

Life Cycle Assessment Studies of Ethylene Production through the Electroreduction of Captured CO₂ from a Quicklime Plant

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Carbon Capture and Utilisation (CCU) is the technology of capturing CO₂ from point sources or ambient air and converting it into valuable products such as ethylene, methanol, formic acid, or urea. The production processes of ethylene by the electrochemical reduction of captured CO₂ emanating from the quicklime plant have been analysed in this study. The conventional method of ethylene production is the steam cracking of hydrocarbon feedstock, usually natural gas, naphtha or ethane. The environmental footprints of those conventional processes have been reviewed from secondary sources. The main objective of this study is to quantify the carbon and other environmental footprints of the ethylene product derived from a CO₂-rich gas stream. The evaluation of environmental footprints for 1 kg of ethylene production has been performed using SimaPro 9.5.0.0 Life Cycle Assessment (LCA) software tool considering the impact assessment methodology IMPACT World+ Midpoint version 1.03 based on the inventoried data of carbon capture & delivery, integrated electrolyser cell and product gases separation processes. The LCA tool calculated 18 mid-point damage categories, including climate change footprint. It is reported that the overall climate change footprint of the CO₂ captured electroreduction processes is about - 0.834 kg CO₂ eq per kg of ethylene and demonstrated the reduction of that environmental impact by 110 - 120 % compared to the conventional processes.

1. Introduction

The global atmosphere is continuously warming up due to anthropogenic emissions caused by increased human activities with every year passed. The Paris Agreement 2015 has been adopted for global collaboration to limit the global temperature increase to below 2 °C (The Paris Agreement, 2015). European Commission presented the European Green Deal Roadmap in 2019 (Parliament, 2020), which sets the targets for achieving no net emissions of greenhouse gases by 2050. In recent years, carbon dioxide (CO₂) emissions have increased at 2.7 % per year. It is suggested that CO₂ emissions must be lowered by at least half by 2050 to keep the global average temperature at a moderate level (Cuellar-Franca and Azapagic, 2015). Carbon Capture and Utilisation (CCU) is the technology of capturing one of the greenhouse gases CO₂ from an industrial point source or direct air capture or geothermal power production with naturally released CO₂ and its subsequent conversion into valuable products. One of the main CCU technologies is the production of chemicals such as ethylene, methanol and others by the electroreduction of captured CO₂. Ethylene alongside hydrogen production by the electrochemical reduction of captured CO₂ emanating from a quicklime plant has been analysed in this study. Ethylene is conventionally produced through the steam cracking of hydrocarbon feedstock, usually natural gas, naphtha, or ethane. Liptow et al. (2013) studied the environmental footprints of ethylene production from woody biomass via fermentation to ethanol followed by dehydration and from ethane-rich shale gas processing to produce ethane and ethane steam cracking in the context of region as Sweden and obtained the Global Warming Potentials (GWPs) of 5.4 and 1.4 kg CO₂ eq per kg of ethylene production, respectively. The GWPs of conventional ethylene production in China (Zhao et al., 2018) from the processes of Shale Gas Steam Cracking (SSC), Methanol to Olefins (NGMTO), Corn-based and Cassava-based Ethanol to Ethylene (ETE)

were determined in the ranges of 0.75 - 1.05, 2.1, 2.7 - 4.1 and 4.3 - 7.4 kg CO₂ eq / kg of ethylene production, respectively. The GWPs of ethylene production from naphtha, ethane, and ethanol using natural gas as the energy source were determined 4.95, 4.175, and 6.7 kg CO₂ eq/kg of ethylene production, respectively, studied by (Ghanta et al., 2014).

There are still significant challenges that affect the scalability and deployment of full-scale ethylene production from captured CO₂ in the following aspects i) phase change solvents ii) optimum hydrodynamic conditions iii) electrocatalyst and iv) membrane separations. Since the development stages of CCU technologies are in the low Technology Readiness Level (TRL), Life Cycle Assessment (LCA) is the most useful method to identify the hotspots for environmental improvement via contribution followed by a sensitivity analysis. In this study, three system units i) CO₂ capture and delivery system, ii) integrated electrolyser cell system and iii) gas separation system have been considered to produce ethylene using captured CO₂ from waste flue gases emanating from a quicklime plant. The goal of the LCA studies of the production of ethylene from a CO₂-rich gas stream is to evaluate the environmental impacts based on inventory data of raw materials, consumables, and energy consumed for these three system units. A suitable functional unit of 1 kg of the ethylene product derived from CO₂-rich gas stream and a cradle-to-gate system boundary for this LCA analysis have been considered. The following key questions have been addressed:

- i) What are the environmental footprints of the ethylene product derived from CO₂-rich gas stream and where are the hotspots to reduce environmental impacts?
- ii) What is the environmental impact reduction of a CCU-based product or service compared to the same product or service derived from fossil carbon sources?

