

# Comparative Life Cycle Assessment of Electrochemical Upgrading of CO<sub>2</sub> to Fuels and Feedstocks

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## Abstract

Development of electrochemical pathways to convert CO<sub>2</sub> into fuels and feedstock is rapidly progressing over the past decade. Here we present a comparative cradle-to-gate life cycle assessment (LCA) of one and two-step electrochemical conversion of CO<sub>2</sub> to eight major value-added products; wherein we consider CO<sub>2</sub> capture, conversion and product separation in our process model. We measure the carbon intensity (i.e., global warming impact) of one and two-step electrochemical routes with its counterparts – thermochemical CO<sub>2</sub> utilization and fossil-fuel based conventional synthesis routes for those same products. Despite inevitable carbonate formation in one-step CO<sub>2</sub> electrolysis, this analysis reveals one-step electrosynthesis would be equally compelling (through the lens of climate benefits) as compared to two-step route. This analysis further reveals that the carbon intensity of electrosynthesis products is due to significant energy requirement for the conversion (70-80% for gas products) and product separation (40-85% for liquid products) phases. Electrochemical route is highly sensitive to the electricity emission factor and is compelling only when coupled with electricity with low emission intensity (<0.25 kg CO<sub>2e</sub>/kWh). As the technology advances, we identify the near-term products that would provide climate benefits over fossil-based routes, including syngas, ethylene and n-propanol. We further identify technological goals required for electrochemical route to be competitive, notably achieving liquid product concentration >20 wt%. It is our hope that this analysis will guide the CO<sub>2</sub> electrosynthesis community to target achieving these technological goals, such that when coupled with low-carbon electricity, electrochemical route would bring climate benefits in near future.

**Keywords:** Life cycle analysis, CO<sub>2</sub> utilization, electrolysis, renewables, CO<sub>2</sub> capture, separation

## 1. Introduction

Increasing industrialization and growing demand of fossil fuels have led rapid rise in green house gas (GHG) emission (e.g., 36 gigatonnes of CO<sub>2</sub> was emitted in 2017), as evident from recent catastrophic weather events.<sup>1,2</sup> This anthropogenic climate change is believed to be irreversible in regards to global warming, ocean acidification,<sup>3</sup> increased precipitation and rise in sea level.<sup>4</sup> To mitigate this climate change, scientists have set the limit of atmospheric concentration of CO<sub>2</sub> to 350 parts per million (ppm).<sup>5</sup> Unfortunately, in recent years, the atmospheric concentration of CO<sub>2</sub> has already crossed 410 ppm,<sup>6</sup> which warrants aggressive measures to develop negative emission technologies<sup>7</sup> that can be rapidly deployed to limit global warming to 2°C by the end of 21<sup>st</sup> century in accordance with Paris Agreement.<sup>8</sup> In this regard, carbon capture and storage (CCS) can play a vital role to substantially mitigate climate change; which however has been facing technical, political and socio-economic setbacks.<sup>9,10</sup> Alternatively, carbon capture and utilization (CCU) is being actively pursued recently, which involves capturing CO<sub>2</sub> either from air or industrial point sources followed by direct or indirect utilization to attain climate and economic benefits.

Over the years, CO<sub>2</sub> has been directly (i.e., non-reductively) used in various industrial processes, including food processing, carbonated beverages, structural materials and enhanced oil recovery (largest direct CO<sub>2</sub> use by far).<sup>5,10</sup> Among various indirect (i.e., reductively) conversion technologies of CO<sub>2</sub> (including thermochemical, electrochemical, electro-thermochemical hybrid, photochemical, biochemical etc.), thermochemical conversion is technologically most advanced (technology readiness level, TRL of 5-8).<sup>11</sup> Thermochemical conversion includes: (1) one-step direct hydrogenation of CO<sub>2</sub>, wherein H<sub>2</sub> is produced from steam-methane-reforming (SMR), (2) two-step process, wherein CO<sub>2</sub> is converted to syngas (via reverse water gas shift (RWGS) or CO<sub>2</sub> reforming process) followed by Fischer-Tropsch (F-T) synthesis of hydrocarbons and oxygenates.<sup>12</sup> Thermochemical process often involves the use of fossil hydrocarbons (e.g., methane) for H<sub>2</sub> production or CO<sub>2</sub> reforming; consequently, the associated GHG emission defeats the climate benefits of CO<sub>2</sub> conversion. Alternatively, commercial water electrolysis to generate hydrogen can be coupled with thermochemical process, making a hybrid thermo-electrochemical process.<sup>13</sup> Despite high TRL of thermochemical CO<sub>2</sub> conversion processes, unfavourable economics at small-scale, thermodynamically limited single-pass CO<sub>2</sub> conversion as well as energy efficiency (EE) are some of the roadblocks for further development and investment to be utilized for distributed CO<sub>2</sub> sources.<sup>13</sup>

Alternatively, there has been rapid progress in one-step ( $\text{CO}_2 \rightarrow \text{products}$ ) or two-step ( $\text{CO}_2 \rightarrow \text{CO} \rightarrow \text{products}$ ) electrochemical conversion of  $\text{CO}_2$  into fuels and chemical feedstocks.<sup>14,15</sup> Today,  $\text{CO}_2$  electrolyzer to produce CO is commercially available at full-scale (from Haldor Topsoe<sup>16</sup> based on high temperature solid-oxide electrolysis cell (SOEC) technology) with a technology readiness level (TRL) of 8.<sup>17</sup> On the other hand, low temperature electrochemical  $\text{CO}_2$  conversion to multi-carbon products is relatively immature (TRL of 2-4) and often limited in lab-scale testing.<sup>13,17</sup> Interestingly, the electrochemical route offers a number of potential opportunities, including modular scaling for small to large-scale applications, lower capital investment, load balancing for electric grid, storage of intermittent renewable electricity (e.g., wind or solar energy) into energy-dense hydrocarbons that can be transported and traded globally etc.<sup>13</sup> With continuous reduction in renewable electricity price, electrochemical  $\text{CO}_2$  conversion technologies could become economically competitive with thermochemical and conventional fossil-based synthesis pathways<sup>12,18</sup>. To date, depending on the reaction conditions, operating parameters and catalyst used, over 16 different chemicals have been produced via electrochemical  $\text{CO}_2$  conversion, including carbon monoxide (CO), formic acid (HCOOH), methane ( $\text{CH}_4$ ), methanol ( $\text{CH}_3\text{OH}$ ), ethylene ( $\text{C}_2\text{H}_4$ ), ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ), n-propanol ( $\text{C}_3\text{H}_7\text{OH}$ ), acetic acid ( $\text{CH}_3\text{COOH}$ ) etc.<sup>19,20</sup> Aside from one-step direct electrochemical conversion of  $\text{CO}_2$ , recent perspectives have emerged highlighting the feasibility of two-step reduction –  $\text{CO}_2$  reduction to CO, followed CO reduction to multi-carbon products (i.e., ethylene, ethanol) (Figure 1).<sup>21</sup> The two-step process can potentially reap multiple benefits, including mature SOEC with high stability, energy efficiency (~45% in first step<sup>16</sup>), with high selectivity towards  $\text{C}_2+$  products in alkaline environment (in second step); overcoming challenges (i.e., low single-pass  $\text{CO}_2$  conversion due to carbonate formation) for one-step  $\text{CO}_2$  conversion to  $\text{C}_2+$  products.<sup>21,22</sup>

