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Hydrogen Utilization in the Sustainable Manufacture of CO_2-Based Methanol

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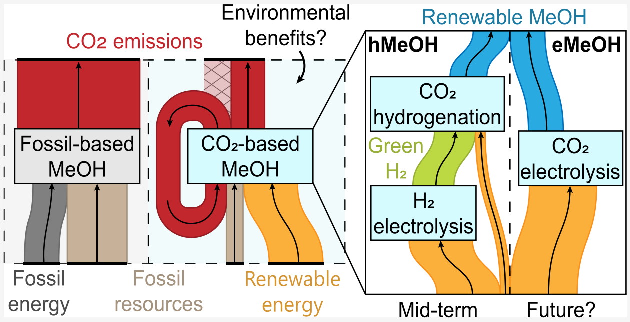

ABSTRACT: Production of alternative CO_2-based products may play a major role in decoupling fossil resources to the economy's needs. CO_2 hydrogenation is one of the most readily operational CO_2 conversion pathways to produce chemicals. Beyond this, electrochemical, photoelectrochemical, and photochemical CO_2 conversion routes have gained attention as long-term direct conversion routes. This work analyzes under what conditions H_2 could be a sustainable intermediate vector in producing renewable hydrogen-based methanol (hMeOH) and compares it with the fossil-based (fMeOH) and the emerging electrochemical-based (eMeOH) routes. The technological and exogenous drivers are identified, and the trade-offs between alternatives are assessed under an integrated life cycle approach. The deployment of low carbon hMeOH is locally conditioned to use electricity with carbon intensities of 150 kg of CO_{2e}/MWh or lower. Higher electrolysis efficiency (>70%) and product concentration (>40 wt %) are needed in the eMeOH route to be competitive with the H_2-based path. Substitution of fMeOH by wind-powered hMeOH could avoid substantial CO_2 emissions (−1.57 kg of CO_{2e}/kg) and fossil resources (−0.61 kg of oil_{eq}/kg) but at the cost of almost triple the impact of land use.

1. INTRODUCTION

Even under an anomalous economic situation affected by COVID-19, global carbon dioxide (CO_2) emissions in 2020 were still over 31.5 Gt of CO_2, a 5.8% drop from the previous year.[1] Considering that to likely contain the global warming to 2 °C we need to become carbon neutral in the next 50 years,[2] international efforts and great economic changes are necessary to sustain a similar rate of decrease without severely affecting the global welfare.

The Paris Agreement,[3] in conjunction with specific Green Deal plans,[4,5] has set an aggressive decarbonization commitment for all economic sectors. The expected energy transition promoted by the massive installation of day-by-day cheaper wind and solar energy, together with improvements in energy efficiency or heat insulation, will provoke a severe reduction in the annual carbon budget in numerous economic activities.[6,7] However, there exist some specific industrial sectors which have intrinsic CO_2 emissions not only related to energy but also with material sources needed in their activities. These are called "hard-to-abate sectors" (e.g., cement, iron and steel, paper, etc.), and additional measures are requested to decouple their production process to the use of fossil resources as identified in several decarbonization roadmaps.[8,9]

In this regard, the use of hydrogen (H_2) as intermediate material and energy has been highlighted for its promising future as a neutral-carbon chemical vector.[10−12] Although the H_2 could be used directly as a raw material or fuel depending on industrial needs, an alternative pathway is its combination with captured CO_2 for producing a value-added product. This group of alternatives would be encompassed in the Carbon Capture and Utilization technologies (CCU), using H_2 and captured CO_2 as feedstocks for producing CO_2-based products. These Power-to-X systems (PtX) are attractive for two aspects: (i) the value-added product is made of recycled carbon (captured from the plant) instead of fossil carbon, so helping in the decarbonization of another activity; and (ii) it could be used as a sink of excess electricity from intermittent renewable resources, which could be helpful in balancing future highly-renewable shared energy grids.[13,14]

Several CO_2-based routes based on H_2 and CO_2 can be found at different technology readiness levels (TRL).[15,16] The thermochemical (TC) conversion of CO_2 presents the highest level of maturity for various products. Among the gaseous products the methane (CH_4) production by CO_2 methanation stands out, which constitutes the power-to-gas route for producing renewable synthetic methane.[17,18] Concerning

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liquid hydrocarbons, the Fischer−Tropsch route for alkanes production and the hydrogenation route for methanol (MeOH) are the primary "power-to-liquids" routes. This work is focused on MeOH, which is remarked as an attractive chemical carrier that serves both as fuel and chemical.[19−21] Its high energy density (22 MJ/kg) and water-like density (792 kg/m^3) make it easy to transport and store, and it has a significant global market volume of 75 Mt/yr in 2015 with expectancies of growing up to 120 Mt/yr by 2025.[22,23] An example of implementation is the "Vulcanol process" from the Carbon Recycling International in Iceland,[24] which produces 4000 tons/yr of CO_2-based MeOH by hydrogenation using renewable energy (geothermal heat and hydroelectricity) and biogenic/industrial CO_2. Another significant demonstration case is the MefCO_2 Project,[25] that aimed to implement a pilot plant at a scale of 1 ton of MeOH per day by hydrogenation of captured CO_2.

