The environmental opportunity cost of using renewable energy for carbon capture and utilization for methanol production

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HIGHLIGHTS

• CO₂ impact of using renewable energy (RE) to produce MeOH from CO₂ quantified.
• Three sources of electricity and CO₂ emissions accounted for.
• RE on grid versus RE for producing MeOH from CO₂ accounted for.
• RE on the grid avoids greater CO₂ than RE for producing MeOH from CO₂.
• Use RE to produce MeOH from CO₂ only if grid intensity is below 67 gCO₂/kWh.

ABSTRACT

Carbon capture and utilization (CCU) to produce methanol is a beneficial pathway to use carbon dioxide (CO₂) and mitigate climate change. Existing life cycle assessments demonstrate that CCU methanol generates a net CO₂ benefit when the hydrogen (H₂), required for hydrogenating the captured CO₂, is generated by electrolyzing water using renewable electricity (RE). However, the findings do not account for the environmental opportunity cost when RE can be supplied to the grid to offset CO₂ intensive electricity instead of electrolyzing water, the energy penalty of capturing CO₂ and the scope for technological improvement. This study quantifies the environmental opportunity cost and determines the net CO₂ emissions when CCU methanol offsets the production of conventional methanol across 14 scenarios. The 14 scenarios account for capturing CO₂ from 3 sources (combined and conventional natural gas, and coal power plants) and generating H₂ with electricity from 3 sources (photovoltaics, wind and the grid). The CO₂ avoided by using RE on the grid is greater than that from producing CCU methanol by 660 to 11960 kg CO₂/ton methanol across the 14 scenarios. Unless the grid CO₂ intensity drops...
1. Introduction

The rapid growth in global carbon-dioxide (CO\textsubscript{2}) emissions and the corresponding increase in the atmospheric CO\textsubscript{2} concentration poses a significant climate risk. Limiting temperature rise to the recommended threshold of 1.5 °C\textsuperscript{1} and minimizing climate-change impacts requires a 45% reduction in global CO\textsubscript{2} emissions from 2010 levels by 2030 and net zero levels by around 2050 [1]. Emerging studies propose carbon capture and utilization (CCU) as an environmentally promising CO\textsubscript{2} mitigation pathway by capturing the CO\textsubscript{2} from waste streams and producing economically valuable products from the captured CO\textsubscript{2} [2].

A recent study shows that CCU has the potential to prevent 7.15 gigatons of CO\textsubscript{2} emissions globally and generate products with a potential market value of 837 billion US dollars by 2030 [3]. Among the products for utilizing captured CO\textsubscript{2}, methanol is an attractive option as it is a vital feedstock for the chemical industry and an important source of transportation fuel. The potential environmental benefits have motivated policy measures in US, the European Union (EU) and China to incentivize the blending of methanol (3–85% by volume) in traditional fossil-fuel based transportation fuels [4]. The global production of methanol has increased by 10% annually from 45 million tons in 2008 to 96 million tons in 2016 [5]. Estimates show that production of methanol from captured CO\textsubscript{2} has the potential to utilize 50 million tons of CO\textsubscript{2} by 2030 [3]. CO\textsubscript{2} utilization from methanol production is expected to increase by 8% annually [6]. Beyond capturing and utilizing CO\textsubscript{2} emissions, methanol produced from captured CO\textsubscript{2} offers the additional environmental benefit of preventing CO\textsubscript{2} emissions by displacing conventional methanol, which is produced from natural gas through steam reformation [7,8].

Given the potential economic and environmental opportunities, facilities dedicated to produce methanol from captured CO\textsubscript{2} have been established in Iceland and Japan [8,9] producing 4000 and 100 tons per year, respectively [10,11]. A survey shows that the “Chemical Intermediate” cluster, which is one of the six major product clusters for CO\textsubscript{2} utilization and includes methanol, has the highest number commercial developers [3]. With significant economic potential [12,13], there is a critical need to prospectively resolve environmental hotspots and identify environmental preferable pathways to further expand the scale of producing methanol from captured CO\textsubscript{2}. Life cycle assessment (LCA), the comprehensive analytical framework to evaluate the environmental impact of products and technology systems, has been applied to investigate various environmental aspects of producing methanol from captured CO\textsubscript{2} [14]. Methanol production from captured CO\textsubscript{2} requires two crucial feedstock production processes - the capture of CO\textsubscript{2} and the generation of H\textsubscript{2}. The methanol is produced by hydrogenating the feedstock of captured CO\textsubscript{2}. LCA studies have shown that methanol produced from captured CO\textsubscript{2} generates a net CO\textsubscript{2} benefit by offsetting conventional methanol produced from natural gas and utilizing a feedstock of captured CO\textsubscript{2} [14], although this benefit can only be realized when renewable electricity (RE) is used for hydrogen generation via electrolysis [11,15–17]. Hydrogen generation through electrolysis of water is an energetic hotspot [11] and the use of RE can decrease the environmental burden of electrolysis [8,16,18]. A recent review concluded that CCU methanol production using wind electricity has a lower CO\textsubscript{2} footprint than conventional methanol [19]. Despite the consensus, existing studies do not account for the following key factors which, when combined, can impact the net life cycle CO\textsubscript{2} benefit of replacing conventional methanol with CCU methanol.

