Life cycle assessment modifications for understanding the effect of carbon dioxide transformations into high value-added products

Inocencio-García, Pablo-José [1]; Otero Meza, Daniel D. [2]; Salcedo Mendoza, Jairo [2]; Cardona Alzate, Carlos-Ariel [*1]

[1] Institute of Biotechnology and Agribusiness, Chemical Engineering Department, Universidad Nacional de Colombia, Manizales, Caldas, Zip Code: 170003, Colombia.

[2] Universidad de Sucre, Carrera 28 No. 5-267, Sincelejo, Sucre, Zip Code: 700001, Colombia.

[*] **Corresponding Author:** ccardonaal@unal.edu.co

Abstract.

The increase in carbon dioxide (CO_2) emissions from industrial activities is a critical driver of climate change, requiring urgent mitigation strategies [1]. The largest industrial CO_2 emitters globally include power generation (coal and natural gas plants), cement production, steel manufacturing, and the chemical industry, which together account for a significant share of anthropogenic emissions [2]. These sectors rely on carbon-intensive processes, making decarbonization a complex challenge. In response, Carbon Capture and Storage (CCS) technologies have been widely explored as a mitigation strategy by capturing CO_2 and a further storage underground to prevent releasing into the atmosphere [3]. Nevertheless, CCS faces economic, technical, and long-term storage concerns, limiting the large-scale adoption. As an alternative, Carbon Capture and Utilization (CCU) technologies have gained attention by valorizing CO_2 as a raw material for the synthesis of fuels, chemicals, and other value-added products. This approach allows the promotion of a circular carbon economy and a decrease in dependence on fossil-based resources [4]. Nonetheless, as depicted by Müller et al. [5], the environmental feasibility of these CCU pathways must be critically assessed to determine whether they truly lead to net CO_2 reductions or merely result in delayed emissions, depending on process efficiency, energy sources, and system boundaries. Furthermore, CO_2-based products provide temporary carbon storage, delaying emissions and mitigating climate impact temporarily. Nevertheless, this benefit is realized only once; once conventional products are fully replaced, emission time profiles stabilize [6].

This study conducts a Life Cycle Assessment (LCA) of three CCU technologies, focusing on the potential to contribute to sustainable production systems. The first stand-alone case considered the synthesis of dimethyl carbonate (DMC), a versatile chemical used as a green solvent and precursor for polycarbonates, under supercritical CO_2 conditions by evaluating, through experimental test, different molar ratios of methanol, propylene glycol and K_2CO_3 for three temperatures (i.e., 60, 80, and 100 °C) [7]. The second stand-alone case evaluated the electrochemical reduction of CO_2 to formic acid, a key compound in hydrogen storage, fuel cells, and as a feedstock for the chemical industry, through the use of Sn-based electrodes and three different electrolytes (i.e., 0.1 M $KHCO_3$, 0.5M K_2SO_4, and 0.1M Na_2SO_4/Na_2CO_3) [8]. The third stand-alone case explored CO-rich syngas production via biomass gasification using CO_2 as a co-gasifying agent, a process to enable the synthesis of synthetic fuels, methanol, and other carbon-based chemicals. This last CO_2 upgrading alternative was evaluated according to the methodology presented by Shen et al. [9], considering sole-air gasification of corn cob and the influence on CO production when co-gasifying at a 15 vol.% CO_2 / 85 vol.% air ratio. Moreover, to deepen the analysis, this study proposed the integration of these three processing pathways, distributing the CO_2 flow based on market demand analysis to evaluate different production scenarios. Four configurations were assessed: i) production of CO-rich syngas and DMC, ii) formic acid and CO-rich syngas production, iii) production of DMC and formic acid, and iv) the combined production of DMC, formic acid, and CO-rich syngas. This approach aimed at understanding how routes integration affected the impact categories considered in the environmental

analysis, providing insights into the trade-offs and potential synergies between different CCU technologies. To enhance the accuracy of the environmental assessment, a modification of the conventional LCA methodology was implemented in the SimaPro software, integrating tailored process modeling, refined energy and material inventory adjustments, and scenario-based sensitivity analysis [5]. The workflow included defining system boundaries for all the scenarios, adapting impact allocation methods, updating energy source profiles, and applying the ReCiPe Midpoint (H) for reaching a comprehensive impact evaluation. Then, the system boundaries were established by a gate-to-gate analysis, referring to the stage of flue gas feed to the capture unit (through the chemical absorption process using monoethanolamine), up to the valorization of CO_2 in the final products. **Figure 1** presents the system boundaries considered for the environmental assessment of this study. The functional unit was defined as 1.0 kg_{CO2} valorized in each scheme. Moreover, was mass allocation methods was defined for the evaluated valorization routes.