Even if it is technically feasible to convert CO_2 into MeOH, this CCU alternative only makes sense when noteworthy environmental benefits are obtained, especially in terms of avoided CO_2 emissions. Several works have assessed the environmental prospects of CO_2-based MeOH produced in the TC route (hMeOH),[26−33] concluding that the high energy needs (electricity and heat) entail that negative CO_2 emissions are obtained only when low-carbon electricity sources are used. Correct integration with the electricity grid mix for considering the renewable energy variability would be critical.[34]

Considering this view, two major questions arise. First question is can the TC route could be substituted with a more beneficial pathway in which no H_2 as intermediate would be involved. The conversion of the CO_2 into MeOH can also be carried out in biological, electrochemical, or photochemical pathways,[33] currently featuring low TRL values (1−4).[15,16] They should evolve to show a higher competitivity level in the future. Among them, the electrochemical (EC) route has a better perspective in the midterm since it comprises scalability, mild temperature and pressure conditions, and the possibility of directly converting the CO_2 into MeOH (eMeOH) from water, CO_2, and electricity.[35−38] Therefore, when comparing the TC and EC routes, the carbon and energy sources may be the same, but the intermediation of the H_2 would be the conditioning element (Figure 1). Some works have explored the comparison between these two alternatives,[39−43] but given the uncertainty in the development of the EC route, most scenarios consider ex-ante scenarios in which the time framework is not clearly defined nor are the conditions that the EC route would need to achieve to be competitive. The second major question is what environmental trade-offs may exist when comparing the production of renewable CO_2-based MeOH with the fossil-based alternative. It is clear that the global warming potential is the critical driver to make feasible the CCU technology, but given the CO_2 recycling and the energy intensity of both EC and TC routes, other impact categories as fossil resource depletion or land use should be considered to provide a holistic overview.

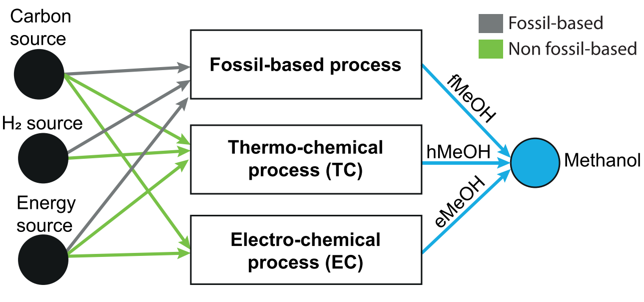

Figure 1. Simplified scheme of the considered routes in this work.

The objective of the work is then the environmental and economic sustainability assessment of using H_2 and CO_2 in a hydrogenation process for producing renewable MeOH and its comparison under scenarios with a defined time horizon with the fossil-based and direct EC-based routes (Figure 1). First, the sustainability assessment from a decarbonization perspective is conducted for the three considered alternatives, identifying the potential interest related to the introduction of renewable methanol (hMeOH and eMeOH) as a substitute. Then, a deeper comparison analysis between the hMeOH and the low-TRL eMeOH alternative is performed. Finally, the impacts on the fossil depletion and land use of the systems analyzed are studied for a broader perspective in the advantages/disadvantages. The novelties of the work are (1) defining the benchmarks in the one-step EC route to compete with the H_2-based TC route and (2) expanding the carbon footprint (CF) assessment with the depletion of fossil resources and land use. We expect this work can help to clarify the conditions and scenarios at which the hydrogen-based MeOH can be a climate-change mitigation alternative and its potential benefits and trade-offs when compared with other alternatives.

2. MATERIAL AND METHODS

2.1. Process Description.

2.1.1. Fossil-Based MeOH Production. Conventional production of MeOH (fMeOH) is performed by steam reforming to produce syngas followed by hydrogenation of the carbon monoxide (CO). The first step (Figure 2) is performed at around 850 °C and 25 bar to reform the CH_4 (eq 1) and displace the equilibrium of the water gas shift reaction (eq 2). Ni-based catalysts are commonly used. Then the CO and CO_2 are hydrogenated in an equilibrium reaction (eq 3 and eq 4) for which a high-pressure loop of around 80 bar and 250−300 °C is used to maximize the conversion into MeOH by Cu-based catalysts.[44]

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{2}$$

$$CO + 2H_2 \leftrightarrow CH_3OH \tag{3}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \tag{4}$$

2.1.2. Thermochemical (TC) CO_2 Hydrogenation. The thermochemical conversion of CO_2 into MeOH (hMeOH) consists of five major stages (Figure 2): (1) capture of the CO_2, (2) H_2 production by water electrolysis; (3) synthesis of MeOH in the hydrogenation reactor; (4) recovery of unreacted CO_2; and (5) distillation of MeOH up to commercial grade.

