Inventories, 2016). Accordingly to the references of A_{CONV} and A_{DH} (Pérez-Fortes et al., 2016; Pérez-Fortes and Tzimas, 2016; Swiss Centre for Life Cycle Inventories, 2016) electricity needs for compressors

and recirculation come from the European grid mix. Nevertheless, these contributions to the CF represent values as low as 0.056 kg·kg^{-1} and 0.086 kg·kg^{-1}, respectively. The three ER alternatives (A_{ER}, $A_{ER-CONV}$ and A_{ER-DH}) and the DH alternative (A_{DH}) have higher electricity requirements than A_{CONV}. The corresponding contribution of the electricity used (renewable) to the CF (expressed as kg of CO_2 emitted per kg of MeOH produced) are 3.43 kg·kg^{-1} (A_{ER}), 1.99 kg·kg^{-1} ($A_{ER-CONV}$), 1.99 kg·kg^{-1} (A_{ER-DH}) and 0.79 kg·kg^{-1} (A_{DH}). In the case of A_{CONV}, no matters if that electricity would come from the grid mix (0.056 kg·kg^{-1}) or from a renewable source such as PV solar (0.002 kg·kg^{-1}) as the consumption is low. On the other hand, it must be kept in mind that due to the integration in A_{DH}, it was demonstrated a reduction of the electricity needs by 46% (Pérez-Fortes et al., 2016) when comparing the integrated (Pérez-Fortes and Tzimas, 2016) and non-integrated (Van-Dal and Bouallou, 2013) configurations. It should be mentioned that a recent study related with a DH plant integrated in a wastewater treatment plant (WWTP) to produce methanol from CO_2 has demonstrated that CO_2 emissions could become negative under the consideration of using the by-product oxygen at the WWTP and the excess of renewable energy for the electrolysis to obtain the required amount of hydrogen (Biernacki et al., 2018).
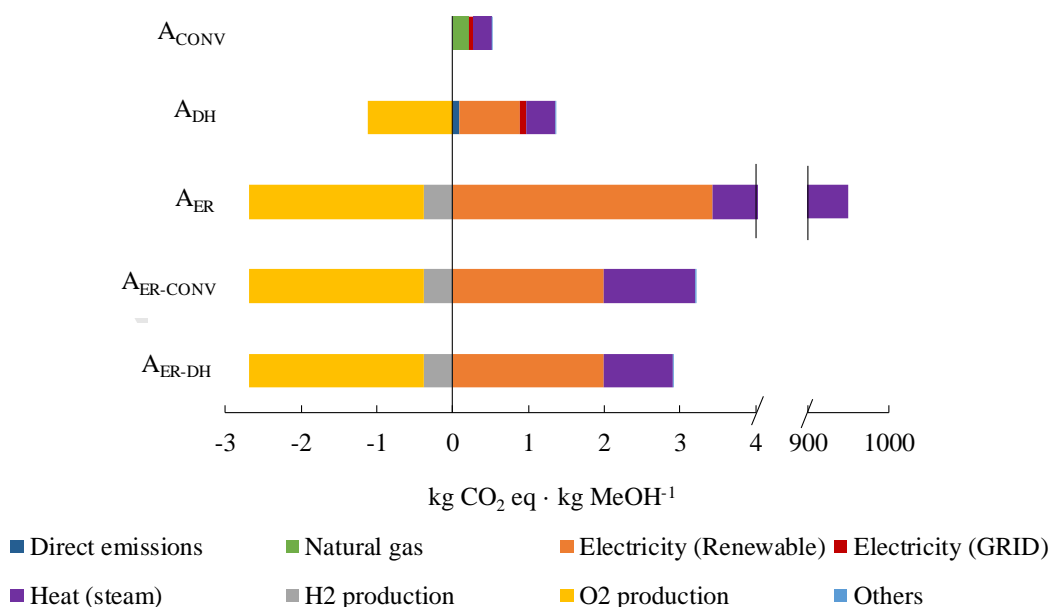
Figure 3. Distribution of GHG emissions in the alternatives A_{CONV}, A_{DH}, A_{ER} (contemporary situation) and the hypothetical scenarios $A_{ER-CONV}$ and A_{ER-DH} (functional unit 1 kg of MeOH at 99.7%wt.)

3.3. Natural resource sustainability

Table 6 presents the main resources used, natural gas for heating and as raw material and H_2, for the production of 1 kg MeOH at the commercial concentration by A_{CONV}, A_{DH}, $A_{ER-CONV}$ and A_{ER-DH}. For a fair comparison, electricity was assumed to be obtained from renewable energy in all scenarios so it is not included in the table. The heat demand is assumed to be exclusively obtained from natural gas. The net consumption of water was not included in this section. From the point of view of natural resources consumption and their environmental implications, the case of conventional fossil fuel utilization, the conventional/commercial fabrication of MeOH exhibits higher consumption of natural gas respect both CO_2 utilization alternatives. It must be taken into consideration that natural gas is the main raw material in the steam-reforming route for the production of the required syngas for the MeOH synthesis. The natural gas consumption for heating purposes will be almost in the same order of magnitude whether in future developments of the ER of CO_2 technique, a MeOH concentration above 40% wt. should be reached in the ER compartment.