(i) **Environmental opportunity cost**: The environmental feasibility of producing methanol from captured CO\textsubscript{2} is predicated upon utilizing low carbon RE for the generation of H\textsubscript{2}. However, the use of RE for H\textsubscript{2} generation forgoes the opportunity to supply RE to the grid and, thereby, avoid CO\textsubscript{2} emissions by offsetting electricity generated from fossil sources. The potential CO\textsubscript{2} emissions that can be avoided by offsetting CO\textsubscript{2}-intensive fossil-fuel electricity on the grid is hereafter referred to as the environmental opportunity cost (EOC) of using RE to produce methanol from captured CO\textsubscript{2}. The EOC is variable as it depends on the CO\textsubscript{2} intensity of the grid electricity offset by the RE, which varies by the source from which the grid electricity is generated (e.g. coal, natural gas, wind). As a result, CCU methanol production may generate a net increase in CO\textsubscript{2} emissions in scenarios where RE can instead prevent a greater amount of CO\textsubscript{2} emissions when it is supplied to the grid.

(ii) **Energy penalty (Elec\textsubscript{p})**: Elec\textsubscript{p} represents the decrease in the electricity output of the power plant [20–22] as the capture of CO\textsubscript{2}, which is required for CCU methanol production, requires heat and electricity [23]. If the power plant from which CO\textsubscript{2} is captured is operating at maximum energy capacity, then the energy penalty is compensated by an external source (hereafter referred to as “external compensation”). In this scenario, electricity is generated without carbon capture in the external power plant. Alternately, if the power plant from which CO\textsubscript{2} is captured is operating below maximum energy capacity, then the energy penalty is compensated by the same plant (hereafter referred to as “internal compensation”). In this scenario, the analysis should account for the carbon capture when electricity is generated internally in the power to compensate for the energy penalty.

(iii) **Technology improvement**: The decrease in material and energy inventory requirements, which accompanies technological and process improvements, decreases the life cycle CO\textsubscript{2} emissions of CCU methanol production.

(iv) **Data uncertainty**: There is a lack of standardized data on the life cycle energy and material inventory required to produce CCU methanol at a commercial scale. As a result, the uncertainty in the inventory data [24,25] and the variability in assumptions used across studies introduces significant uncertainty in the value of the life cycle CO\textsubscript{2} determined for CCU methanol production [19,26].

To account for the above factors, we determine the net life cycle CO\textsubscript{2} impact from CCU methanol, which accounts for the post-combustion CO\textsubscript{2} capture from power plants, H\textsubscript{2} generation, methanol production, the CO\textsubscript{2} avoided by offsetting conventional methanol, the EOC of the RE used and the energy penalty of carbon. We determine the threshold value of the grid CO\textsubscript{2} intensity at which RE use for CCU methanol production generates a greater benefit than the supply of RE to the grid. To account for technological improvements, we determine the net CO\textsubscript{2} emissions and the threshold value for CCU methanol production under the current technological condition and at the thermodynamic limit, wherein the material and energy requirements are assumed to be the theoretical minimum. We determine the life cycle CO\textsubscript{2} impact of CCU methanol based on material and energy inventory collected from 58 studies [11,15–18,27–69] and conduct an uncertainty analysis to determine the impact of data uncertainty on the results.
2. Methods

2.1. CCU methanol production - key processes and inventory requirement

The key processes for CCU methanol production are – capture and compression of CO₂, generation of H₂ through electrolysis of water, compression and transportation of CO₂ and H₂, and the hydrogenation of CO₂ to produce methanol.

MEA based post-combustion CO₂ capture: We assume that CO₂ is captured using a post-capture monoethanolamine (MEA) based system as it has a high (>90%) carbon capture efficiency [27,28,70], is capable of capturing CO₂ from dilute concentrations [71], can be retrofitted to existing power plants, is the most commercially mature technology [72,73] and is more widely deployed than pre-combustion and oxy-fuel systems [70]. We consider CO₂ capture from power plants as it accounts for 28% of the overall CO₂ emissions in the U.S [74] and is therefore a good candidate for carbon capture. For a detailed explanation of the physical principles of the capture of CO₂ using MEA, the reader can refer to literature [27-47] (section S3 SI) and is summarized in Fig. 1.