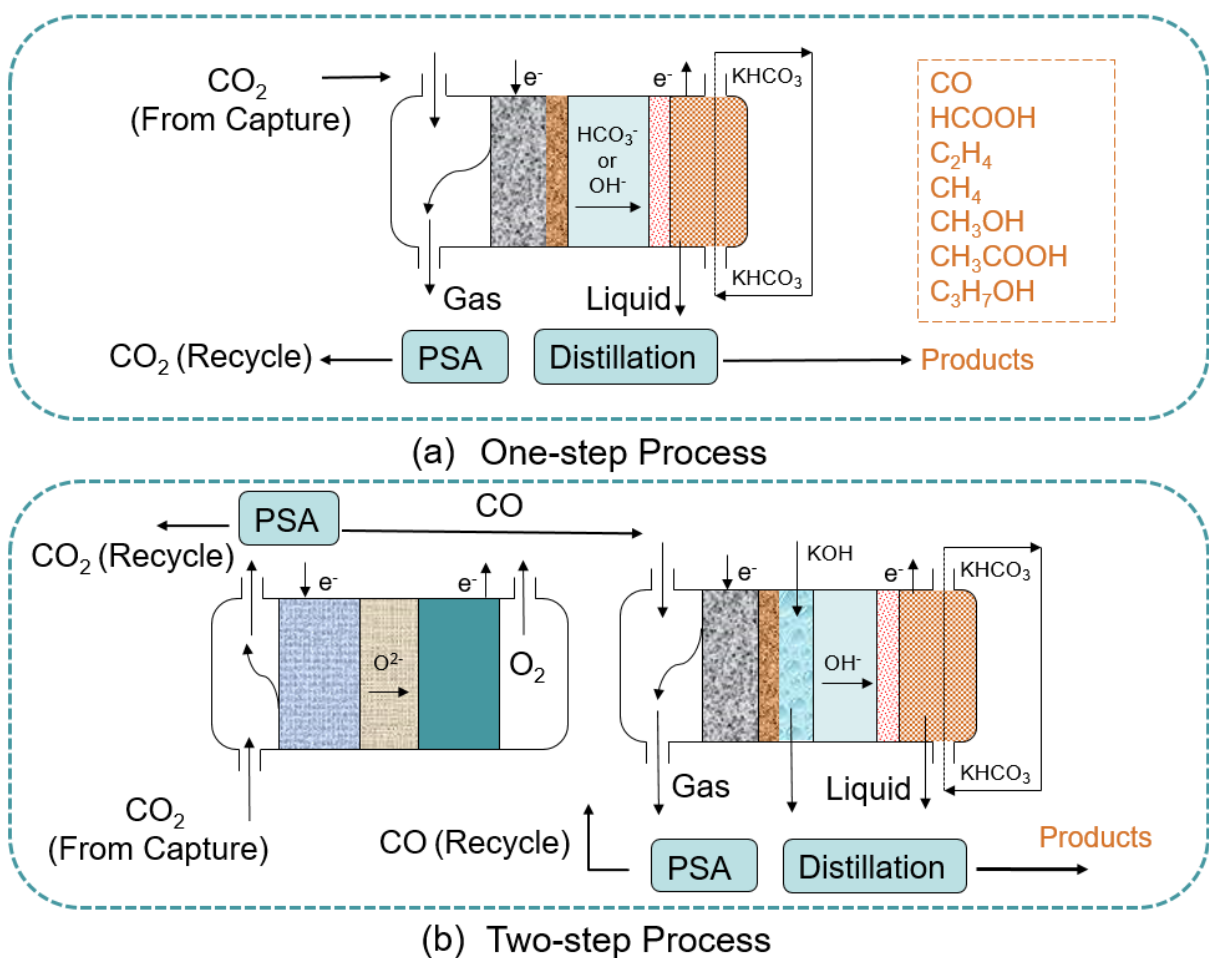
All the processes mentioned herein signify diverse pathways and opportunities for alternative utilisation of  $\text{CO}_2$  to enable negative emission technology.<sup>9,23</sup> While recent studies<sup>10-13</sup> have highlighted some of the potential pathways for near-term deployment due to their technological maturity and economical feasibility over others, concerns remain on the climate benefits of these potential pathways. Life cycle assessment (LCA) is one such standardized tool to assess environmental sustainability of any process/product. LCA is a holistic approach that considers environmental impacts from all materials and energy flows associated throughout the life cycle of a process/product. As a result, LCA tool can guide government, policy makers, other stakeholders

to environmentally assess a range of CCU technologies.<sup>23</sup> However, heavy reliance on data quality as well as complex nature of CCU process resulted in limited studies on thermochemical CO<sub>2</sub> conversion approach for products, including formic acid,<sup>24</sup> methyl formate,<sup>25</sup> methane, methanol and derived polymers<sup>26,27</sup> and C<sub>1</sub>, C<sub>2</sub> chemicals<sup>27,28</sup> production. LCA studies, specifically on electrochemical CO<sub>2</sub> conversion technologies, are often limited to one particular product (i.e., Formate or HCOOH),<sup>29,30</sup> hybrid thermo-electrochemical process (i.e., electrochemical CO<sub>2</sub>-to-CO followed by F-T),<sup>31</sup> or focused heavily on CO<sub>2</sub> capture and conversion process, ignoring the significant contribution of downstream separation process.<sup>32,33</sup> Furthermore, systematic studies on the potential climate benefits of one and two-step electrochemical routes over thermochemical and conventional routes are scarce. To this end, the present study aims to bridge this knowledge gap by performing a comparative environmental assessment of electrochemical CO<sub>2</sub> conversion routes with thermochemical CO<sub>2</sub> conversion and conventional routes (i.e., fossil-fuel based).

In this study, we sought to answer few key questions: looking through the lens of climate benefits, how compelling is the two-step process over one-step electrosynthesis? how does electrochemical CO<sub>2</sub> conversion routes compare with that of thermochemical as well as conventional routes? Which of the CO<sub>2</sub> derived products are environmentally compelling? What are the key technological goals that need to be achieved for electrochemical CO<sub>2</sub> conversion pathways to be environmentally competitive? To answer these questions, we have performed a comprehensive cradle-to-gate LCA for eight commonly reported electrochemical CO<sub>2</sub> conversion products involving all three major phases of life cycle (i.e., CO<sub>2</sub> capture, electrochemical conversion and separation of products). We have used GWI (global warming impact, kg CO<sub>2</sub>e) as midpoint indicator to assess these three selected processes. Finally, we performed sensitivity analysis to reveal the impact of three most sensitive parameters – grid emission factor (GEF), EE and product feed concentration (wt%) and compared in terms of GWI among electrochemical, conventional and thermochemical systems.

## 2. System Description

The scope of this LCA includes environmental assessment of one and two-step electrochemical CO<sub>2</sub> conversion pathway (Figure 1) as compared with that of thermochemical route and conventional fossil-based routes. Main products under study are the eight C<sub>1</sub>-C<sub>3</sub> products for electrochemical CO<sub>2</sub> conversion and conventional (fossil or bio based) routes, while five C<sub>1</sub>-C<sub>2</sub> products (i.e., CO, HCOOH, CH<sub>4</sub>, CH<sub>3</sub>OH and C<sub>2</sub>H<sub>4</sub>) for thermochemical CO<sub>2</sub> conversion, as the later is yet to be developed for C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>COOH and C<sub>3</sub>H<sub>7</sub>OH product.



**Figure 1:** Schematic illustration of the (a) One-step (CO<sub>2</sub>→products) electroconversion using membrane electrode assembly (MEA) and (b) two-step (CO<sub>2</sub>→CO→products) electroconversion, wherein step 1 (solid oxide (SOEC) converts CO<sub>2</sub>→CO and step 2 (flow cell) converts CO→products. Capture phase involves NGCC based power plant (3 vol% CO<sub>2</sub>) with thermal amine scrubbing.

## 2.1 One and Two-step Electrochemical CO<sub>2</sub> Conversion

**Table 1:** One and two-step electrochemical CO<sub>2</sub> reduction products and associated parameters along with their global production

CO <sub>2</sub> derived products		Half-cell electrochemical reaction	Voltage vs NHE (E <sup>0</sup> )	Stoichiometric CO (kg CO/kg product)	Stoichiometric CO <sub>2</sub> (kg CO <sub>2</sub> /kg product)	Molar mass per electron transfer	Global production (Mtonne/year) <sup>34,35</sup>
<b>HCOOH</b>	<b>One-step</b>	CO <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> → HCOOH	-0.19	-	0.956	23.01	0.6
<b>CO</b>	<b>One-step</b>	CO <sub>2</sub> + 2H <sup>+</sup> + 2e <sup>-</sup> → CO + H <sub>2</sub> O	-0.103	-	1.57	14.00	150 <sup>1</sup>
<b>CH<sub>4</sub></b>	<b>One-step</b>	CO <sub>2</sub> + 8H <sup>+</sup> + 8e <sup>-</sup> → CH <sub>4</sub> + 2H <sub>2</sub> O	0.17	-	2.74	2.00	250
	<b>Two-step</b>	CO + 6H <sup>+</sup> + 6e <sup>-</sup> → CH <sub>4</sub> + H <sub>2</sub> O	0.26	1.74		2.67	
<b>CH<sub>3</sub>OH</b>	<b>One-step</b>	CO <sub>2</sub> + 6H <sup>+</sup> + 6e <sup>-</sup> → CH <sub>3</sub> OH + H <sub>2</sub> O	0.017	-	1.37	5.34	110
	<b>Two-step</b>	CO + 4H <sup>+</sup> + 4e <sup>-</sup> → CH <sub>3</sub> OH	0.07	0.87		8.01	
<b>C<sub>2</sub>H<sub>4</sub></b>	<b>One-step</b>	2CO <sub>2</sub> + 12H <sup>+</sup> + 12e <sup>-</sup> → C <sub>2</sub> H <sub>4</sub> + 4H <sub>2</sub> O	0.08	-	3.14	2.34	140
	<b>Two-step</b>	2CO + 8H <sup>+</sup> + 8e <sup>-</sup> → C <sub>2</sub> H <sub>4</sub> + 2H <sub>2</sub> O	0.17	1.99		3.51	
<b>C<sub>2</sub>H<sub>5</sub>OH</b>	<b>One-step</b>	2CO <sub>2</sub> + 12H <sup>+</sup> + 12e <sup>-</sup> → C <sub>2</sub> H <sub>5</sub> OH + 3H <sub>2</sub> O	0.085	-	1.91	3.84	77
	<b>Two-step</b>	2CO + 8H <sup>+</sup> + 8e <sup>-</sup> → C <sub>2</sub> H <sub>5</sub> OH + H <sub>2</sub> O	0.18	1.21		5.75	
<b>CH<sub>3</sub>COOH</b>	<b>One-step</b>	2CO <sub>2</sub> + 8H <sup>+</sup> + 8e <sup>-</sup> → CH <sub>3</sub> COOH + 2H <sub>2</sub> O	0.098	-	1.47	7.51	18
	<b>Two-step</b>	2CO + 4H <sup>+</sup> + 4e <sup>-</sup> → CH <sub>3</sub> COOH	0.30	0.93		15.01	
<b>C<sub>3</sub>H<sub>7</sub>OH</b>	<b>One-step</b>	3CO <sub>2</sub> + 18H <sup>+</sup> + 18e <sup>-</sup> → C <sub>3</sub> H <sub>7</sub> OH + 5H <sub>2</sub> O	0.10	-	2.19	3.34	0.2
	<b>Two-step</b>	3CO + 12H <sup>+</sup> + 12e <sup>-</sup> → C <sub>3</sub> H <sub>7</sub> OH + 2H <sub>2</sub> O	0.20	1.39		5.00	

<sup>1</sup> CO is industrially produced as syngas in captive facilities (i.e., steam-methane-reforming (SMR)) and is not marketed in bulk. This production volume is thus on the basis of global syngas production volume.