2. Methods and data inventories

LCA is a methodology to account for the environmental impacts of a product or service throughout its entire life cycle. It provides a holistic approach to evaluate environmental performance by considering the potential impacts from all stages of raw material extraction, manufacture, product use and end-of-life stages. This LCA methodology was standardised in the 1990s by the International Organisation for Standardization (ISO), which is comprised primarily of two standards: ISO 14040 (ISO 14040, 2006a) and 14044 (ISO 14044, 2006b) and is still updated and extended regularly. It involves compilation of relevant input and output data in context of goal and scope of the study, subsequent evaluation of their associated environmental impacts using an appropriate impact assessment methodology and finally interpretation of the results with respect to the aims of the analysis. The framework of LCA methodology comprises four stages:

- i) goal and scope definition,
- ii) inventory analysis,
- iii) impact assessment and
- iv) interpretation

To perform LCA analysis of the production processes of the ethylene by the electrochemical reduction of captured CO₂ emanating from the quicklime plant, SimaPro 9.5.0.0 LCA software tool developed by PRé Sustainability B.V. (PRé Sustainability, 2023), has been used. An appropriate Life Cycle Impact Assessment (LCIA) methodology is required to translate a product's life cycle inventory data to the potential environmental impacts. In this LCA analysis, the IMPACT World+ Midpoint version 1.03 LCIA methodology (Bulle et al., 2019) has been applied for the evaluation of the midpoint impact categories. This LCIA methodology is based on the latest scientific knowledge and incorporates a wide range of environmental impact categories, including mainly climate change, resource depletion, water use, land use, and human toxicity. The ecoinvent v3.9.1 database (ecoinvent, 2023), has been used for all Life Cycle Inventory (LCI) datasets.

The life cycle inventory modelling framework defines how data is gathered and processed during the LCI stage of LCA and how interactions with other product systems are handled. The LCI data of three system units for ethylene production through electroreduction of captured CO₂ from a quicklime plant has been gathered and calculated based on the Process Flow Diagram (PFD), shown in Figure 1 and secondary sources. The flow rates of different components of the flue gas, emanating from the quicklime plant of capacity 504 ton/day and lifetime of 15 years, have been taken as feed to the absorber (Kazepidis et al., 2019). The phase change CO₂ capturing solvent that was selected for the absorber was secondary amine, N-methyl cyclohexylamine (MCA) since it exhibits the best performance based on some criteria such as CO₂ loading, absorption rate, cyclic capacity, etc. (Papadopoulos et al., 2019). The inventory for the construction of the absorber and decanter made of carbon steel along with insulation has been calculated based on literature data (Kazepidis et al., 2021). Asbestos cement has been used for insulation. The absorber captured almost 90 % CO₂ of the flue gas stream and the single pass conversion for CO₂ was about 78 %. The energy efficiency of the electrolyser was about 40 %. The current density at electrolyser was taken as 250 mA/cm². A heater was used to increase the temperature of the captured solution to phase change the temperature to 90 °C. In the electrolyser unit, the captured solution

has been passed through the Cu-sputtered (Maniam et al., 2023) cathode where CO₂ has been reduced to produce different product gases. Faradaic efficiencies of product gases H₂, C₂H₄, C₂H₅OH, CH₄ and HCOOH were 84.7 %, 10.1 %, 4.3 %, 3.3 %, and 2.1 % (Li et al., 2019).

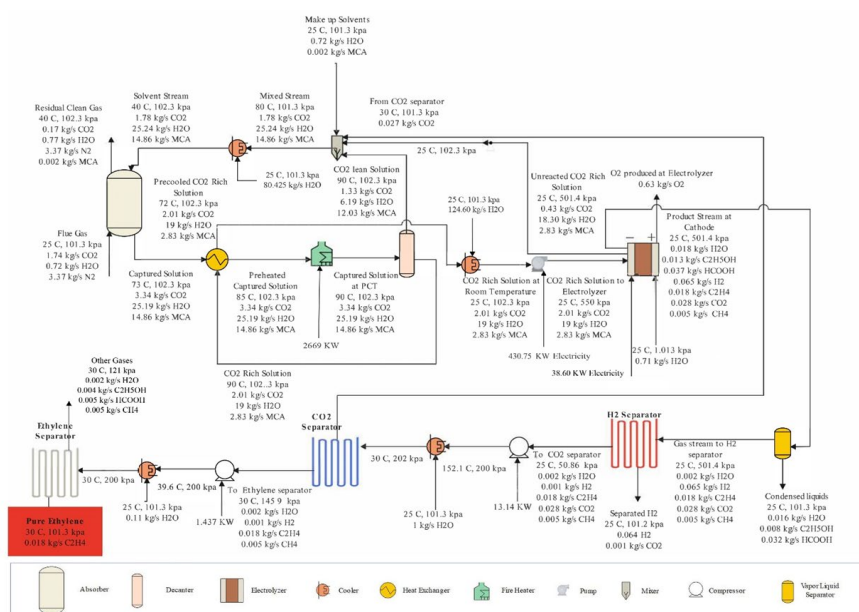


Figure 1: The PFD of ethylene production through electroreduction of captured CO₂ from a quicklime plant