H₂ generation: Over 95% of the global hydrogen is produced from fossil fuels [75] and research and development efforts are currently investigating alternate renewable energy pathways, which are less carbon intensive [76]. We consider H₂ production through the electrolysis of water using RE sources (wind and photovoltaics) as it accounts for 4% of the globally produced H₂ [75] and is currently the only commercially viable, environmentally benign alternative to H₂ produced from fossil fuels [18]. We assume that the electrolysis is conducted in an alkaline electrolysis cell as it is the most widely deployed water electrolysis technology [48,65,66,76]. The inventory required for H₂ generation from water electrolysis was collected from 22 studies (section S4 in the SI) and is summarized in Fig. 1.

The system boundary to determine the net CO₂ impact of CCU methanol is depicted in Fig. 2 and includes two functionally equivalent systems – (i) CCU methanol production (upper dashed box) and electricity generation with carbon capture and (ii) conventional methanol production from natural gas (lower dashed box) and electricity generation without CO₂ capture.

The processes contributing to the overall CO₂ emissions from CCU methanol systems include the capture, compression and transportation of CO₂, generation, compression and transportation of H₂, hydrogenation of CO₂ to produce methanol, and the CO₂ that is not captured when preferable to alternatives [70,81,82]. CO₂ is compressed to a pressure of 110 bar (greater than the critical pressure of 73.8 MPa [83,84]) to ensure the transportation is in a super-critical state and avoid a two-phase flow [29,84]. H₂ is assumed to be compressed to 110 bar, which ensures transportation in a liquefied state and is consistent with values reported in literature in the range of 69–100 bar [18,85,86]. The transportation distance for H₂ and CO₂ is assumed to be 200 km and the pressure drop from transportation of H₂ and CO₂ is 0.12 [85] and 0.1 bar/km [29], respectively. Therefore, we assume that there is no recompression of H₂ or CO₂ as the pressure after 200 km of transportation is 85 and 86 bar, which is higher than 80 bar required for hydrogenation of CO₂ to produce CCU methanol [15,30,67]. Further details on the inventory required for CO₂ and H₂ compression and pipelines are presented in S5, S6, S7 and S8 in the SI.

Methanol production from hydrogenating CO₂: CCU methanol is produced through the catalytic hydrogenation of captured CO₂. In the presence of catalysts (Cu/ZnO/Al₂O₃), CO₂ reacts with H₂ to form methanol at a pressure of 50–100 bar, a temperature of 210–270 °C and the H₂:CO₂ molar ratio of 3:1 [11,15,18,65,87]. The methanol that is produced is separated from water and residual gases and purified through distillation [11]. Detailed descriptions of the chemical and the physical principles and the reaction mechanism for methanol generation from hydrogenation of CO₂ are available in the literature [11,65]. The inventory requirements are summarized in Fig. 1 and further detailed in section S2 in the SI.

2.2. System boundary

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electricity is generated (typically 10% for MEA-based capture process). The energy penalty and the CO$_2$ flows for external and internal compensation are depicted in red and green, respectively.

2.3. Functional unit

To enable a functionally equivalent comparison between the CCU and conventional methanol system, this study uses a functional unit of 1 ton of methanol and Elec$_{p}$ kWh of electricity, which has a mean value of 927 kWh (SI Table S15). This helps quantify the CO$_2$ impact when 1 ton of CCU methanol offsets 1 ton of conventional methanol produced from natural gas. In the CCU methanol system, Elec$_{p}$, which was used for CCU methanol production, is instead supplied to the grid in the lower box and results in the EOC. Units: Electricity flows in kWh/ton methanol, CO$_2$ flows in kg/ton methanol.

The energy penalty and the CO$_2$ flows for external and internal compensation are depicted in red and green, respectively.

2.4. Determining the life cycle CO$_2$ impact from the inventory requirement

We use the LCA software package SimaPro [88] to determine the life cycle CO$_2$ impact of the inventory required for the key processes described in the above mentioned sections. In SimaPro, we use the global warming mid-point impact category in the TRACI [89] impact assessment method to determine the CO$_2$ impact from the inventory requirements (explained in the sections below).

\[
\text{CO}_2\text{-Emissions from CCU Methanol (CO}_2\text{CCU-MeOH)} = \text{CO}_2\text{-CCU-MeOH}_{\text{Gen}} + \text{CO}_2\text{-CCT} + \text{CO}_2\text{-H}_2\text{GCT} + \text{CO}_2\text{-Not-Cap} + \text{CO}_2\text{-Infra} + \text{CO}_2\text{-Elec}_p
\]  

(1)

CO$_2$ emissions from CCU methanol production (CO$_2$CCU-MeOH Gen): CO$_2$CCU-MeOH Gen is determined from the life cycle inventory required to produce 1 ton of CCU methanol through the hydrogenation of captured CO$_2$ (Table S2 SI). In SimaPro, the inventory is characterized for global warming impact in the TRACI [89] impact assessment method. CO$_2$CCU-MeOH Gen is determined to be 20.2 kg CO$_2$/ton CCU methanol (Section S2 SI).