The electrolyzer for electrochemical CO<sub>2</sub> conversion can be thought of as a blueprint of commercially available water electrolyzer.<sup>36,37</sup> It involves multiple proton-electron transfer steps, leading to single or multi-carbon CO<sub>2</sub> derived products. Based on the mode of operation and ion transport medium, various configuration for CO<sub>2</sub> electrolyzers are available, including alkaline flow cell and membrane electrode assembly (MEA).<sup>12,38,39</sup> Due to the close proximity of thermodynamic voltages for various CO<sub>2</sub> derived products (see Table 1), high selectivity towards one particular product is challenging; which subsequently influences downstream separation energy and associated carbon footprint.<sup>40</sup> Electrochemical CO<sub>2</sub> reduction reaction involves multiple reaction steps, wherein multiple products (e.g., CO, CH<sub>3</sub>OH and C<sub>2</sub>H<sub>4</sub>) share similar reaction pathway, leading to selectivity challenge for multi-carbon products.<sup>19</sup> While high selectivity, current density and low overpotential have been demonstrated for one-step CO<sub>2</sub> reduction to multi-carbon products in alkaline environment,<sup>19,39-41</sup> the inherent carbonate formation in such electrolyte often leads to significant loss of CO<sub>2</sub> and consequently low CO<sub>2</sub> single-pass conversion efficiency (up to ~43%).<sup>38,42,43</sup> In this context, two-step electrochemical CO<sub>2</sub> conversion approach is appealing; since the first step i.e., the electrolyzer for CO<sub>2</sub>-to-CO conversion is commercially available today at full-scale with high stability and selectivity towards CO (~100%).<sup>16</sup> Recent studies have demonstrated that two-step process (i.e. CO electroreduction) can minimize overpotential and facilitate CO-CO dimerization, leading to increased single-pass conversion,<sup>44</sup> current density and selectivity (including C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>OH and C<sub>3</sub>H<sub>7</sub>OH).<sup>21,22,45</sup> The key performance parameters that govern the energetics of electrochemical conversion process are overpotential, and faradaic efficiency (FE), which defines the EE of the electrolyzer. On the other hand, single-pass CO<sub>2</sub> conversion efficiency determines the energy cost of CO<sub>2</sub> capture, and downstream product separation processes.<sup>33,43,46</sup> Table 1 summarizes the eight electrochemical CO<sub>2</sub> conversion products, their half-cell reactions, thermodynamic voltage, stoichiometric CO and CO<sub>2</sub> per kg product, molar mass per electron transfer, and global production.

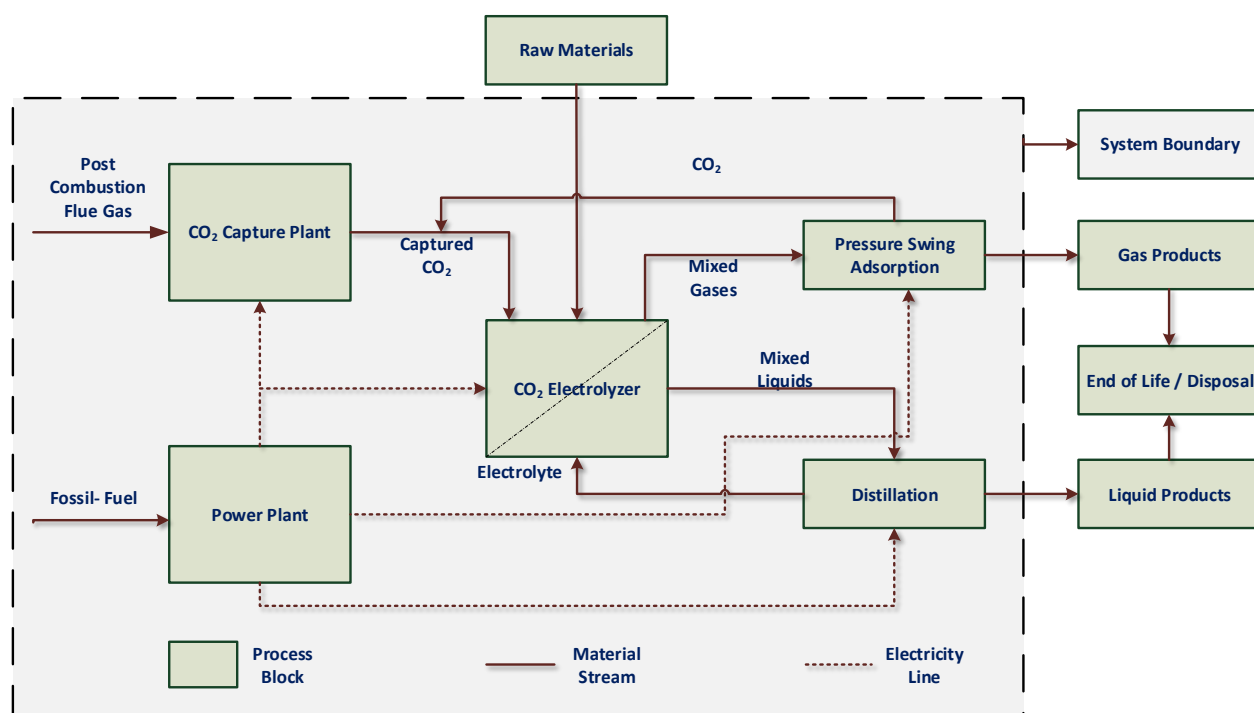
## **2.2 Thermochemical Utilization of CO<sub>2</sub>**

Thermochemical conversion combining heat, pressure and catalysts is an alternative technology for CO<sub>2</sub> conversion into hydrocarbons and oxygenated products.<sup>13</sup> The primary aspect for product formation is hydrogenation of CO<sub>2</sub>, utilising CO<sub>2</sub> from post-combustion capture process and H<sub>2</sub> from fossil-based SMR process (10.6 kg CO<sub>2</sub>e/kg H<sub>2</sub>)<sup>47</sup> associated with water-gas-shift reaction.<sup>48</sup>

We considered five products (i.e., CO, HCOOH, CH<sub>4</sub>, CH<sub>3</sub>OH and C<sub>2</sub>H<sub>4</sub>) that can be produced using this approach and is included in this comparative study. Detail process outlook for each product is included in Supporting Information (Table S1).

### 2.3 Conventional Routes

Industrially mature conventional fossil-based processes for the eight products studied herein were used to benchmark the climate benefits of the electrochemical CO<sub>2</sub> conversion routes. Commonly, these are fossil-fuel derived routes (with an exception for bio-ethanol) and reaction mechanisms are product specific. Natural gas primarily acts as the fossil equivalent for most of the products (due to high availability of methane). Descriptions of these conventional processes are provided in Supporting Information (Table S2).



**Figure 2:** Cradle-to-gate system boundary for the LCA study (represented by dashed line). Overall environmental assessment is based on energy requirement in each phase. Emissions contribution from use phase, construction and decommissioning phases for electrolyzer were excluded. Functional unit is 1 kg of each product of interest. Raw materials include construction materials for electrolyzer, capture unit and separation units.



### 3. LCA Materials, Methods and Assumptions

We followed the ISO 14040/14044 framework to perform this LCA study. We incorporated major elements under goal & scope definition, life cycle inventory, impact assessment and sensitivity analysis as summarized in Table 2.