The CO_2 capture can be performed by a variety of technologies and to different point sources. Chemical absorption with monoethanolamine (MEA) is the most mature technology in the field,[45,46] but alternatives with other solvents, adsorption on solids, or membrane technologies can also be applied.[47−49] The point sources can vary from coal power plants to different industrial sectors, the CO_2 concentration being in the range of 1.5−30% v/v.[50] The water electrolysis is performed in alkaline or PEM electrolyzers with overall energy

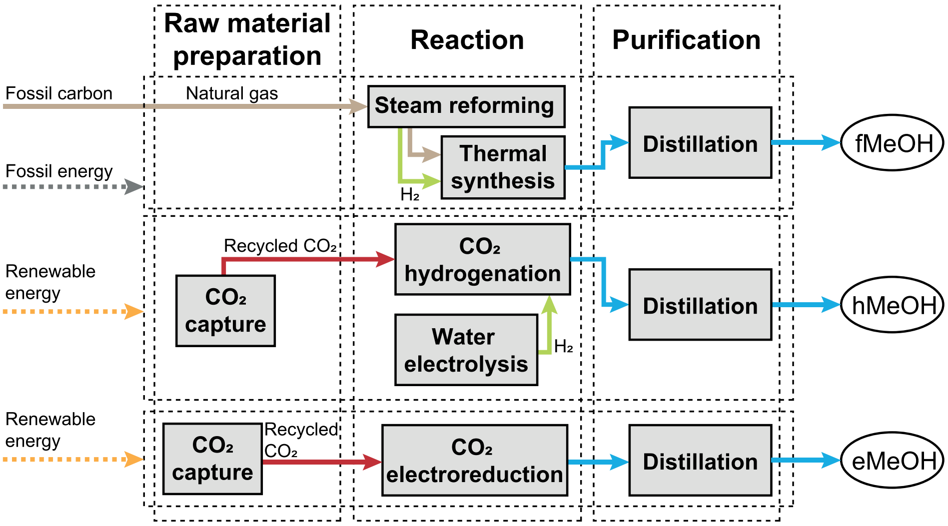

Figure 2. Conceptual diagram for the fossil, thermochemical (TC), and electrochemical (EC) routes for producing MeOH.

efficiencies around 60−70%.[51] Typical electrodes are IrO_2 on the anode side for producing the water oxidation (eq 5) and Pt on the cathode for catalyzing the hydrogen evolution reaction (eq 6)

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{5}$$

$$4H^+ + 4e^- \rightarrow 2H_2 \tag{6}$$

The MeOH synthesis is performed at intermediate temperatures of 200−300 °C and 50−100 bar of pressure. The MeOH is produced from eq 4, while the competing equilibrium CO/CO_2 in the water gas shift reaction (eq 2) also occurs. Catalysts of Cu, ZnO, or AlO_3 are the most used for CO_2 hydrogenation.[52] A gas−liquid separator is then used to recover the gas mix, while the diluted methanol goes into a distillation column to achieve a higher concentration of the MeOH.

2.1.3. Electrochemical (EC) CO_2 Reduction. The electrochemical reduction (ER) of CO_2 avoids the need to produce H_2 and directly yields MeOH (eMeOH) by direct CO_2 reduction. This process comprises four major steps: (1) capture of the CO_2, (2) electroreduction of CO_2 into MeOH and subproducts; (3) recovery of unreacted CO_2; and (4) distillation of MeOH up to commercial-grade (Figure 2).

Steps 1, 3, and 4 are similar to the TC route. The CO_2 electroreduction occurs in an electrochemical reactor, frequently in alkaline or PEM configurations with flowing electrolytes and GDE configurations on the cathode to improve current densities.[53] On the anode side, the water-splitting reaction (eq 5) usually happens with IrO_2 as the catalyst. There are two groups of reactions on the cathode: one related to reducing the inlet CO_2 (eq 7) and a second one with the evolution of hydrogen (eq 6). The catalyst must be very selective to MeOH, but parallel CO_2 reduction reactions to other products can occur. This work assumes that only MeOH and H_2 can be produced from the reactor. Cu is the most common catalyst, mainly in the form of copper oxides (Cu_2O). The process occurs at room temperature and pressure.[54−57]

$$CO_2 + 6e^- + 6H^+ \rightarrow CH_3OH + H_2O \tag{7}$$

2.2. Life Cycle Methodology. *2.2.1. Goal and Scope.* This study aims to compare the environmental profile of producing renewable MeOH using H_2 as an intermediate against the conventional fossil-based MeOH and alternative direct electrochemical CO_2-based MeOH pathways. This work additionally pursues the determination of the impacts of these routes on the use of resources (consumption of fossil resources and land use) and the emission of greenhouse gases (global warming impact). In this way, it would be possible to unveil the environmental trade-offs and limitations that the use of H_2 for producing renewable MeOH could bring in the decarbonization of hard-to-abate sectors. To this end, the functional unit used in the whole study is 1 kg of MeOH at a commercial concentration (99.7 wt %).