CO$_2$ emissions from capture, compression and transportation of CO$_2$(CO$_2$CCT): CO$_2$CCT is determined from the life cycle inventory

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CO$_2$ emissions from capture, compression and transportation of CO$_2$(CO$_2$CCT): CO$_2$CCT is determined from the life cycle inventory

\[
\text{Elec}_p = \text{Elec}_p \text{without cap} (927 \text{ kWh})
\]

\[
\text{CCU methanol (1 ton)}
\]

\[
\text{CO}_2\text{ emitted (CO}_2\text{CCU-MeOH Gen)}
\]

\[
\text{CO}_2\text{ emitted (CO}_2\text{H}_2\text{GCT)}
\]

\[
\text{CO}_2\text{ emissions – H}_2\text{ gen, comp & transp}
\]

\[
\text{Elec}_p \text{ supplied to grid (produces env opp cost CO}_2\text{ Opp Cost)}
\]

\[
\text{CCU methanol (1 ton)}
\]

\[
\text{Conventional Methanol (1 ton)}
\]

\[
\text{CO}_2\text{ emitted (CO}_2\text{Conv-MeOH Gen)}
\]

\[
\text{Elec}_p \text{ without cap} (\text{Elec}_p)
\]

\[
\text{100% CO}_2\text{ emitted without CC (CO}_2\text{Elec}_p\text{ without cap)}
\]
CO₂ emissions from capture, compression and transportation of H₂ (CO₂ H₂ GCT): CO₂ H₂ GCT is determined from the life cycle inventory required to capture, compress and transport the H₂ feedstock required to produce 1 ton of CCU methanol (Section S4 SI). In SimaPro, the CO₂ emissions from the production of electricity (Elec) is the same as in the conventional methanol pathway (Elec). The CO₂ emissions from generating electricity (CO₂ Elec) is 463 kg CO₂/t methanol (Table S12 SI).

CO₂ emissions in the Conventional Methanol Pathway (CO₂ Conv_MeOH): CO₂ Conv_MeOH is determined from Eq. (2)

\[ \text{CO}_2\text{Conv}\text{MeOH} = \text{CO}_2\text{Conv}\text{MeOH}_{\text{Gen}} + \text{CO}_2\text{Elec}_{\text{without\_cap}} - \text{CO}_2\text{Opp\_Cost} \]  

2.6. Scenario analysis to explore the variation in the net CO₂ emissions from CCU methanol

The net CO₂ emissions from CCU methanol is impacted by the source from which CO₂ is captured, the source of electricity used to electrolyze water, and the source used to compensate for the energy penalty of CO₂ capture. For example, the CO₂ emissions from electricity without CO₂ capture in the conventional methanol pathway (CO₂ Elec_without_cap) in lower dashed box in Fig. 2) will be higher when CO₂ is captured from a coal than a combined cycle natural gas plant as coal electricity is more CO₂ intensive than a combined cycle plant. Similarly, the CO₂ emissions from water electrolysis will depend on whether grid, wind or solar electricity is used. The life cycle inventory indicates the grid mix used in the process. The life cycle inventory of the grid mix used in this study is provided in Table S15 SI. The life cycle inventory provides a consistent composition of electricity across the region of interest, which facilitates a consistent comparison as an equal magnitude of electricity (Elec) is offset by the CCU methanol.

\[ \text{Elec}_{\text{without\_cap}} \] is produced along with 1 ton of methanol. Elec_{without_cap} facilitates a consistent comparison as an equal magnitude of electricity (Elec) is offset by the CCU methanol. CO₂_{Elec_{without_cap}} is determined to be 51, 70 and 122 kg/ton CCU methanol when CO₂ is captured from a combined cycle natural gas, natural gas and coal power plants, respectively (Section S3 SI).
CO₂ footprint. Furthermore, the net CO₂ emissions will change depending on whether the energy penalty is compensated externally or internally.