**Table 2:** Overview of methodology and assumptions

Items	Methods	Assumptions
System boundary and functional unit	<ul style="list-style-type: none"> <li>- cradle-to-gate (utility, capture, conversion, separation)</li> <li>- 1 kg of each product</li> </ul>	<ul style="list-style-type: none"> <li>- no end-of-life or disposal of products</li> <li>- no emissions from use phase</li> <li>- insignificant emissions from construction and decommissioning phases</li> </ul>
CO <sub>2</sub> capture	<ul style="list-style-type: none"> <li>- post combustion CO<sub>2</sub> capture</li> <li>- 0.354 kWh/kg CO<sub>2</sub> as capture energy</li> </ul>	<ul style="list-style-type: none"> <li>- NGCC power plant as flue gas source (3 vol% CO<sub>2</sub>)</li> <li>- thermal amine scrubbing/absorption of CO<sub>2</sub></li> <li>- integrated on-site capture and conversion system</li> </ul>
Electrochemical CO <sub>2</sub> / CO conversion	<ul style="list-style-type: none"> <li>- energy calculated based on cell voltage and required current</li> <li>- multi-product system: H<sub>2</sub> as by-product, O<sub>2</sub> from OER</li> <li>- EE of the CO<sub>2</sub> electrolyzer based on HHV of products</li> <li>- SOEC is considered for CO<sub>2</sub>→CO</li> <li>- For CO, functional unit is 1 kg CO+0.216 kg H<sub>2</sub> for consistent comparison</li> <li>- MEA is used for CO<sub>2</sub>→other products</li> <li>- Flow cell electrolyzer for CO→products</li> </ul>	<ul style="list-style-type: none"> <li>- 90% FE for each product</li> <li>- 0.3 V each for anodic and cathodic overpotential</li> <li>- 10% of conversion energy as BOP</li> <li>- product crossover in MEA is considered</li> <li>- insignificant impact of water extraction, pre-treatment on overall GWI</li> <li>- negligible contribution of O<sub>2</sub>, H<sub>2</sub>O on GWI: no further allocation</li> </ul>
Product separation	<ul style="list-style-type: none"> <li>- PSA (Skarstrom cycle) for gaseous product separation</li> <li>- distillation (RadFrac-Aspen Plus V10) for liquid product separation</li> </ul>	<ul style="list-style-type: none"> <li>- 10 wt% product feed concentration in distillation column</li> <li>- no implication in electrolyzer performance due to 10 wt% product concentration</li> <li>- energy conversion efficiency: distillation (thermal to electrical)-95%</li> </ul>
GWI assessment and sensitivity analysis	<ul style="list-style-type: none"> <li>- based on total required electrical energy (kWh/kg product) and grid intensity (kg CO<sub>2</sub>e/kWh)</li> <li>- sensitivity on EE, GEF and product feed concentration</li> <li>- stoichiometric CO<sub>2</sub> credit</li> <li>- carbon credit from H<sub>2</sub> generation</li> </ul>	<ul style="list-style-type: none"> <li>- GEF for 50% renewables share (in Canada)</li> <li>- methanol as reference for sensitivity analysis</li> </ul>

### 3.1 System Boundary and Functional Unit

We assessed the CO<sub>2</sub> emissions associated with electrochemical CO<sub>2</sub> conversion route using cradle-to-gate LCA, involving CO<sub>2</sub> capture, conversion and product separation (without considering end-of-life/disposal of products), as shown in Figure 2. The boundaries for this assessment thus include utility (i.e., primarily electricity), CO<sub>2</sub> capture, electrochemical CO<sub>2</sub> conversion and separation of products. We excluded any difference in emissions associated with the use phase of the products (i.e., gate-to-grave) from the scope of this assessment by assuming each CO<sub>2</sub> derived product is a perfect substitute for the one currently produced via conventional process. We also excluded emissions associated with construction and decommissioning of the systems (e.g., CO<sub>2</sub> capture, electrolyzer, separation units etc.), as their contribution is insignificant as compared to the operation phase of the process.<sup>32,49,50</sup>

We assumed a functional unit of 1 kg of each CO<sub>2</sub> derived product. We note that recently published LCA guidelines on CCU<sup>51</sup> suggested energy-based and mass-based functional units for fuels and chemicals, respectively. However, such guidelines are critical when assessing the entire (cradle-to-grave) life cycle of the process and is not applicable for cradle-to-gate LCA. The GWI (kg CO<sub>2</sub>e/kg product) is the sole environmental measure considered for assessing the three aforementioned processes. The GWI of the overall process was calculated based on electrical energy required (kWh/kg product) in each phase (i.e., capture, conversion and separation) and grid intensity (kg CO<sub>2</sub>e/kWh).

### 3.2 Post combustion CO<sub>2</sub> Capture

For the capture stage, post combustion CO<sub>2</sub> capture from flue gas was considered. Assumed source for flue gas is a natural gas combined cycle (NGCC) power plant with 3 vol% CO<sub>2</sub>. Here we assumed thermal amine scrubbing/chemical absorption of CO<sub>2</sub> in monoethanolamine with subsequent CO<sub>2</sub> desorption or solvent regeneration.<sup>52,53</sup> For an optimum 90% CO<sub>2</sub> capture efficiency, 0.354 kWh/kg CO<sub>2</sub> captured was considered.<sup>54</sup> We note that this value is approximately one quarter of the energy required for a standalone (without heat integration) monoethanolamine based CO<sub>2</sub> capture process (~1.2 kWh/kg CO<sub>2</sub> captured),<sup>52,61</sup> due to efficient heat integration with steam cycle to regenerate the solvent.<sup>55</sup> Based on electrochemical CO<sub>2</sub> reduction reaction stoichiometry (Table 1), we calculated the required capture energy per mass (kWh/kg product) for

each product. We excluded energy requirement for storage and transportation of captured CO<sub>2</sub> assuming integrated on-site capture and conversion system in this analysis.<sup>56</sup>

### 3.3 Electrochemical CO<sub>2</sub> Conversion

We assumed high-temperature SOEC for one and two-step electrochemical routes involving CO<sub>2</sub>→CO conversion. Based on commercially available Haldor Topsoe's eCOs™ unit, we assumed 6 kWh/Nm<sup>3</sup> CO as the total process energy required, which also includes a gas separation unit to produce high purity CO (99.99%).<sup>16</sup> For consistent comparison with thermochemical and conventional processes (as CO is commercially available as syngas (CO+H<sub>2</sub>)), functional unit has been considered as 1 kg CO+0.216 kg H<sub>2</sub> for electrochemical process. Thus, conversion energy for CO also contains energy required to produce that additional 0.216 kg H<sub>2</sub> via water electrolysis. For the remaining seven products, we assumed a low-temperature (MEA) cell for CO<sub>2</sub> reduction (Figure 1a) and flow cell for CO reduction (Figure 1b), wherein each of the seven products to be generated with 90% selectivity, along with H<sub>2</sub> as a by-product with 10% selectivity at the cathode, and O<sub>2</sub> from anodic oxygen evolution reaction (OER); resulting in a multi-product system.

We calculated thermodynamic potential based on Gibb's free energy of formation (free energy values are provided in Table S3) for both one-step and two-step electrochemical routes. We assumed 0.3 V overpotential both for anodic and cathodic reactions (total 0.6 V) for low-temperature MEA and flow cell at an assumed optimistic current density of 300 mA/cm<sup>2</sup> based on the literature reports.<sup>57,58</sup> While the reported overpotential and selectivity (or FE) varies across various products,<sup>19,38</sup> we assumed constant overpotential for all the eight products for consistent comparison. Based on the recent literature, the single pass conversion of CO<sub>2</sub> is theoretically limited to 50% for CO<sub>2</sub>→CO in a MEA and flow cell, regardless of the testing conditions (i.e., CO<sub>2</sub> feeding rate, operating current density, and reaction temperature<sup>43</sup>). Consequently, a significant amount of CO<sub>2</sub> feed is consumed due to inevitable carbonate formation at the cathode-membrane interface through side-reactions with OH<sup>-</sup> anions that are locally generated during the electrolysis.<sup>43,59</sup> When an anion exchange membrane is used, the consumed CO<sub>2</sub> could transport (alone with the products) across the membrane (i.e., membrane crossover)<sup>59</sup> in the form of CO<sub>3</sub><sup>2-</sup> and subsequently releasing CO<sub>2</sub> along with O<sub>2</sub> in acidic/neutral anolyte.<sup>60</sup> Experimental studies indicate that for every 2 electrons transferred, one CO<sub>3</sub><sup>2-</sup> cross over the membrane and degassed out of anolyte as one CO<sub>2</sub> molecule.<sup>61</sup> Taking into account the number of electrons transferred and

reaction stoichiometry (Table 1), we thus calculated the maximum achievable single-pass CO<sub>2</sub> conversion efficiency of 50%, 20%, 25%, 25%, 25%, 33% and 25% for HCOOH, CH<sub>4</sub>, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>COOH, C<sub>3</sub>H<sub>7</sub>OH, respectively. Assuming neutral anolyte (0.01 M KHCO<sub>3</sub>), we estimated the energy required to separate CO<sub>2</sub> (generated from carbonate and bicarbonate) from O<sub>2</sub> (generated from OER) using a PSA unit. We calculated the EE based on higher heating value (HHV) of the products (see Table S4 for HHV values and Supporting Information for detail calculation). Analogous to commercial proton exchange membrane (PEM) water electrolyzer performance, we also assumed 10% of the energy required for electrochemical conversion of CO<sub>2</sub> as the balance of plant (BoP) energy, which includes energy required to run pumps, coolers etc.<sup>62</sup>

### 3.4 Product Separation

In case of one-step electrosynthesis using MEA cell, the gas products (i.e., C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub>) from the cathode effluent needs to be separated from unreacted CO<sub>2</sub> and by products (i.e., H<sub>2</sub>). Depending on the CO<sub>2</sub> feeding rate, the gaseous product stream from the cathode can have 5-70% unreacted CO<sub>2</sub><sup>38,43,44</sup> that needs to be separated to achieve high product purity. On the other hand, the crossover CO<sub>2</sub> needs to be separated from O<sub>2</sub> from the anode effluent. Based on commercial and operational feasibility to obtain high purity, pressure swing adsorption (PSA) was considered for gas product separation. In previous experimental studies (one-step using MEA cell), due to membrane cross-over, the liquid products (i.e., ethanol, HCOOH) were found in the anolyte as well as at the cathode effluent with concentration as high as 4 wt%.<sup>38,59,63</sup> Industrially mature distillation process was considered to separate liquid (i.e., alcohol) products<sup>17,64,65</sup> Likewise, in two-step electrosynthesis, a PSA unit is first used to separate CO from unreacted CO<sub>2</sub> which is then fed to the 2<sup>nd</sup> stage for CO reduction reaction (CORR) (Figure 1b). The liquid and gas products in the 2<sup>nd</sup> stage were separated using distillation and PSA, respectively.