2.2.2. System Boundaries and Assumptions. Cradle-to-gate system boundaries are proposed, including those from the CO_2 capture to the product purification. Product use and further end-impacts are out of the scope of this work. Previously confirmed less relevant stages as the production of secondary chemicals (e.g., electrolytes) are not considered because of their unsubstantial contribution, as evaluated in a previous study.[58] Cathode replacement is neglected assuming significant improvements in the electrode lifetimes, as described in Rumayor et al.[59] Carbonate formation is assumed to be minimized by proper cell design as it severely impacts the performance.[60] CO_2 capture is modeled assuming a flue gas from a coal power plant and using the inventory from previous authors,[49] but it must be noted that additional needs could be required depending on the impurities in the CO_2 point source. The captured CO_2 is allocated with the CCU product (MeOH in this case), but in fact, the CO_2 savings are shared with the product from the CO_2 source. Additional discussion regarding the CO_2 allocation can be found in Muller et al.[61] Byproducts produced in the CO_2-based routes (e.g., O_2, H_2) are not valorized and so considered as purged out of the system. Ideally, they would be valorized and considered as other secondary products with a particular avoided burden, but it is not clear if it would be possible to couple the different productions and sell all its products in the market. It should also be considered that additional process details could be given to take into account other complexities, but given the scope of this work, only the major units and key performance contributors are considered. Further detailed engineering approaches can be found in specialized works.

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2.2.3. Scenarios and Life Cycle Inventories. Life cycle inventories are obtained from a built-in process model for each of the major units as described in previous works.[62,63] A life cycle inventory (LCI) combines (i) process values from the literature for the TC unit, the CO_2 capture, and other secondary units; (ii) a black-box model for the ER unit; and (iii) a set of simulations with Aspen Plus for the distillation step. It is defined in three cases of study depending on the time horizon considered:

- **Today**: In today's scenario we compare the environmental impacts of the fossil-based MeOH with the renewable MeOH from CO_2 hydrogenation in the Vulcanol process. This case study considers that the EC technology is not ready for massive deployment, and the TC route is limited to local frameworks. The fossil-based LCI is given from the Ecoinvent database 3.7,[64] while the Vulcanol datasheet is used for the CO_2-based MeOH LCI.[65] Two subscenarios are defined for the conventional route: (1) electricity needs to be covered by the European grid mix, as given in the original inventory; (2) electricity needs are fully covered with wind energy, assuming an optimistic locally beneficial situation.
- **Near Future (2020−2030)**: This case studies the local conditions that make viable (carbon negative) the implementation of the hMeOH route. This scenario assumes that the H_2 has become an attractive alternative for decarbonizing certain applications, but with an ongoing energy transition, there is a significant location variability in the availability of low-carbon electricity. The hMeOH route is the only viable high-scale decarbonization alternative, considering that the eMeOH route is still uncompetitive and at a low TRL. The process values used for the LCI are taken in a range from experimental work.[26,28,30,41] Additional information on energy demands used is shown in Table S1 in the Supporting Information.
- **Mid-future (2030−2050)**: In this case, the hMeOH route is used as a reference to define the electroreduction benchmarks that the eMeOH route would need to achieve to become a competitive alternative in terms of carbon footprint. Then the environmental impacts of the CO_2-based MeOH with today's conventional fMeOH are compared. This case assumes that wind and solar energy dominate the energy landscape and that heating is electrified by electric boilers with 96% energy efficiency.[66] The hMeOH route uses the best-case LCI from the "near future" case study, assuming that (i) heat for CO_2 capture is electrified; (ii) H_2 electrolysis improves up to 70% efficiency; (iii) there is optimal heat integration in the MeOH synthesis and purification. The LCI for the eMeOH route is obtained by a mathematical process model of the reaction and purification stages described in previous studies.[58,67,68] The electroreduction variables used in the model are summarized in Table 1. The low TRL scenario is based on the parameters reported from the best lab-scale performer.[57] The high TRL values use similar hypotheses in the parameters as other general ex-antes LCA/TEA assessments,[40,69,70] so considering an optimistic future-like scenario.