We perform a scenario analysis to determine the sensitivity of the net CO₂ emissions from CCU methanol to the above-mentioned parameters. We explore 14 scenarios (Table 1) based on

(i) Three sources from which CO₂ is captured – Fossil fuel power plants are favorable candidates for CO₂ capture as the electricity sector accounts 34% of the total greenhouse gas emissions in the USA and coal and natural gas plants account for 98% percent of the CO₂ emissions from the electricity sector [94]. We consider a coal power plant, a conventional natural gas power plant or a combined cycle natural gas power plant for carbon capture.

(ii) Three sources of electricity - the grid, wind and PV - for water electrolysis and hydrogenation of CO₂. We consider wind as it is the largest RE source in the USA and has a low GHG footprint [95] and, therefore, reduce the CO₂ burden of electrolyzing water. We include PV as it is the fastest growing source of RE along with wind [96] and has shown a 72% reduction in the cost of electricity generation at a utility scale from 2010 [97], which makes it economically attractive for water electrolysis. We consider two grid-based scenarios to compare the net CO₂ emissions when CCU methanol is produced using renewable and grid electricity.

(iii) Two sources for compensating for the energy penalty – we explore scenarios where the energy penalty is compensated externally or internally.

The net CO₂ emissions is determined using Eq. (4) for each of the 14 scenarios.

2.7 Net CO₂ emissions from CCU methanol at thermodynamic limit and minimal environmental opportunity cost

The net CO₂ emissions from CCU methanol can be minimized by decreasing the CO₂ emissions from CCU methanol production and the
**Table 1**
Scenario to explore the net CO₂ emissions from CCU methanol production. The inventory requirements for CO₂ capture, H₂ generation and CCU methanol production (Fig. 1) and the energy penalty, which equals 927 kWh/ton methanol (Table S13 SI), remains the same across scenarios.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>CO₂ Source</th>
<th>Electricity required for water electrolysis (CO₂/kWh)</th>
<th>Energy penalty compensated by external power plant or internally (same plant)</th>
<th>CO₂ intensity of electricity used to compensate the penalty (g CO₂/kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Natural Gas</td>
<td>Grid (13900 kWh/ton methanol, US Average = 499 g CO₂/kWh)</td>
<td>External</td>
<td>499</td>
</tr>
<tr>
<td>2</td>
<td>Combined Cycle Plant (459)</td>
<td>PV (13900 kWh/ton methanol)</td>
<td>External</td>
<td>499</td>
</tr>
<tr>
<td>3</td>
<td>Natural Gas Plant (674)</td>
<td>CO₂/kWh)</td>
<td>External</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>Coal Plant (1240)</td>
<td>External</td>
<td>External</td>
<td>499</td>
</tr>
<tr>
<td>5</td>
<td>Natural Gas Plant (674)</td>
<td>Wind (13900 kWh/ton methanol, 27 g CO₂/kWh)</td>
<td>External</td>
<td>499</td>
</tr>
<tr>
<td>6</td>
<td>Coal Plant (1240)</td>
<td>External</td>
<td>External</td>
<td>111</td>
</tr>
</tbody>
</table>

This analysis models CO₂ capture at the thermodynamic limit through the minimum work required to separate CO₂. The minimum work to separate CO₂ at 90% efficiency at a concentration of 12% in flue gas is 43.8 kWh/ton CO₂ (101,102).

Technical improvements for the water electrolysis can be achieved through efficiency improvements in wind and solar PV systems and the electrolysis process to produce hydrogen. We model the thermodynamic limit by assuming the crystalline Si PV module operates at the Shockley-Queisser limit of 30% [98], which is the maximum possible efficiency of crystalline Si modules, and the wind turbine operates at the maximum possible Betz limit of 59% [99]. The minimum energy required to generate H₂ through water electrolysis is 39.4 kWh/kg H₂ [100].

We assume isothermal compression under ideal conditions to determine the energy required to compress CO₂ and H₂ to 110 bar at the thermodynamic limit, which is 66.5 and 1,455 kWh/ton of CO₂ and H₂, respectively (SI Section S12). This analysis assumes that the capture of CO₂ and the generation of H₂ occurs at the site where methanol is produced through the hydrogenation of the captured CO₂. As a result, at the thermodynamic limit, we assume that there is no pipeline infrastructure required to transport CO₂ and H₂ to the site of CCU methanol production.

At the thermodynamic limit, the CO₂ and H₂ required to hydrogenate CO₂ and produce methanol is determined from the stoichiometry of the reaction. Therefore, to produce 1 ton of CCU methanol, 1.37 tons and 0.187 tons of CO₂ and H₂ are required [18]. As the reaction is exothermic [18], we assume no energy is required under ideal thermodynamic conditions.