The required energy for the PSA unit is taken from a biogas upgrading plant (0.25 kWh/m<sup>3</sup>)<sup>66</sup> and assumed to be the same for all gaseous products, as this variation is negligible as compared to the other energy intensive processes.<sup>33,70</sup> We assumed CO<sub>2</sub> separated via PSA will be recycled to offset the CO<sub>2</sub> feed (Figure 2).

To separate liquid products (HCOOH, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, CH<sub>3</sub>COOH, C<sub>3</sub>H<sub>7</sub>OH), conventional distillation column (RadFrac) was modeled using Aspen Plus V10 software. Condenser and reboiler heat duties are the most significant contributors to overall energy required per mass of

product separation. While alcohols are commercially separated using distillation process industrially, separation of HCOOH using distillation is extremely energy intensive due to the close boiling point of HCOOH and H<sub>2</sub>O. Alternatively, liquid-liquid extraction process has been demonstrated to purify formic acid solution up to 95 wt%.<sup>67,68</sup> However, economic feasibility for liquid-liquid extraction at commercial scale is yet to be evaluated.<sup>46,69</sup> Thus, in this analysis, distillation is considered for consistent comparison across different liquid products. We note that the single-pass liquid product accumulation in the electrolyte is very low (~0.03 wt%),<sup>18</sup> leading to highly energy intensive downstream separation process. Consequently, we assumed the electrolyte will be recirculated until the product concentration reaches 10 wt%, which would then be directed to the distillation column to achieve desired distillate concentration to meet the market specifications (~85-99 wt%). We also note that the impact of product accumulation on the electrolyzer performance has not been studied yet, and for simplicity, we assumed the electrolyzer performance remains unchanged even at 10 wt% product concentration. Later, we have discussed the implications of product concentration using sensitivity analysis. Design and operational parameters (i.e., reflux ratio, number of trays, feed pressure and temperature) were optimized to estimate distillation energy requirement. However, more detail design optimization as well as provision of other extensive methods (i.e., extractive etc.) are beyond the scope of this study as Aspen modeling is connected to multiple units for a whole process to be optimized. Finally, based on the efficiencies of reboiler and condenser, 95% energy conversion efficiency (i.e., thermal to electrical) was assumed for distillation.<sup>70</sup>

### **3.5 Cradle-to-Gate GWI Assessment**

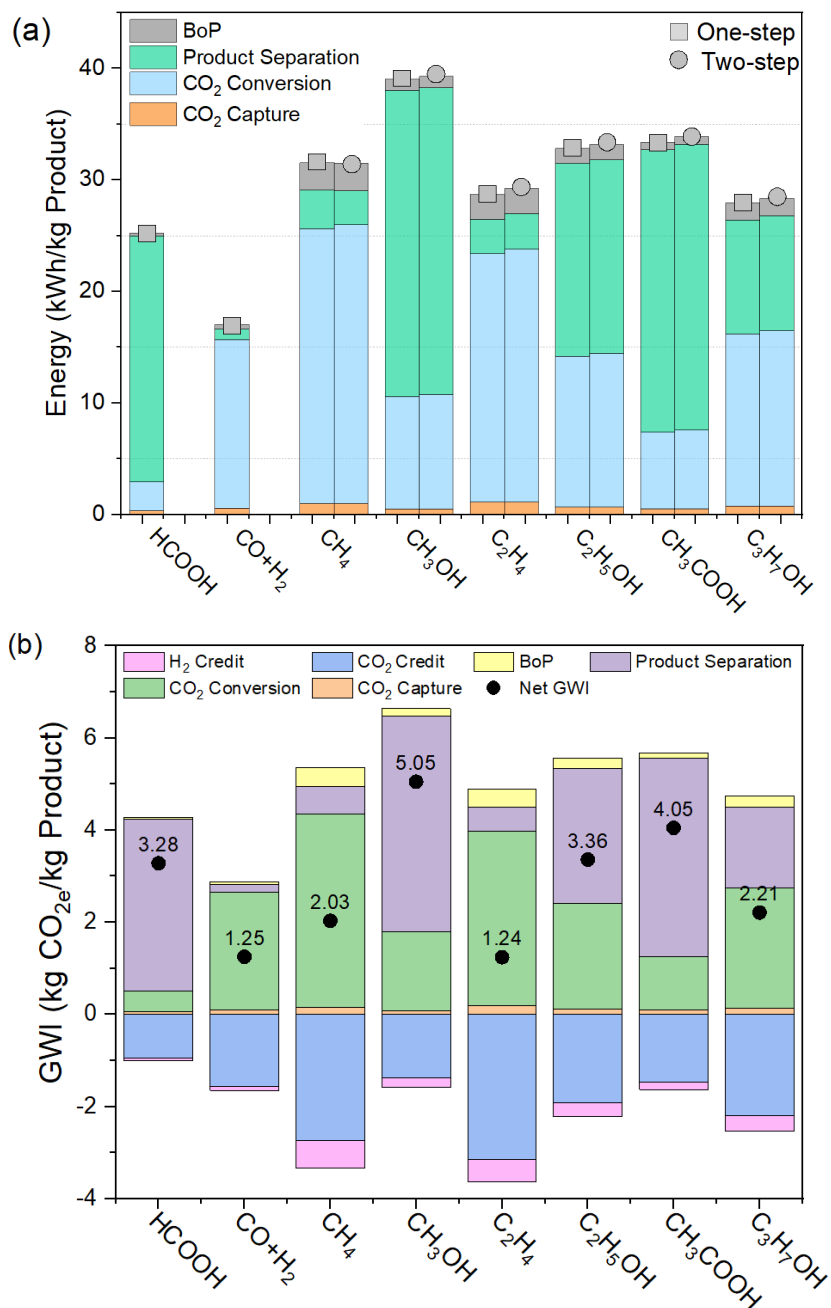
We lumped the energy required in different phases (capture, conversion, and separation) on the basis of per mass of product (i.e., the functional unit). The basis of the energy calculation is 1000 kg product/day. To calculate product specific impact for equivalent systems, we considered product substitution or avoided burden approach.<sup>71</sup> We assumed similar environmental impact of SMR and water electrolysis (50 kWh/kg H<sub>2</sub>) for H<sub>2</sub> supply at 0.17 kg CO<sub>2e</sub>/kWh. In this analysis, the stoichiometric H<sub>2</sub> production is negligible (due to 10% selectivity) as compared to the CO<sub>2</sub> derived products. However, the carbon credit from H<sub>2</sub> is noticeable (0.05 – 0.60 kg CO<sub>2e</sub>/kg product) owing to high GWI from conventional SMR process (10.60 kg CO<sub>2e</sub>/kg H<sub>2</sub>).<sup>47</sup> Thus, this credit from H<sub>2</sub> was used to calculate overall GWI as this much CO<sub>2e</sub> can be avoided by producing

H<sub>2</sub> electrochemically. On the other hand, while stoichiometric O<sub>2</sub> production is relatively high (0.40 – 4.43 kg O<sub>2</sub>/kg product) in CO<sub>2</sub> electrolysis, the GWI associated with cryogenic distillation for commercial O<sub>2</sub> separation is insignificant (0.019 kg CO<sub>2</sub>e/kg O<sub>2</sub> at supercritical condition for 95% purity),<sup>72</sup> resulting in negligible carbon credit (0.01-0.08 kg CO<sub>2</sub>e/kg product) from O<sub>2</sub> by-product (see details in Supporting Information). Given the fact that the anolyte will be recovered after downstream product separation for reuse, the carbon footprint of 0.01 M KHCO<sub>3</sub> production would be insignificant<sup>73</sup> and thus excluded from GWI analysis. We also calculated effect of water extraction and purification on GWI and found to be negligible (0.78 kWh/tonne H<sub>2</sub>O)<sup>74</sup> (see details in Supporting Information).

We calculated the product specific GWI by assuming a grid emission factor (GEF in kg CO<sub>2</sub>e/kWh) and taking CO<sub>2</sub> credit (subtracting kg CO<sub>2</sub> required/kg product based on stoichiometry) and carbon credit from H<sub>2</sub> (kg CO<sub>2</sub>e/kg product based on stoichiometry and GWI of SMR process, see details in Supporting Information) into account. Considering high share of renewables in Canada (mostly due to hydroelectricity), National Energy Board, Canada reported a grid emission factor (GEF) of 0.12 kg CO<sub>2</sub>e/kWh with 66% renewables share in 2016.<sup>75</sup> We assumed a conservative value of 0.17 kg CO<sub>2</sub>e/kWh (50% renewables share) for this analysis. We also performed sensitivity analysis to reveal the impact of GEF on overall GWI.