2.2.4. Impact Categories, Indicators, and Software. An attributional Life Cycle Assessment (LCA) has been performed to the scenarios and system boundaries considered. Given the low TRL of the EC technology, it is performed as an ex-ante LCA, in which the technology is preliminarily assessed prior to its industrial application.[71] The methodology has followed the international LCA standards ISO 14040:2006 and 14044:2006.[72,73] The impact category method selected was the Hierarchist ReCiPe 2016 v1.1 (H). It is considered the midpoint impact category of climate change, fossil depletion, and land use. The Global Warming Potential (GWP_{100}), Fossil Depletion Potential (FDP), and agricultural Land Occupation Potential (LOP) are used as their respective indicators. The main software was OpenLCA[74] using the GaBi Professional Database 2020,[75] with some exceptions using the Ecoinvent Database 3.7.[76]

Table 1. Scenarios Considered Regarding the Level of TRL Achieved in the CO_2 Electrochemical Reactor for Producing eMeOH

parameter	low TRL	high TRL
Faradaic efficiency (%)	55	90
electrolysis energy efficiency (%)	35	70
single-pass CO_2 conversion	30	30
[MeOH] (wt %)	10	40

3. RESULTS AND DISCUSSION

3.1. Carbon Footprint of Today's Methanol Manufacture. Figure 3 shows the carbon footprint assessment under today's case study. The conventional production of MeOH has a global warming potential (GWP) of 0.584 kg of CO_{2e} per kg of MeOH, with the heating needs (0.254 of kg CO_{2e}/FU) and the CH_4 used as feedstock (0.231 of kg CO_{2e}/FU) being the major contributors. These CH_4 emissions could be even bigger as they can be severely affected by the natural gas precedence, the distribution leaks being a critical factor to manage.[77] If the energy needs are decarbonized ("Wind-powered industry"), the total GWP of conventional fMeOH decreases to 0.295 kg of CO_{2e}/FU. The remaining emissions are mainly related to the need for CH_4 during the steam

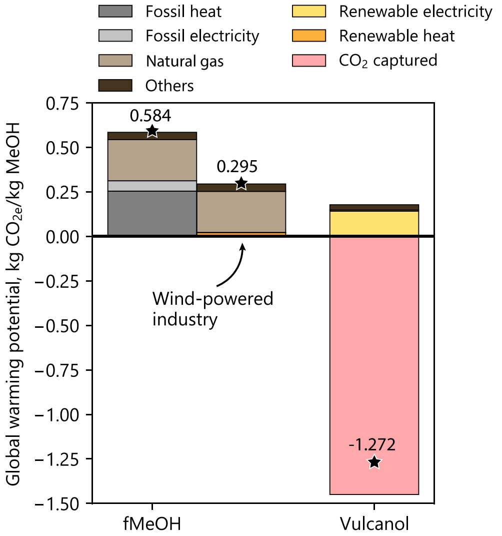

Figure 3. Global warming potential (kg CO_{2e}/kg MeOH) of today's conventional methanol manufacture (powered by current grid mix or wind energy) and alternative H_2-based Vulcanol process.

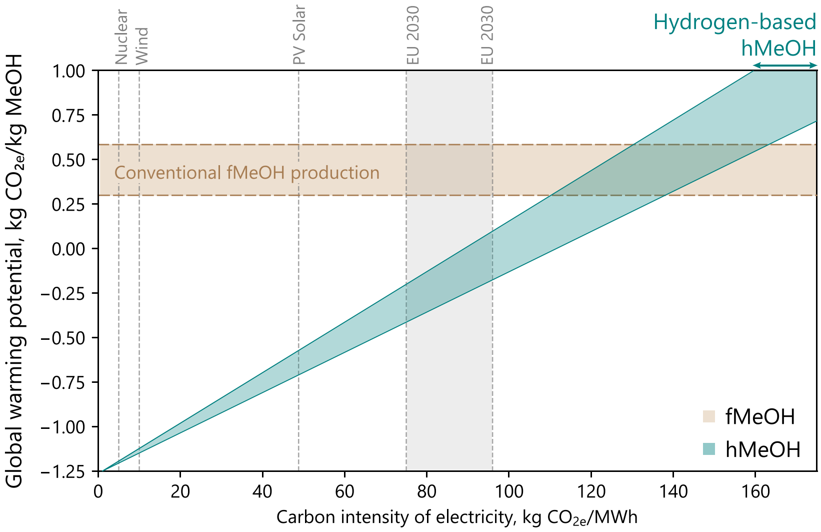

Figure 4. Global warming potential (kg CO_{2e}/kg MeOH) of hMeOH as a function of the carbon intensity from the electricity supply. The global warming potential of conventional fMeOH is presented with a beige area (0.303−0.584 kg of CO_{2e}/kg MeOH). The filled area for hMeOH is calculated from the range of reported electricity and heat needs in the TC conversion process.