**Minimizing the environmental opportunity cost:** The EOC of using RE for CCU methanol decreases if the CO₂ intensity of the grid decreases (CO₂ Elec_grid in Eq. (3)) and the resulting CO₂ emissions offset by RE on the grid decreases. This analysis determines the threshold value of the CO₂ intensity of the grid electricity (CO₂ Grid_Thresh) at which the EOC of utilizing RE for CCU methanol is zero. At this threshold value, the CO₂ avoided by using RE to produce CCU methanol is equal to the CO₂ avoided by supplying RE to the grid.

Therefore, when CO₂ Elec_grid equals CO₂ Grid_Thresh:

\[
\text{CO}_2_{\text{CCU-MeOH}} - \text{CO}_2_{\text{Conv-MeOH}} = \text{CO}_2_{\text{Op-Cost}}
\]

If the grid CO₂ intensity exceeds the threshold, then it is environmentally favorable to supply the RE to the grid. Alternately, if the grid CO₂ intensity is lower than the threshold, it is environmentally favorable to utilize the RE for CCU methanol production.

3. Results and discussion

3.1. Net CO₂ emissions from CCU methanol production – contribution analysis

When the EOC is not accounted for, the net CO₂ emissions is the difference between the positive values of emissions from CCU and conventional methanol production. For example, when 1 ton of CCU methanol offsets 1 ton of conventional methanol in scenario 6, the net CO₂ emitted is –160 kg (inset table Fig. 3). The negative value indicates that CCU methanol offsetting conventional methanol avoids the emission of 160 kg of CO₂. When the EOC is not considered, the CO₂ emissions from CCU methanol production is greater or comparable to conventional methanol production in 6 out of the 14 scenarios (scenarios 1, 2, 3, 4 and 5 and scenario 9 in Figure S1 in SI). This is primarily due to the CO₂ emissions from hydrogen generation (CO₂ H₂ GCT) and the energy penalty of carbon capture (CO₂ Elec_grid).

The inset table in Fig. 3 also presents the net CO₂ benefit of CCU methanol production at the thermodynamic limit.
the CO$_2$ emitted from producing conventional methanol (+1170 kg) and the EOC (-6240 kg). Despite being less carbon-intensive than conventional methanol production, CCU methanol production forgoes an opportunity to avoid a greater amount of CO$_2$ by supplying RE to the grid in the remaining 8 scenarios (scenarios 6 to 8 in Fig. 3 and scenarios 10 to 14 in Figure S1 in SI).

The results demonstrate the importance of including the EOC and the energy penalty of CO$_2$ capture when determining the net CO$_2$ impact of CCU methanol, which is not accounted for in existing literature [8,11,15,17]. It is important to note that the EOC is determined based on the average CO$_2$ intensity of the US grid (CO$_2$_Elec$_{grid}$ = 499 g CO$_2$/kWh in Eq. (3)). Fig. 5 explores the sensitivity of the EOC to the grid CO$_2$ intensity. As a result, we determine if it is better to use RE for CCU methanol production or on the grid at different CO$_2$ footprints of grid electricity.

Scenarios 1 and 2 show that when grid electricity is used, the CO$_2$ footprint of CCU methanol is around 7 times that of conventional methanol, which is primarily due to the CO$_2$ emissions from H$_2$ generation. A 7 time increase in the CO$_2$ footprint is in contrast to a previous study by Pérez-Fortes et al. [15] which reported that CCU methanol is less CO$_2$ intensive than conventional methanol. However, the system boundary used in Pérez-Fortes et al. did not account for the CO$_2$ impact of CO$_2$ capture and H$_2$ generation. A subsequent expansion in the system boundary to account for CO$_2$ impact of CO$_2$ capture and H$_2$ generation makes the CO$_2$ impact of CCU and conventional methanol obtained from Pérez-Fortes et al. similar to that reported in this study (SI Section S18). The change in results of Pérez-Fortes et al. study with an expansion of the system boundary further emphasizes the need to account for the broader life cycle CO$_2$ emissions from the upstream processes of CO$_2$ capture and H$_2$ generation when quantifying the net CO$_2$ impact of CCU methanol.

The results do not change based on the downstream application in which CCU methanol is used as CCU methanol will essentially be offsetting conventional methanol. For example, consider a scenario where CCU methanol can potentially offset conventional methanol which is being used as transportation fuel. The CO$_2$ trade-off between the two types of methanol is quantified by the “Env opp cost accounted” row in the inset table in Fig. 3, which clearly shows that replacing conventional with CCU methanol in the transportation fuel will produce a net increase in CO$_2$ emission (e.g. 6080 kg CO$_2$/ton methanol in scenario 6 in Fig. 3). Alternately, conventional methanol will have a lower CO$_2$ burden than CCU methanol in any downstream application when the EOC of RE use is accounted for.