In order to assess environmental performance of electrochemical with respect to thermochemical CO<sub>2</sub> conversion and conventional routes, respective GWIs for the later two were collected from literature, and LCA databases (GaBi, ecoinvent). For consistent comparison, identical cradle-to-gate approach was considered for all the three processes. GWIs values for both conventional and thermochemical processes have been adopted from previous report.<sup>76</sup> For both conventional and thermochemical process, there are further non-common/precursor products (i.e., H<sub>2</sub>, CO can be co-produced as syngas). However, for simplicity, system boundary of electrochemical route was not adjusted or expanded to include the inference of such co-production.

## 4. Results and Discussion



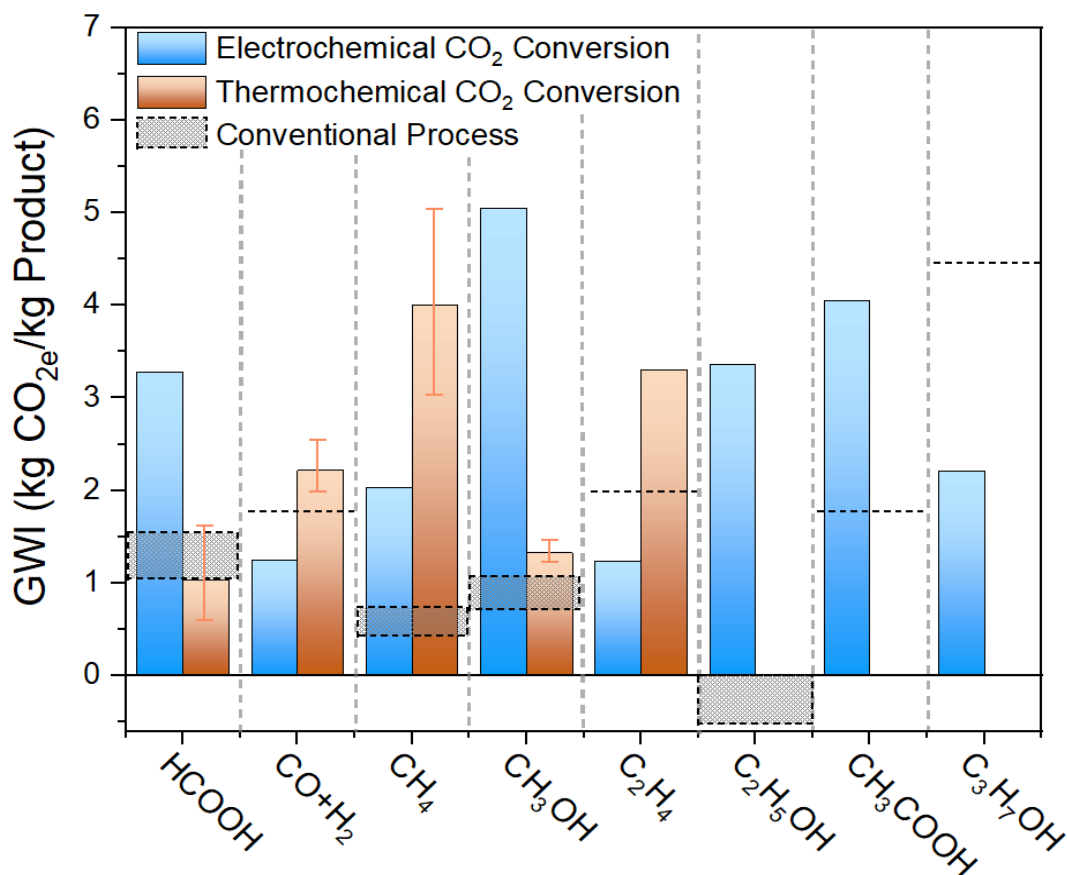
**Figure 3:** a) Energetic assessment of electrochemical CO<sub>2</sub> conversion. Detailed breakdown is shown in Table S5. b) Cradle-to-gate carbon intensity (i.e., GWI) for one-step vs two-step electrochemical CO<sub>2</sub> conversion routes. Detail breakdown is provided in Table S8. GEF is considered as 0.17 kg CO<sub>2e</sub>/kWh (50% renewable share, see details in Table S6).<sup>75</sup> For syngas, we assumed that required hydrogen (0.216 kg/kg CO) will be produced by water electrolysis.

Figure 3(a) shows the required energy breakdown for the eight products (one-step and two-step electrochemical routes) in capture, conversion, and separation phases (see details in Table S5). As indicated in Figure 3(a), the energy requirement for CO<sub>2</sub> capture is insignificant (~1-8% of total energy) as compared to CO<sub>2</sub> conversion and product separation processes. We note that CO<sub>2</sub> required per kg product in one-step route is equal to that in two-step route based on stoichiometry; which leads to same energy requirement for CO<sub>2</sub> capture in both routes. In contrast to capture energy, the energy required for CO<sub>2</sub> conversion varies widely across various products, as shown in Figure 3(a). While thermodynamic voltage and the stoichiometric CO<sub>2</sub> per kg product for the eight products are at close proximity to each other, their molar mass per electron transfer varies widely (i.e., 2-23). Thus, difference in thermodynamic voltage, and stoichiometric CO<sub>2</sub> per kg product, as shown in Table 1, has insignificant effect on the energy required for CO<sub>2</sub> conversion and is primarily governed by the molar mass per electron transfer. For instance, CH<sub>4</sub> and HCOOH require the highest (24.65 kWh/kg) and lowest conversion energy (2.59 kWh/kg) and is attributed to lowest (2.0) and highest (23.01) molar mass per electron transfer, respectively, as indicated in Table 1. It is interesting to note that despite the inevitable carbonate formation in one-step CO<sub>2</sub> electroreduction, the energy required for CO<sub>2</sub> conversion via two-step route is negligibly (~1%) higher than that in one-step process. While in one-step process, an additional PSA unit is required to separate cross-over CO<sub>2</sub> from the anode gas stream, an additional PSA is required to separate CO/CO<sub>2</sub> in two-step process, resulting in an equivalent system requirement.

Apart from conversion energy, we observed that the downstream product separation process plays a significant role, specifically with distillation for liquid product separation. Lower concentration of liquid product (10 wt%) which is inevitable to ensure steady electrolyzer performance, is responsible for far-reaching downstream separation energy. For example, distillation of CH<sub>3</sub>OH needs the highest energy (26.43 kWh/kg, 68% of total energy required, See details in Table S5) due to its physico-chemical properties (e.g., polarity, miscibility, volatility) as well as ability to achieve ~99% purity (in the absence of azeotropic property with water). In contrast, the energy required for gas product separation (i.e., CO, CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub>) is substantially low due to the energy efficient PSA process (0.25 kWh/ Nm<sup>3</sup>).<sup>66</sup> Although CH<sub>4</sub> and C<sub>2</sub>H<sub>4</sub> exceed others in terms of conversion energy, their energy of separation is much lower compared to liquid products, indicating the importance of separation energy optimization for liquid products to reap overall life cycle climate benefits.