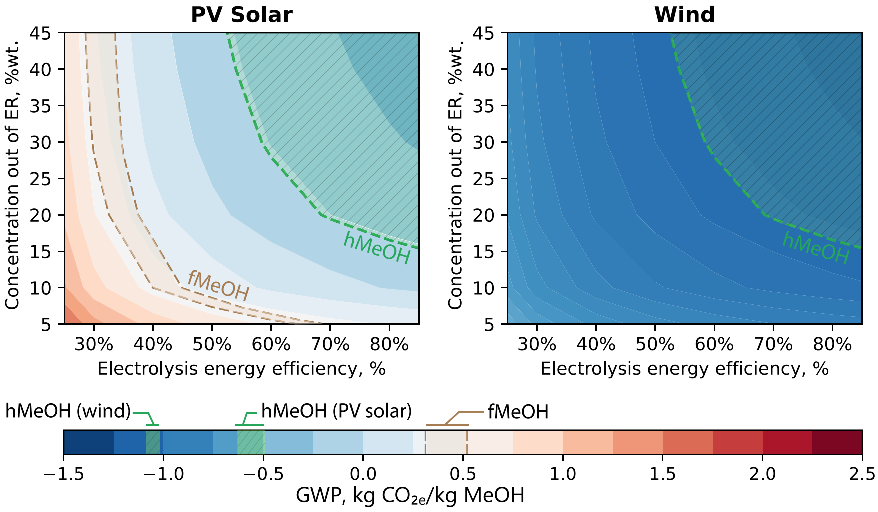

Figure 5. GWP of eMeOH production (kg CO_{2e}/MeOH) as a function of the electrolysis energy efficiency (%) and product concentration (wt %). The dashed green area represents the carbon footprint range for hMeOH production.

reforming process. The Vulcanol process has a direct GWP of 0.178 kg of CO_{2e}/FU, with electricity for H_2 production counting for almost 80%. As the carbon feedstock is CO_2 captured from a geothermal source, it must be attributed negative emissions of −1.450 kg of CO_{2e}/FU, resulting in a net GWP of the Vulcanol process of −1.272 kg of CO_{2e}/FU. These results show that, even if the conventional production of MeOH uses low-carbon energy sources, there are still inherent CO_2 emissions related to the material needs that the CCU alternative avoids. In this way, substituting conventional fMeOH with hMeOH from the Vulcanol process would avoid more than 1.5 kg of CO_{2e}/FU even in the conventional industry decarbonizes, indicating the potential CO_2 savings when using captured CO_2 as the carbon source.

3.2. Thermochemical CO_2 Conversion for a Decarbonized MeOH Production.

Figure 4 displays the GWP of the renewable MeOH produced from CO_2 hydrogenation under the near-future case study as a function of the electricity carbon intensity supplied to the process. Since the TC process consumes a significant amount of energy, the energy source is critical, with H_2 electrolysis already consuming around 10 kWh/FU. To supply energy mixes with carbon intensities higher than 100−140 kg, CO_{2e}/kWh produces hMeOH with a GWP higher than the conventional fossil-based process (around 0.3−0.6 kg of CO_{2e}/FU), making the CCU process unfeasible. The transition toward wind and solar power along the whole EU is expected to produce a mean carbon intensity in 2030 of 75−97 kg of CO_{2e}/kWh,[78] which would be already enough to have hMeOH with a GWP between −0.198 kg of CO_{2e}/FU and 0.114 kg of CO_{2e}/FU. The benefits of using dedicated low-carbon technologies enhance even more this reduction, up to the point of achieving a similar GWP to the Vulcanol process, on the order of −1.1 kg of CO_{2e}/FU when wind/nuclear power is used.

3.3. Future Alternatives for Renewable MeOH Production.

The midfuture case study for the period 2030−2050 included the EC route as a potential competitor with the H_2-mediated TC route. The question was what conditions would be needed to make the process competitive in terms of carbon footprint. Figure 5 shows the GWP of the eMeOH as a function of the most critical electroreduction performance variables: the electrolysis energy efficiency and the product concentration. Two energy sources are used: in the first case, PV solar energy is supplied, resulting in that energy efficiencies around 40%, and a concentration of at least 20 wt % would be the minimum benchmark to be viable compared with the conventional process, but being far away from the hydrogen-based hMeOH. In the second case wind energy is supplied, and so the eMeOH would provide clear CO_2 savings compared with fMeOH even at a similar performance as in current lab-scale experiments. The eMeOH could technically compete with the hMeOH if further efforts are made to push the energy efficiencies close to 70% and product concentration around 40 wt %, which would minimize the massive energy needs in the electroreduction and the distillation process. Only under this situation, could the EC route be comparable with the TC route. Considering that actual lab-scale performers[54−57,79] are obtaining an energy efficiency around 20−35% and concentration lower than 10 wt %, it is clear that significant research needs to be done to find better electrocatalysts, improve cell configurations, and optimize the operating conditions. Other liquid hydrocarbons such as formic acid (HCOOH) are closer to these values (best performers[80−83] around 60% efficiency and 20 wt %), which gives positive prospects of finding similar conditions in the future for the MeOH.