The EOC assumes that RE used for CCU methanol production results is supplied to the grid. However, a certain portion of the generated RE is curtailed and not supplied to the grid [103–105]. In this scenario, using the curtailed RE to produce CCU methanol will not incur an EOC. For example, in scenario 6 in Fig. 3, CCU methanol offsetting conventional methanol makes the CO$_2$ impact of CCU and conventional methanol obtained from Pérez-Fortes et al. similar to that reported in this study (SI Section S18). The change in results of Pérez-Fortes et al. study with an expansion of the system boundary further emphasizes the need to account for the broader life cycle CO$_2$ emissions from the upstream processes of CO$_2$ capture and H$_2$ generation when quantifying the net CO$_2$ impact of CCU methanol.

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**Fig. 4.** Solid bars represent CO$_2$ emissions from CCU methanol production when grid (scenarios 1 to 2) and PV electricity (scenarios 3 to 8) is used for water electrolysis. Dashed bars represent CO$_2$ impact of producing conventional methanol and supplying PV electricity to the grid. Tabulated values present the range of the net CO$_2$ emitted when 1 ton of CCU methanol offsets 1 ton of conventional methanol and the EOC of PV electricity is accounted for. The circled numbers correspond to the scenarios in Table 1. Positive values represent CO$_2$ emissions and negative values represent avoided CO$_2$ emissions. *RE is not used in scenarios 1 and 2 as CCU methanol is produced using grid electricity. As a result, the EOC is zero in scenarios 1 and 2.
methanol avoids 160 kg of CO\textsubscript{2} but incurs an EOC of 6080 kg CO\textsubscript{2}. Therefore, CCU methanol production is environmentally preferable to conventional methanol only when there is a 97% or greater reduction in the EOC (6080 to 160 kg CO\textsubscript{2}). Alternately, CCU methanol will have a lower CO\textsubscript{2} impact than conventional methanol if a minimum of 97% of the overall RE used for CCU methanol production is curtailed electricity. However, such high curtailment rates are very unlikely as curtailment rates have been reducing and are around 1 to 15% in the U.S \cite{103-105}.

The values in the inset table in Fig. 3 demonstrate that the net CO\textsubscript{2} emitted is lower when CO\textsubscript{2} is captured from coal plants than combined cycle or conventional natural gas plants. This is because CCU methanol production offsets electricity that is generated without CO\textsubscript{2} capture (CO\textsubscript{2} Elec without_cap in Figs. 2 and 3). Offsetting coal electricity without CO\textsubscript{2} capture prevents an emission of 1240 g CO\textsubscript{2}/kWh, which is greater than 459 or 674 g CO\textsubscript{2}/kWh of emissions prevented by offsetting combined cycle or conventional natural gas electricity without CO\textsubscript{2} capture, respectively (SI Section S9). The results provide the rationale to maximize the net CO\textsubscript{2} benefit of CCU methanol by ranking power plants for CO\textsubscript{2} capture based by fuel type. The highest priority for CO\textsubscript{2} capture should be assigned to coal plants followed by conventional and combined cycle plants.

The CO\textsubscript{2} burdens of the energy penalty of CO\textsubscript{2} capture, the methanol production from CO\textsubscript{2} and H\textsubscript{2}, and the infrastructure requirements (H\textsubscript{2} and CO\textsubscript{2} air compressors, H\textsubscript{2} and CO\textsubscript{2} pipeline, water electrolysis cell) are negligible.

### 3.2. Net CO\textsubscript{2} emissions from CCU methanol production – uncertainty analysis

The values in the inset table in Fig. 4 represent the upper and lower bound of the difference between the CO\textsubscript{2} emissions from CCU and conventional methanol. The variation is due to the uncertainty in the life cycle inventory requirements for CCU methanol production, the source from which CO\textsubscript{2} is captured and the choice of the electricity source used for compensating for the energy penalty. Despite this uncertainty, the positive values of the upper and lower bounds show that when the EOC is accounted for, the CO\textsubscript{2} avoided by supplying PV electricity to the grid is greater than the CO\textsubscript{2} avoided from producing CCU methanol by \(+700 \text{ to } +11960 \text{ kg/ton methanol (inset table in Fig. 4).} \) Similarly, when wind electricity is used, the results are \(+660 \text{ to } +11525 \text{ kg CO}\textsubscript{2}/\text{ton methanol (SI Section S11).} \)

### 3.3. Environmental opportunity cost and net CO\textsubscript{2} emissions from CCU methanol at the thermodynamic limit