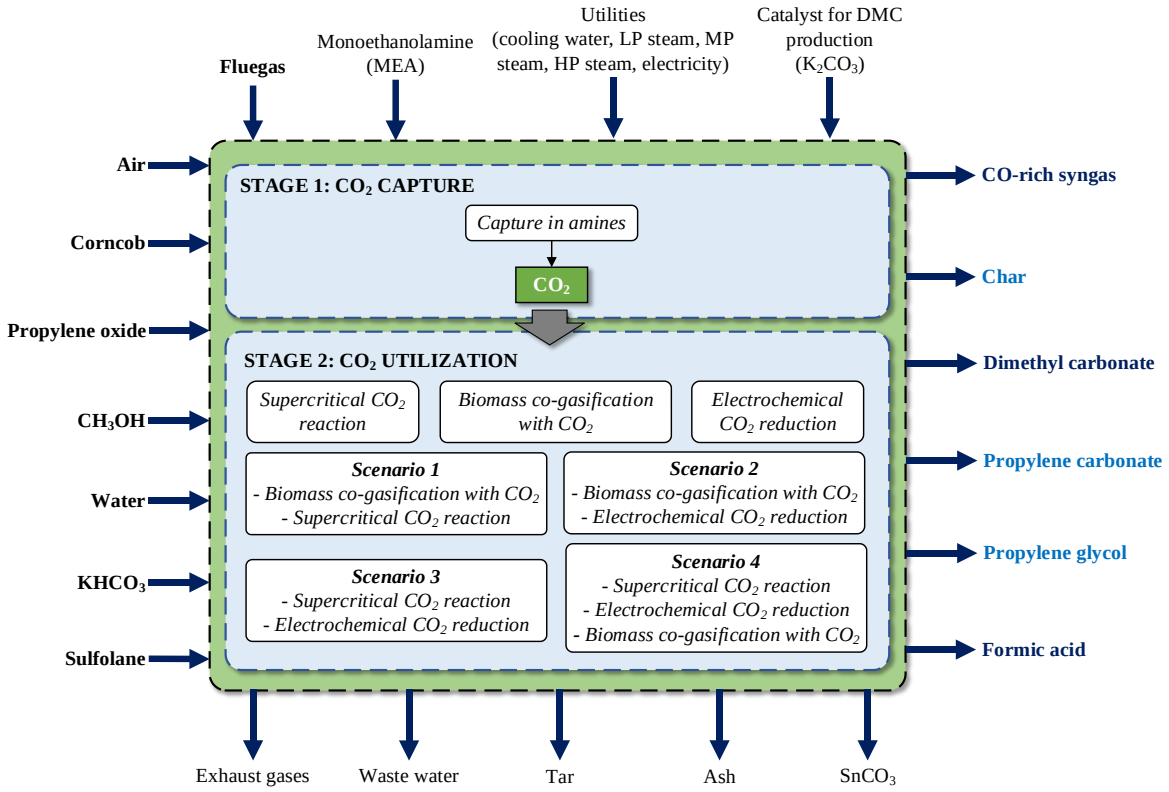

Figure 1. System boundary for environmental assessment of the proposed CCU schemes.

Under the mass allocation approach, CO_2 uptake was treated as negative emissions before eventually release. Moreover, an end-of-life (EoL) model, as positive emissions, was adopted to ensure CO_2 balance. Regarding the assumptions considered, infrastructure for compression, transportation, and distribution was neglected since CO_2 capture and chemical synthesis occurred on-site, with a 5% purge of outlet gases to prevent inert gas accumulation. Given the unique nature of CO_2 utilization in LCA, new indicators were needed beyond traditional carbon footprints and resource use, as CO_2 functions both as a waste product and a raw material. Results interpretation in these schemes is crucial to accurately assess climate benefits, as conventional indicators may not considered temporary storage, delayed emissions, and sequestration potential of CO_2-based products. Then, new tailored indicators were defined to ensure a more comprehensive evaluation of environmental trade-offs and long-term sustainability in CCU systems.