Figure 6 shows the contribution shares for the two eMeOH subscenarios and hMeOH scenarios for the GWP assessment when supplying PV solar energy. The high TRL eMeOH route and the hMeOH route perform in similar net GWP of around −0.5 kg of CO_{2e}/FU, reducing almost 1 kg of CO_{2e}/FU compared with the fossil-based route. The low TRL eMeOH presents a net GWP of 2.06 kg of CO_{2e}/FU, not decreasing the conventional fMeOH route impact (0.303−0.584 kg of CO_{2e}/FU). The purification process is more relevant in the eMeOH route, especially in the low TRL subscenario where the lower product concentration out of the reactor (10 wt %) aggravates the total energy requirements during the MeOH purification. The comparison between stages for the three MeOH routes is shown in Table 2.

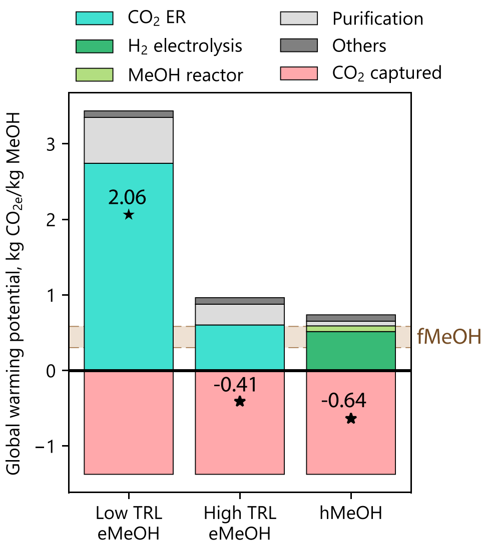

Figure 6. GWP breakdown (kg CO_{2e}/kg MeOH) for producing MeOH in the considered EC (eMeOH) and TC (hMeOH) routes when PV solar energy is supplied. The beige area stands for GWP of the fMeOH production.

Table 2. Global Warming Potential Comparison (kg of CO_{2e}/kg of MeOH) for the Considered MeOH Routes[a]

product	raw material preparation	reaction	purification
fMeOH	0.233	0.296	0.055
hMeOH	0.084−1.374[b]	0.591	0.062
eMeOH (high TRL)	0.086−1.374[b]	0.603	0.275
eMeOH (low TRL)	0.091−1.374[b]	2.743	0.607

[a] The fMeOH uses electricity from the current grid mix, while hMeOH and eMeOH use electricity from PV solar energy. [b] Net CO_2 captured and consumed in the process.

Some scenarios have shown significant reductions in the GWP when substituting the fossil-based fMeOH with renewable MeOH (hMeOH or high TRL eMeOH). Figure 7 displays for the scenarios in the midfuture case study the assessment of three indicators: Global Warming Potential (GWP), Fossil Depletion Potential (FDP), and Land Use Occupation Potential (LOP). Two energy sources are analyzed: wind energy and PV solar energy. A first conclusion is that powering the CCU system (TC or EC routes) with wind energy reduces between 2 and 3 times the environmental impacts compared to when using solar energy. The reason is that wind energy requests fewer abiotic resources to generate electricity, especially those related to Si production, where extraction and manufacturing consume significantly more fossil resources and occupied land. A second conclusion is that in climate change and fossil depletion the CCU system outperforms conventional MeOH production, due to the use of recycled carbon to minimize CO_2 emissions while displacing the needs of fossil carbon. For example, considering the mean values of wind and PV energy, the hMeOH scenario would proportionate an average CO_2 savings of −1.36 kg of CO_{2e}/FU and reduce the use of fossil resources by −0.57 kg of oil_{eq}/FU. Regarding the land, the high energy intensity of both TC and EC processes, in combination with the higher land requirements of renewable energies, impact the total land use with an increase of 2.4 times in the best case (hMeOH with wind energy) and 26.6 times in the worst case (Low TRL eMeOH with PV energy). Examining the values, conventional fMeOH has a LOP impact of 0.0032 m^2 annual $crop_{eq}$ per year, while the mean for the hMeOH scenario is 0.0168 m^2 annual $crop_{eq}$ per year, around eight times its conventional value.

However, it must be noted that one of the major limitations in this study is that the electricity supply is being oversimplified by assuming average capacity factors, and then the mismatch between generation and demand throughout the year is not evaluated. Electricity supply is being balanced by an ideal integration with the electricity grid, which is not a realistic assumption given the significant daily and seasonal variability of renewable energy. Supporting energy storage systems could be used to compensate for these variations within the production plant and provide a sustained number of hours to be operational, which could be essential to ensure the economic viability of the facility. Figure S3 in the Supporting Information shows an estimation about the effect of introducing energy storage systems on GWP and FDP, clearly indicating increments of more than 30% in both indicators