Table 6. Raw materials and resource consumption of A_{CONV}, A_{DH}, $A_{ER-CONV}$ and A_{ER-DH}

Raw materials and resource consumption						
	Unit	A_{CONV}	A_{DH}	A_{ER}	$A_{ER-CONV}$	A_{ER-DH}
Natural gas *(heat)**	m³	0.178	0.118	>300	0.452	0.342
Natural gas at high pressure*	m³	0.652				
Hydrogen	kg		0.188**			

* Calculated using a reference higher/gross heating value of 39 MJ·Nm⁻³ (Swiss Centre for Life Cycle Inventories, 2016)

**Hydrogen for stoichiometric mixture in the direct reaction of the recycled CO_2 with hydrogen

Previous results have not considered the avoided amount of CO_2. However, it should be taken in mind that this study is using the conventional manufacture route as a benchmark for the evaluation. Then, the CO_2 utilization alternatives showed (A_{DH} and A_{ER} and their hypothetical scenarios) have the advantage that they are avoiding an amount of CO_2 respect A_{CONV}. This value, defined by the amount of CO_2 used per amount of MeOH produced, was determined in A_{DH}, A_{ER}, $A_{ER-CONV}$ and A_{ER-DH} as 1.374 $kg \cdot kg^{-1}$. In order to take another step forward on the future developments of A_{ER}, three additional scenarios were created and evaluated in terms of CFs. On one hand, $A_{ER-ideal}$ shows the ideal case in which FE is maximum (100%) and the cell potential (E) is minimum (1.214 V). This case would indicate the minimum attainable energy consumption (in the ER cell) and the minimum steam requirement (for distillation). These consumption values were calculated per unit of mass of MeOH produced as 6.10 $kWh \cdot kg^{-1}$ (energy from renewable) and 0 $MJ \cdot kg^{-1}$ (steam), respectively. On the other hand, two additional scenarios labelled as $A_{ER-CONV-1}$ and $A_{ER-DH-1}$ were created. Those scenarios come from $A_{ER-CONV}$ (40% wt. MeOH) and A_{ER-DH} (67% wt. MeOH) but now ideal conditions of E_{cell} and FE were considered. $A_{ER-ideal}$, $A_{ER-CONV-1}$ and $A_{ER-DH-1}$ are taking into account the avoided amount of CO_2 and they have the absence of by-products (i.e. O_2 and H_2) being ER the only influence in the CF.
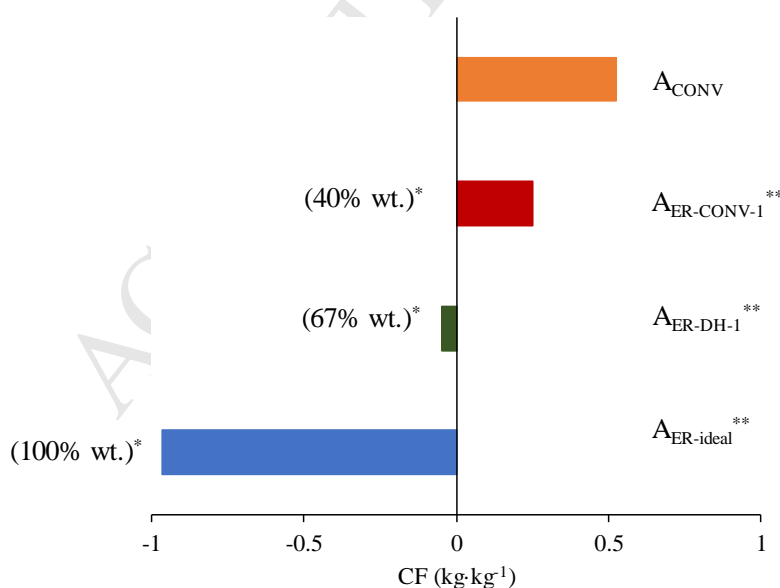
* Concentration of MeOH at the outlet stream of ER.

** $A_{ER-CONV-1}$, $A_{ER-DH-1}$ and $A_{ER-ideal}$ were created using ideal conditions of E_{cell} (1.214V) and FE (100%).