Among the stand-alone technologies analyzed, CO-rich syngas production proved to be the most environmentally promising, primarily due to the high yield (i.e., 44.74 wt. %) and validated CO_2 capture efficiency. Moreover, the biochar generated during the process enhances CO_2 sequestration, leading to a climate change impact value of 0.22 $kg_{CO2\text{-}eq}/kg_{CO2\text{-}valorized}$. Conversely, DMC production contributed significantly to environmental burdens due to the reliance on chemical precursors such as methanol and propylene oxide, resulting in an impact of 1.16 $kg_{1,4\text{-}DB\text{-}eq}/kg_{CO2\text{-}valorized}$. In the case of formic acid production, the low technological maturity and low yield (i.e., 14.57 wt. %) required high voltage inputs and frequent electrode regeneration due to surface precipitation and corrosion, leading to an aggravated impact of 0.59 $kg_{CO2\text{-}eq}/kg_{CO2\text{-}valorized}$. Finally, Scenario 1, where the integration of CO-rich syngas and DMC production was considered, was identified as the most promising among the proposed configurations. The use of more mature technologies in this scenario resulted in lower process mass and energy intensities, leading to more favorable environmental impact category values compared to the other integration scenarios. Thus, new indicators emerge to assess CO_2 utilization in CCU systems: i) CO_2 utilization efficiency, to differentiate between processes merely capturing CO_2 and those converting the gas into valuable products, ii) net carbon sequestration, to evaluate whether CO_2 utilization leads to long-term emission reductions or simply shifts emissions without contributing to overall sequestration, iii) recyclability of CO_2-derived products, to assess the potential of each product for reuse at the end of their life cycle, promoting a circular economy, iv) CO_2 recovery potential, to quantify the amount of CO_2 captured, utilized, or stored relative to total system emissions, reflecting the ability to close the carbon loop, v) CO_2 emissions avoidance, to measure the emissions prevented by using CO_2 as a feedstock instead of fossil-based resources, vi) CO_2 retention time, to determine how long the carbon remains stored before being released, and vii) CO_2 sequestration rate, to quantify the net amount of CO_2 permanently or temporarily sequestered both in geosphere or hydrosphere, as through photosynthesis. Finally, the techno-economic efficiency of CO_2 utilization was also considered as an additional indicator to integrate economic viability with environmental performance, balancing the costs of capture, conversion, and production with the value generated. Finally, through the normalization of results for CO_2 utilization, fair comparisons were ensured by accounting for temporary storage, delayed emissions, and system-specific impacts, enabling more accurate sustainability assessments.

This study highlighted the importance of LCA in evaluating CCU technologies, providing a comprehensive understanding of CO_2 utilization pathways and the potential environmental trade-offs. LCA demonstrated to be a crucial tool for identifying the most sustainable strategies by assessing the material, energy, and environmental implications of different CCU routes. By integrating LCA into the decision-making process, the enhancement of CO_2 valorization efficiency and the development of climate-mitigation technologies contributing to the reduction of greenhouse gas (GHG) emissions can be achieved.

Keywords: *Carbon Capture and Utilization; Life Cycle Assessment; Dimethyl carbonate (DMC) synthesis; Electrochemical CO_2 reduction; Biomass gasification with CO_2; Greenhouse Gas (GHG) mitigation.*

Acknowledgments.
This research work was funded within the framework of the research project "Aprovechamiento y valorización sostenible de residuos sólidos orgánicos y su posible aplicación en biorrefinerías y tecnologías de residuos a energía en el departamento de Sucre" code BPIN 2020000100189.

References.

[1] S. Wang *et al.*, "Distinguishing Anthropogenic CO2 Emissions From Different Energy Intensive Industrial Sources Using OCO-2 Observations: A Case Study in Northern China,"

Journal of Geophysical Research: Atmospheres, vol. 123, no. 17, 2018, doi: 10.1029/2018JD029005.

[2] M. Shabbir Alam *et al.*, "The impacts of globalization, renewable energy, and agriculture on CO2 emissions in India: Contextual evidence using a novel composite carbon emission-related atmospheric quality index," *Gondwana Research*, vol. 119, 2023, doi: 10.1016/j.gr.2023.04.005.

[3] U. Singh, A. Garg, and A. K. Singh, "Sustainable development goals as means to motivate CO2 capture and storage in Indian geologic formations," *Mar Pet Geol*, vol. 160, 2024, doi: 10.1016/j.marpetgeo.2023.106668.

[4] S. Sollai, A. Porcu, V. Tola, F. Ferrara, and A. Pettinau, "Renewable methanol production from green hydrogen and captured CO2: A techno-economic assessment," *Journal of CO2 Utilization*, vol. 68, 2023, doi: 10.1016/j.jcou.2022.102345.

[5] L. J. Müller, A. Kätelhön, M. Bachmann, A. Zimmermann, A. Sternberg, and A. Bardow, "A Guideline for Life Cycle Assessment of Carbon Capture and Utilization," *Front Energy Res*, vol. 8, 2020, doi: 10.3389/fenrg.2020.00015.

[6] T. Koljonen, H. Siikavirta, R. Zevenhoven, and I. Savolainen, "CO2 capture, storage and reuse potential in Finland," *Energy*, vol. 29, no. 9–10, 2004, doi: 10.1016/j.energy.2004.03.056.

[7] Y. Wen *et al.*, "Direct synthesis of dimethyl carbonate and propylene glycol using potassium bicarbonate as catalyst in supercritical CO2," *Polish Journal of Chemical Technology*, vol. 17, no. 1, 2015, doi: 10.1515/pjct-2015-0010.

[8] X. Lu, D. Y. C. Leung, H. Wang, M. K. H. Leung, and J. Xuan, "Electrochemical Reduction of Carbon Dioxide to Formic Acid," *ChemElectroChem*, vol. 1, no. 5, 2014, doi: 10.1002/celc.201300206.

[9] Y. Shen, X. Li, Z. Yao, X. Cui, and C. H. Wang, "CO2 gasification of woody biomass: Experimental study from a lab-scale reactor to a small-scale autothermal gasifier," *Energy*, vol. 170, 2019, doi: 10.1016/j.energy.2018.12.176.