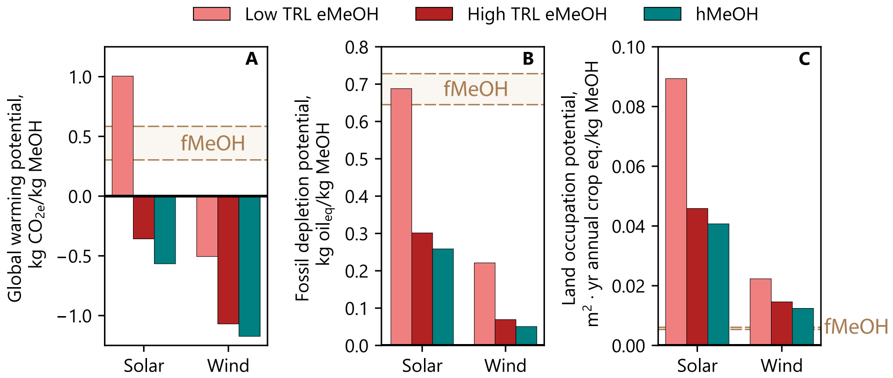

Figure 7. Assessment of alternative eMeOH and hMeOH routes compared with the fossil-based fMeOH production in (A) global warming potential (kg CO_{2e}/kg MeOH); (B) fossil depletion potential (kg oil_{eq}/kg MeOH); and (C) land occupation potential ($m^2 \cdot yr$ annual $crop_{eq}$/kg MeOH). The beige area represents conventional fMeOH production.

when at least 20% of the energy comes from batteries. Further consideration in the intermittent use of stored energy when achieving higher values of technology implementation should be addressed.

4. CONCLUSIONS

This work envelops the environmental benefits and trade-offs that hydrogen utilization could bring to society when coupled with CO_2 for producing renewable MeOH (hMeOH) in comparison with the current fossil-based (fMeOH) and future electrochemical-based methanol (eMeOH). Regarding the 2030/2050 climate neutrality objectives, the decarbonization of fuels and chemicals must be tackled, and methanol, one of the major global commodities, needs critical technological changes in the coming years. In the near term, implementing CCU alternatives by hydrogenating CO_2 to MeOH (hMeOH) can be a local solution when renewable electricity and ready-to-capture industrial CO_2 are available. For the period from 2030 to 2050, the production of hMeOH can be an interesting climate mitigation technology when paired with energy carbon intensities of 150 kg of CO_{2e}/MWh or lower. Considering the rapid evolution and massive installation of wind/PV solar in projected national plans and the economic incentives for carbon reduction in industries, development at a larger scale of electro-intensified plants using H_2 for producing hMeOH could bring a CO_2 emissions reduction between 1.25 and 7.9 kg of CO_{2e} per kg of H_2 produced. When electricity is supplied at carbon intensities between 10 and 100 Kg CO_{2e}/MWh

Regarding the long run (2050 in advance), we evaluated the electrochemical conversion of CO_2 as an emerging technology that could displace the H_2-based route thanks to its flexibility and avoidance of H_2 as an intermediary. We concluded that electrochemical-based MeOH (eMeOH) could be a compelling alternative when electrolysis performance reaches a 70% energy efficiency and 40% product concentration. In that future foresight, the complete transition from today to renewable-powered MeOH production could be translated into substantial savings of CO_2 emissions (0.99−1.57 kg of CO_{2e}/kg MeOH) and fossil resources (0.44−0.61 kg of oil_{eq}/kg MeOH), depending on the electricity source and conversion pathway. However, given the electro-intensification of the CCU alternatives and the minor power density of wind/solar resources, the total land use impact would increase from 2.4 to 26.6 times the actual impact for MeOH production (fMeOH).

This study provides a comprehensive perspective about the environmental prospects of using H_2 for MeOH production and defines scenarios in time and space in which alternatives as the direct CO_2 electroreduction may arise. Additional considerations in economics should be addressed in future studies, as well as exploring other competitive options. Given the high dependency on electricity supply, photochemical alternatives for producing H_2 or directly MeOH could be of significant interest to study. Finally, the evaluation of optimized local solutions concerning hydrogen storage, energy supply, and unit integration should be attended. We hope that all these advances may help in the future in the penetration of CCU alternatives as a climate change mitigation solution and the transition from a fossil and linear-based economy to a circular and nonfossil one.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.1c04295.

Energy demands for CO_2 hydrogenation, considerations of process units, and electroreduction modeling details (DOCX)

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Notes

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■ ABBREVIATIONS

CC = climate change
CF = carbon footprint
CCU = Carbon Capture and Utilization
ER = electro-reduction
EC = electrochemical
eMeOH = electroreduction-based MeOH
FDP = fossil depletion potential
hMeOH = hydrogen-based MeOH
LOP = land occupation potential
LCA = life cycle assessment
LCI = life cycle inventory
PtX = Power-to-X
TC = thermochemical
TEA = technoeconomic assessment

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