Figure 4. CF of the scenarios A_{CONV}, $A_{ER-CONV-1}$, $A_{ER-DH-1}$ and $A_{ER-ideal}$

The results obtained (Figure 4) display negative values of CFs in $A_{ER-DH-1}$ (-0.045 kg·kg^{-1}) and $A_{ER-ideal}$ (-0.963 kg·kg^{-1}) that would indicate a net CO_2 reduction. A reduction of CO_2 of -0.963 kg·kg^{-1} is the maximum possible considering just ER (under the hypothesis of the chosen CF of the PV solar energy) and dismissing the by-products generated. Furthermore, the hypothetical $A_{ER-CONV-1}$ led to a CF value (0.250 kg·kg^{-1}) that is the half of the real CF value of A_{CONV} (0.525 kg·kg^{-1}) indicating a reduction of CO_2 emissions if better conditions in the ER_{cell} were attained in future.

3.4. Remaining challenges and perspectives

MeOH manufacture routes based on the utilization of CO_2 could be a powerful choice against the depletion of fossil resources and the curbing of CO_2 emissions that are boosting the Global Warming. On one hand, the results obtained have demonstrated that some valorisation options, as DH of CO_2 are truly near to be environmentally competitive, especially in areas with excellent renewable resources due to its disadvantage in terms of high electricity consumption. On the other hand, alternatives based on ER of CO_2 have clear advantages but still needs further improvements. Despite found to be at its first stages (TRL 3-5), it is expected to progress very rapidly. Using renewable energy is one of the most important approaches to achieve an even carbon cycle. A future challenge relies on the heat to come also from a renewable source (Philibert, 2017). However, to scale up the ER technology it must be necessary to improve some technical aspects to produce MeOH at higher concentrations. This goal would be enough to decrease the large demand of steam in the purification stage that can finally neutralised the CF values respect the conventional production process (A_{CONV}) attracting an industrial interest in a more sustainable route. It is imperative to develop efficient and selective electrocatalysts that promote the kinetically lethargic CO_2 reduction process. The latest trends are showing a shift from the typical homogeneous catalysts based on metal-organic complexes (eg. complexes

composed of transition metal atom (Co or Ni) and phthalocyanine ligands (Meshitsuka et al., 1974)) to the emergent inorganic metal compounds and carbon-based materials (Zhang et al., 2018) pass through the heterogeneous electrocatalysts (eg. Mo–Bi bimetallic catalyst (Sun et al., 2016)). N-doped graphene/CNTs were theoretically predicted to be a good electrocatalyst for effective MeOH production at the applied potential from –1.29 V to –0.49 V (Zhang et al., 2018). It is clear that some combinations of alloys and intermetallic compounds or novel composite materials are still waiting to be explored. Other factors such as electrolytes (composition and pH), cell configuration (eg. microfluidic or membrane-based, recirculation) could to be also a target to improve. Proper research advances will overcome these challenges so the alternative is expected to be at the same TRL as direct hydrogenation in the future contributing to their industrial application and to alleviate the environmental problems associated with the fossil-dependence routes.

Conclusions

Undoubtedly, CO_2 valorisation alternatives for the production of methanol can be strategic low-carbon choices against the conventional fossil-dependant route. However, the development of the electrochemical reduction of CO_2 for the production of MeOH remains in its infancy. This study demonstrates that the CF of two alternatives based on CO_2 utilization (electrochemical reduction and direct hydrogenation of CO_2) could even or be below the values of the conventional route. It was evidenced a net replacement in the consumption of fossil fuels. Nevertheless, these alternatives are found at different technological readiness level. Some efforts are still needed within the ER of CO_2 in its long way to become practical and competitive. One of the most important conditions is the utilization of renewable energy especially in the alternative based on direct hydrogenation of CO_2 where the electrolyser demands the majority of the electricity. The benefit of using renewable energy could be neglected by the large steam requirements to date in the purification stage, particularly in ER of CO_2 option. In this case, a target concentration of MeOH at the outlet stream of the ER compartment around 40% wt. must be kept in mind as it will anticipate a carbon neutral cycle

respect the conventional route. However, 67% wt. of MeOH at the outlet stream of the ER compartment would be the target value in order to compete with the lasts direct hydrogenation configurations. Integration of the avoiding mass of CO_2 per unit of mass of MeOH produced under ideal conditions of ER has led to a CF of -0.963 $kg \cdot kg^{-1}$, indicating a possible reduction of CO_2 up to this value. A future challenge also includes the circumstance that the steam could come also from a renewable source. Systematic studies of selective and durable electrocatalytic materials and electrochemical reactor design are essential to realize the goal as soon as possible, turning this process into a practical and industrially viable option. Nonetheless, the successful results obtained so far represent important steps toward more low-carbon methanol synthesis.

Acknowledgments

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- MeOH production by electro-reduction (ER) and direct hydrogenation were compared.
- Carbon footprint (CF) of the NG-based commercial process was used for reference.
- Use of PV solar energy is essential to achieve a carbon even MeOH.
- MeOH concentration above 40% wt. would even the CF of ER to the reference.
- ER could lead to lower natural resources consumption compared to commercial route.