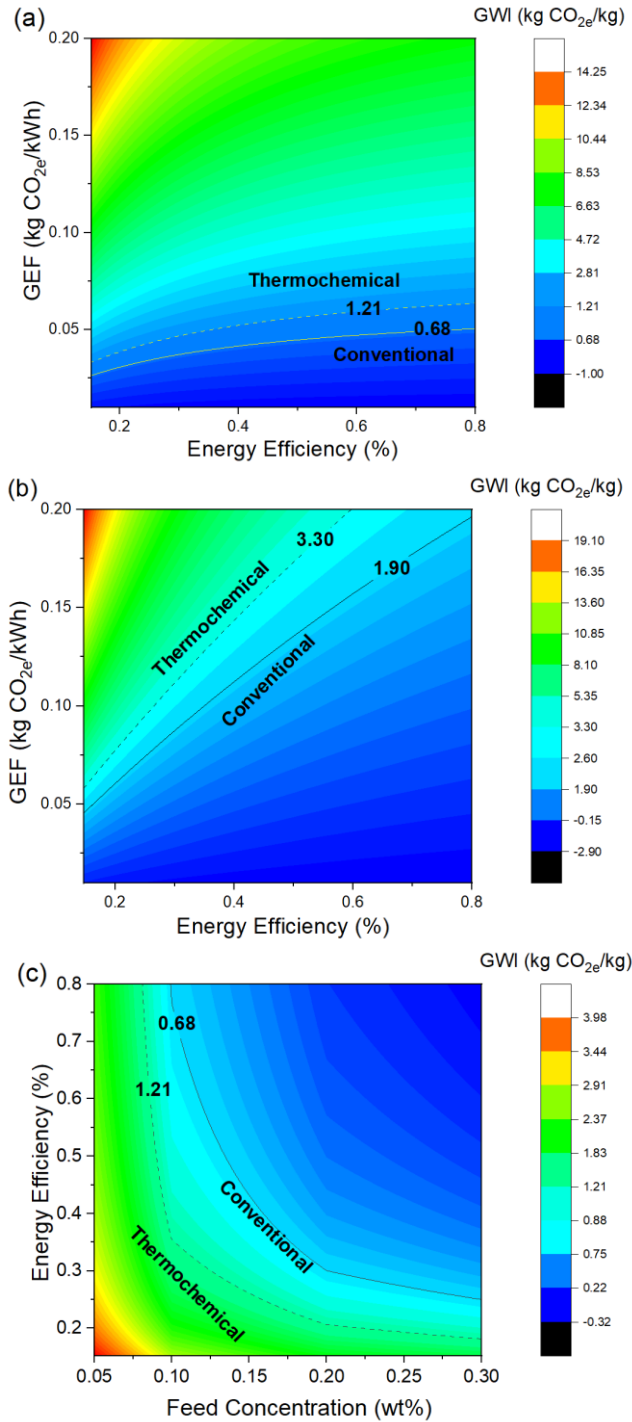


The GWI for the electrochemical CO<sub>2</sub> derived products (one-step and two-step) were calculated (Figure 3b) primarily based on the overall energy requirement (Figure 3a) throughout the life cycle and grid intensity (i.e., GEF) (see details in Table S8). To our knowledge, no LCA study is available in the literature that analyzes solely the production CO. However, several LCA studies analyzed the production of synthesis gas (H<sub>2</sub>/CO=3, molar ratio) as a feedstock to produce methanol, dimethyl ether etc.<sup>77,78</sup> Therefore, to compare the GWI of electrochemical CO<sub>2</sub>→CO production with synthesis gas, hydrogen supply (0.216 kg H<sub>2</sub>/kg of CO) is considered using water electrolysis (50 kWh/kg H<sub>2</sub>) and shown in Figure 3b. Our analysis reveals that the production of methanol has the highest GWI (5.05 and 5.16 kg CO<sub>2e</sub>/kg for one-step and two-step, respectively), and is attributed to the energy intensive separation process involved in electrochemical pathway (Figure 3(a)). In contrast, C<sub>2</sub>H<sub>4</sub> has the lowest GWI (1.24 kg CO<sub>2e</sub>/kg) among all the products of interest, due to the highest carbon credit from CO<sub>2</sub> feedstock and by-product H<sub>2</sub>.



**Figure 4:** GWI comparison among electrochemical and thermochemical CO<sub>2</sub> conversion routes. The GWI of fossil-based conventional routes are also shown. GEF is considered as 0.17 kg CO<sub>2e</sub>/kWh (50% renewable share,<sup>75</sup> see details in Table S6).

We then sought to reveal how these GWI of electrochemical process compares with those of conventional process and thermochemical CO<sub>2</sub> conversion processes. As illustrated in Figure 4 (and Table S9), most electrochemical CO<sub>2</sub> derived products are likely to involve higher carbon footprint due to the energy intensive conversion and separation phases. Assuming a GEF of 0.17 kg CO<sub>2</sub>e/kWh, we identified syngas (CO+H<sub>2</sub>), C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>7</sub>OH as the viable products to provide climate benefits over conventional process for cradle-to-gate phases. This analysis reveals that syngas (CO+H<sub>2</sub>) and C<sub>2</sub>H<sub>4</sub> would be the most compelling products (GWI ~ 1.25 kg CO<sub>2</sub>e/kg CO+0.216 kg H<sub>2</sub> and ~1.24 kg CO<sub>2</sub>e/kg C<sub>2</sub>H<sub>4</sub>), which would provide annual climate benefits of 74 and 92 Mtonne CO<sub>2</sub>e, respectively assuming present day global production volume (~150 and 140 Mtonne, respectively) compared to conventional process. In contrast, conventional process for C<sub>2</sub>H<sub>5</sub>OH production provides climate benefits (GWI ~ - 0.5 to 0 kg CO<sub>2</sub>e/kg C<sub>2</sub>H<sub>5</sub>OH), which is the result of biomass based metabolic corn fermentation with little energy usage making it a green production system. Thus, for electrochemical CO<sub>2</sub> utilization to produce C<sub>2</sub>H<sub>5</sub>OH to provide climate benefits, extensive process optimization would be necessary to match this far-fetched value. Likewise, for electrosynthesis of liquid products, including methanol and formic acid, significant reduction in the required energy (possibly from the separation phase) could bring climate benefits as compare those from fossil-based routes.

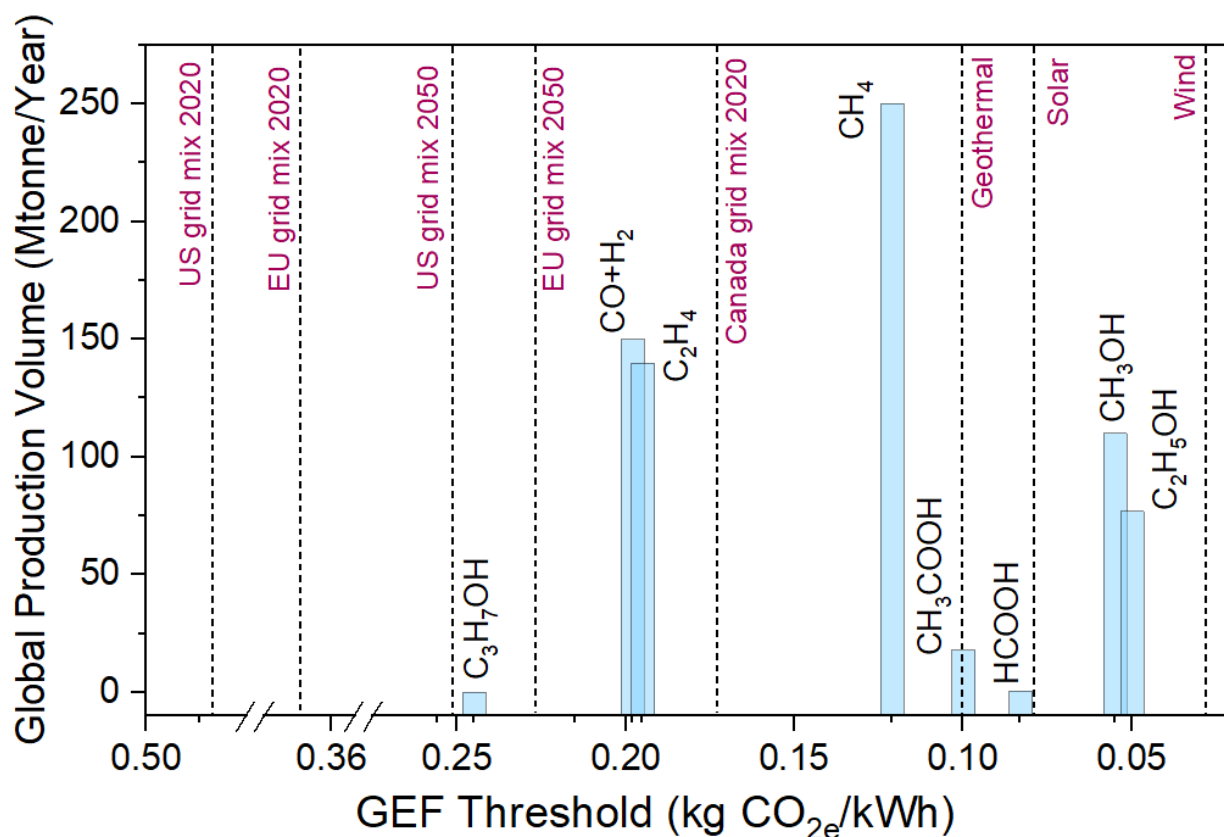


**Figure 5** a) Effect of GEF and energy efficiency of CO electrolyzer on GWI (assuming 10 wt% methanol concentration) for CH<sub>3</sub>OH electro-synthesis, b) Effect of GEF and energy efficiency of CO electrolyzer on GWI for C<sub>2</sub>H<sub>4</sub> electro-synthesis c) Effect of CH<sub>3</sub>OH product feed concentration and EE on GWI; considering GEF = 0.05 kg CO<sub>2e</sub>/kWh. Solid line denotes GWI for conventional

synthesis, while dashed line denotes the same for thermochemical CO<sub>2</sub> conversion process. GWI has been calculated based on total energy required for two-step process.

To this end, we performed sensitivity analysis involving key performance indicators, including GEF, EE, and product feed concentration for CO electrolysis. Figure 5(a), (b) shows the impact of GEF and EE on overall GWI (with CH<sub>3</sub>OH and C<sub>2</sub>H<sub>4</sub> as examples, results for other products are provided in Figure S1). Based on the reported performance (i.e., EE of 20% for the CO<sub>2</sub>→CH<sub>3</sub>OH electrolysis<sup>79</sup>), and 10 wt% feed concentration for distillation, it can be seen that GEF needs to be <0.05 kg CO<sub>2</sub>e/kWh to compete with conventional and thermochemical processes.<sup>80,31</sup> The insignificant impact of EE on the GWI is due to the fact that the required energy for CO conversion is only ~25% of the total energy demand for CH<sub>3</sub>OH electrosynthesis (Figure 3a). In contrast, for gas products (e.g., C<sub>2</sub>H<sub>4</sub>), the EE has significant impact on the GWI, as the conversion energy dominates the overall energy requirement (Figure 3a). For instance, assuming GEF of 0.15 kg CO<sub>2</sub>e/kWh, EE over >42% and >55% for C<sub>2</sub>H<sub>4</sub> would bring environmental benefits as compared to thermochemical CO<sub>2</sub> conversion and conventional process, respectively.