By quantifying the EOC, the results in Fig. 5 determines if the CO\textsubscript{2} avoided by using RE to produce CCU methanol is greater than the supplying RE to the grid for varying CO\textsubscript{2} intensities of the grid electricity (y-axis). The results are bounded between the baseline and the thermodynamic limit of CCU methanol production, which are represented on the left and right extreme of the x-axis, respectively. In the green region, the CO\textsubscript{2} avoided by using RE for CCU methanol production is greater than the CO\textsubscript{2} avoided by supplying RE to the grid (i.e. EOC is negative). In the brown region, the CO\textsubscript{2} avoided by supplying RE to the grid is greater than the CO\textsubscript{2} avoided by using RE for CCU methanol production (i.e. EOC is positive). To contextualize the results, we include the current and projected (2050) grid CO\textsubscript{2} intensities of the eight North American Electric Reliability Corporation (NERC) reliability regions in plots (a) and plot (b), respectively.

At the threshold grid CO\textsubscript{2} intensity value of 67 g CO\textsubscript{2}/kWh, the CO\textsubscript{2}
avoided by using RE for CCU methanol production equals the CO₂ avoided by supplying RE to the grid (Eq. (5)). The CO₂ intensity of the current US average grid and the eight NERC reliability regions are in the brown region of the graph (Fig. 5 (a)) and higher than 67 g CO₂/kWh. Therefore, it is environmentally preferable to supply RE to the grid than use RE for CCU methanol production for the current grid condition in the US. Based on the projected CO₂ intensity values of the grid in 2050 (Fig. 5 (b)), the results show that supplying RE to the grid will most likely continue to be environmentally preferable to using RE to produce CCU methanol.

More importantly, the results show that even if the CCU methanol production reaches thermodynamic limits (extreme right on x-axis), supplying RE to the US grid will continue to be the environmentally preferable in 2020 and 2050. This is because current and projected values for the CO₂ intensity of the US average grid mix and the NERC reliability regions are in the brown region and are higher than the threshold values of 82 g CO₂/kWh. The thermodynamic analysis shows that despite maximum possible improvements in the water electrolysis process, the EOC will continue to be the dominant factor in determining if RE should be used for CCU methanol production or be supplied to the grid.

4. Conclusion

This work quantifies the life cycle CO₂ impact of offsetting the production of conventional methanol with CCU methanol across 14 scenarios, which account for the (i) environmental opportunity cost of supplying RE to the grid (ii) two alternatives to compensate for the energy penalty of capturing CO₂ – internal and external (iii) three sources for the captured CO₂ – coal, natural gas and combined cycle natural gas plants and (iv) three sources of electricity – the grid, PV and wind. The LCA includes the key processes for CCU methanol production – capture of CO₂ using post-combustion capture MEA systems, compression and transportation of CO₂, generation of H₂ through water electrolysis, compression and transportation of H₂. Furthermore, the analysis accounts for the uncertainty in the material and energy inventory required to produce CCU methanol.

CCU methanol has a higher or a comparable CO₂ footprint than conventional methanol in 6 out of the 14 scenarios primarily due to the CO₂ emissions from H₂ generation and compensating for the energy penalty of carbon capture. In the remaining 8 scenarios, the CO₂ emissions from producing CCU methanol is lower than conventional methanol. Despite the uncertainty in the data, the findings show that the CO₂ benefit from supplying RE to the grid is greater than utilizing RE for CCU methanol production across the 14 scenarios. Unless the CO₂ intensity of the grid mix is lower than 67 g CO₂/kWh, utilizing RE on the electricity grid will produce a greater CO₂ benefit than in CCU methanol production. Similarly, the grid CO₂ intensity should be lower than 82 g CO₂/ kWh when the CCU methanol production system operates at thermodynamic limits, which is unlikely in the US before 2050. The results demonstrate the need to account for the broader systems-level CO₂ impacts when transitioning to large-scale CCU pathways such as methanol.

CRediT authorship contribution statement

Dwarakanath Ravikumar: Conceptualization, Methodology, Software, Validation, Formal analysis, Data curation, Writing - original draft, Writing - review & editing. Gregory Keoleian: Conceptualization, Validation, Resources, Visualization, Writing - review & editing. Shelle Miller: Conceptualization, Validation, Resources, Visualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.apenergy.2020.115770.

References


[23] Ravikumar D, Seager TP, Cucurachi S, Prado V, Mutel C. Novel method of sensitivity analysis improves the prioritization of research in anticipatory life


Merrill MD. Water electrolysis at the thermodynamic limit. Florida State University; 2007.


NREL Reducing Wind Curtailment through Transmission Expansion in a Wind Vision Future; 2015.