Based on previous discussion in this section (Figure 3), separation energy has appreciable impact on overall GWI. In order to investigate further, Aspen modeling was performed for distillation to generate commercial concentration for CH<sub>3</sub>OH (~99%) with 5 wt%, 10 wt%, 20 wt% and 30 wt% feed concentration. As shown (Figure S2) the required energy for separation increases exponentially when feed concentration drops below 30 wt%. Thus, with GEF of 0.05 kg CO<sub>2</sub>e/kWh and 30% EE, product feed concentration >20 wt% is required to bring environmental benefits (Figure 5(c)). Thus, electrochemical synthesis of liquid products at higher concentration is by far the most challenging and requires more focus to achieve technological maturity to an extent. In this regard, adoption of two-step electrochemical CO<sub>2</sub> conversion (Figure 1) can play a vital role to achieve higher concentration of liquid products. Ripatti et al. reported electrosynthesis of 1 M acetate via CO reduction.<sup>44</sup> By optimizing mass transport inside the cell, 95-98% purity for acetate was obtained with >70% single-pass conversion efficiency when 40 wt% CO with N<sub>2</sub> was utilized as feed.<sup>44</sup> Although generation of higher carbon liquid products like CH<sub>3</sub>COOH, C<sub>3</sub>H<sub>7</sub>OH and C<sub>2</sub>H<sub>5</sub>OH is thermodynamically challenging, recent reports have emerged to produce these liquids in mM concentration range.<sup>81</sup> Moreover, recent breakthroughs to electrochemically



**Figure 6** Identification of environmentally compelling CO<sub>2</sub> electrosynthesis products. Reference values have been taken for US grid mix 2020,<sup>83</sup> EU grid mix 2020 & 2050,<sup>76</sup> Canadian grid mix 2020<sup>75</sup> and geothermal, solar, wind energy<sup>84</sup> cases. Projected GEF (US grid mix 2020, 2050)<sup>84</sup> is provided in Table S7 respectively.

produce highly concentrated HCOOH up to 12 M<sup>81</sup> and 20 wt%<sup>82</sup> assures future research opportunities to explore the same for other multi-carbon fuels and chemicals.

Finally, we sought to identify environmental threshold values for the electricity supply to reveal under which conditions electrochemical CO<sub>2</sub> reduction products would bring climate benefits as compared to their conventional synthesis routes. We also considered present day annual global production volume for these eight products (Figure 6). We further assumed an optimistic scenario, wherein liquid products would be readily separated from the CO<sub>2</sub> electrolyzer (as demonstrated for HCOOH)<sup>81,82</sup> without requiring energy intensive downstream separation process. With these assumptions and assuming 60% EE for CO<sub>2</sub> or CO electrolysis, we calculated the GEF threshold below which each of these products would bring climate benefits as compared to their respective

conventional synthesis routes. As shown in Figure 6, products with high global demands, including  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CO}+\text{H}_2$ , would not be environmentally compelling to produce via one or two-step electrolysis in present day (year 2020) and projected (year 2050) carbon intensity of US and European Union (EU) grid mix. While  $\text{C}_3\text{H}_7\text{OH}$ , seem to be the most compelling product, its present-day annual production volume will provide little incentive to produce this electrochemically. It is important to note that carbon footprint of electrochemical route is strongly dependent on the carbon intensity (i.e., GEF) of the electricity used, unlike thermochemical or conventional processes and the above scenario is highly dependent on the geographical location. Given the continuous adoption of higher renewables share in global energy sector, operation of electrochemical system with 100% renewable energy (i.e., carbon intensity  $<0.1$  kg  $\text{CO}_2\text{e}/\text{kWh}$ ) would extract larger climate benefits than conventional or thermochemical routes. Considering the example of eastern Canada, emissions from reservoir-based hydropower is only 0.017 kg  $\text{CO}_2\text{e}/\text{kWh}$ ,<sup>85</sup> which would bring potential superior climate benefit from electrochemical process for all of the products of interest. For instance, considering 5.7 Mtonne ethylene production in Canada in 2015, the electrochemical route would reduce  $\sim 18$  Mtonne  $\text{CO}_2\text{e}/\text{year}$  from ethylene production as compared to conventional synthesis route.<sup>86</sup>

## 5. Conclusion and Outlook

One of the drivers in performing the above analysis is to provide a broad-brush assessment on how and under what scenario electrochemical  $\text{CO}_2$  reduction products would be environmentally compelling as compared to thermochemical  $\text{CO}_2$  utilization and conventional or fossil-based (except ethanol) pathways. This study reveals that the energy required for  $\text{CO}_2$  capture contributes only 1-8% of the overall energy requirement and associated  $\text{CO}_2$  emissions for electrochemical  $\text{CO}_2$  utilization pathway. However, notable energy requirement for electrochemical conversion (70-80% of total energy) and product separation (40-85% of total energy) were found for gas and liquid products, respectively. Through the lens of climate benefits, this analysis shows two-step electrosynthesis is equally compelling as compared to one-step route. However, the potential benefits of two-step process, including higher conversion efficiency and selectivity towards multi-carbon products may outweigh any additional energy requirements for the separation phases. The electrochemical route is highly sensitive to the electricity emission factor and would be compelling over thermochemical and conventional route only when it is coupled with low-carbon electricity i.e.,  $<0.25$  kg  $\text{CO}_2\text{e}/\text{kWh}$ . To put this into perspective, present day share of renewable in U.S.

electricity generation mix is ~20% resulting in a grid emission factor of ~0.43 kg CO<sub>2</sub>e/kWh.<sup>83,84</sup> Following energy information administration (EIA) projection, it would take over 50% share of renewables to achieve < 0.25 kg CO<sub>2</sub>e/kWh from U.S. electricity generation mix. However, to reap such benefits, it would be equally critical to achieve high energy efficiency (>60%) of CO<sub>2</sub> electrolysis for all the products of interest. While energy efficient (~45%) CO<sub>2</sub> electrolyzer is commercially available today to produce CO, such high performance is yet to be reported for other gas and liquid products. Furthermore, for liquid products, in order to reduce downstream separation energy and associated CO<sub>2</sub> emissions, higher product concentration (>20 wt%) needs to be achieved through performance improvement (via catalyst design, optimization of reaction condition) and system design of CO<sub>2</sub> electrolyzer (e.g., membrane, gas diffusion electrode, and electrolyzer design). Recent reports have demonstrated feasibility of achieving such high concentration for CO<sub>2</sub> electroreduction to HCOOH; however, the same for other liquid products are yet to be reported. As the technology advances, assuming minimum separation energy for all the CO<sub>2</sub> derived products, this analysis further reveals near-term electrochemical CO<sub>2</sub> derived products that would provide climate benefits over fossil-based routes, including CO+H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>7</sub>OH. Given the level of technological maturity (TRL 2-4)<sup>13</sup>, and considering annual production volume, we identify syngas (CO+H<sub>2</sub>) and C<sub>2</sub>H<sub>4</sub> as the most compelling product with annual emissions reduction potential of ~74 and 92 Mtonne CO<sub>2</sub>e, respectively compared to conventional route when coupled with low-carbon electricity (0.17 kg CO<sub>2</sub>e/kWh). Finally, incorporation of ~100% renewable energy sources will clearly specify the potential of electrochemical system to restrain dependency on fossil-fuels and penetrate more into energy, fuel and chemical sectors.

This study sets the stage to develop further comprehensive LCA studies on electrochemical CO<sub>2</sub> conversion and the technologies it could potentially be paired with. For instance, syngas (CO+H<sub>2</sub>) is often used as an industrially important intermediate chemical precursor to produce a number of highly demanded products, for example via Fischer-Tropsch process. Therefore, future LCA studies should consider integrating further downstream processes to make a “final” CO<sub>2</sub> derived product, involving storage, transportation, construction and decommissioning phases. Future studies should also consider other environmental measures (e.g., fossil or resource depletion, land use etc.) to reveal true benefits of electrochemical routes with fossil-based and bio-based ones. Another area where future studies could be focused on is the avoidance of use phase for CO<sub>2</sub>

derived products. Commercially, these products can compete with and displace other market products which will create consequential environmental impact. Also, the time dependence or cumulative nature of environmental impact that can come from CO<sub>2</sub> utilization over larger time period needs to be considered<sup>11</sup>. It thus is obvious that there are opportunities for a more rigorous study focusing on overall process optimization and aforesaid limitations, uncertainties in relation to environmental benefits. Approach for such study could be cradle-to-grave which will produce more extensive results along with parallel environmental comparison with other alternative CO<sub>2</sub> utilization techniques (i.e., bio-electrochemical, plasma) as well as in different geographic regions. It is our hope that the present study will guide the CO<sub>2</sub> electrolysis community to target overcoming the technological goals to make CO<sub>2</sub> derived products environmentally compelling as compared to other routes of CO<sub>2</sub> removal. This study will also aid environmentalists, investors, and policy-makers to make informed decisions on CO<sub>2</sub>-based products and conversion technologies in accordance with Paris agreement, innovation for cool earth forum (ICEF) roadmap<sup>11</sup> and other strategical planning.

### **Author Contributions**

Conceptualization, M.G.K.; Formal Analysis, S.K.N.; Methodology, Investigation, Original Draft Writing, Review & Editing, S.K.N., S.M, and M.G.K.; Funding Acquisition, M.G.K.

### **Conflicts of Interests**

There are no conflicts to declare.

### **Acknowledgements**

The authors would like to acknowledge the financial support provided by Canada First Research Excellence Fund (CFREF) at University of Calgary for this study.



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