The construction of the electrolyser was considered in the inventory. Coal, iron, natural gas, limestone, and oil were considered as building materials for the electrolyser (Varbanov and Friedler, 2008). The amount of copper catalyst cold sprayed on the cathode was considered as 15 mg/cm². The separation of gases taken place was considered in 4 stages and calculated in Aspen Hysys. Firstly, they are passed through a vapour-liquid separator where the separation of ethanol and water vapour takes place. Additionally, the liquid product from the separator is then passed to the distillation column which was designed in Aspen Hysys to get co-product ethanol. Then the remaining gas stream was passed through a hydrogen polymeric membrane separator where 98 % recovery and 99 % purity in the hydrogen product stream were considered. Similarly, the residual stream passed through the polymeric membrane where CO₂ separated and mixed with the recycled phase change solvent stream. CO₂ recovery was assumed as 98 % and the operating temperature and pressure were considered as 30 °C and 2 bar respectively (Hossain et al., 2020). Then the remaining residual stream mainly containing ethylene passed through the polydimethylsiloxane (PDMS) membrane. In this study, 100 % ethylene recovery and selectivity ratio of ethylene to CO₂ in the PDMS membrane considered as 2. The operating conditions for ethylene separation through the PDMS membrane were considered from the literature (Tan and Rodrigue, 2019).

Most of the CCU systems are multifunctional because they connect two or more product systems. In this study, ethylene is the main product alongside hydrogen produced from captured CO₂ of the flue gas stream of the quicklime plant. Hence, quicklime is co-produced alongside ethylene and hydrogen. There are mainly 2 approaches of solving multifunctionality problems (Müller et al., 2020). One is system expansion where it expands the functional unit to include other functions of the product systems than those which were originally stated in the goal and scope definition. If this expanded function is still meaningful, the multi-functionality problem is resolved. System expansion with substitution is another way of solving the multifunctionality problem in CCU systems. In this second approach one of the co-products substitutes conventional production, and the avoided environmental burdens are credited to the remaining system. For CCU systems, the substituted process is usually the production of the main product without carbon capture. Hence, the CCU system is credited for the otherwise emitted CO₂. The benefit of this solution is that it compares the CO₂-based product and the reference product "directly" as the result expresses the difference in emissions from the main product with and without capture. In this study, the second approach has been used.

3. Results and discussion

Carbon capture and delivery, electrolyser and product gases separation units have been modelled in terms of functional unit of 1 kg ethylene production for evaluating the environmental impacts. The cradle to gate LCA studies of these three units have been performed using the SimaPro 9.5.0.0 LCA tool, considering the LCIA methodology IMPACT World+ Midpoint version 1.03.

The quantification of 18 midpoint impact categories have been evaluated such as climate change (short term), climate change (long term), mineral resource use, human toxicity, ozone layer depletion, freshwater acidification, marine eutrophication and others for these units. The percentages that each unit contributes to a total are depicted as 100 % stacked column for 18 midpoint impact categories and is shown in Figure 2.

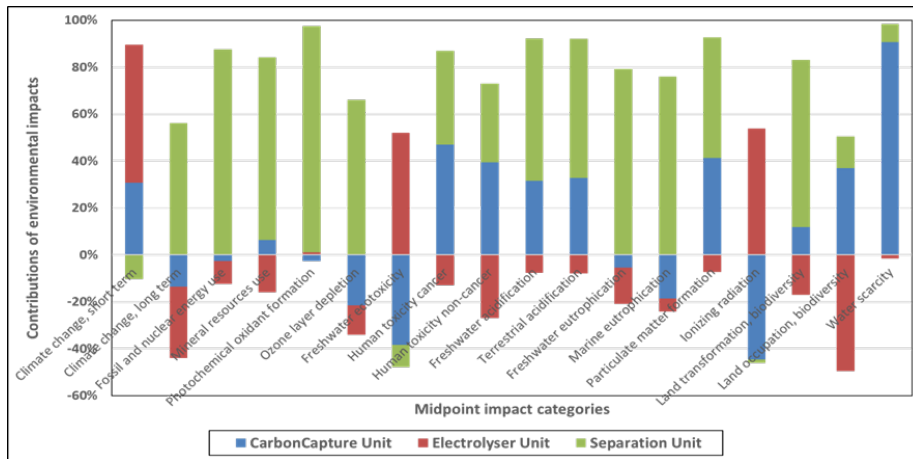


Figure 2: Contributions of 18 midpoint impact categories for three units

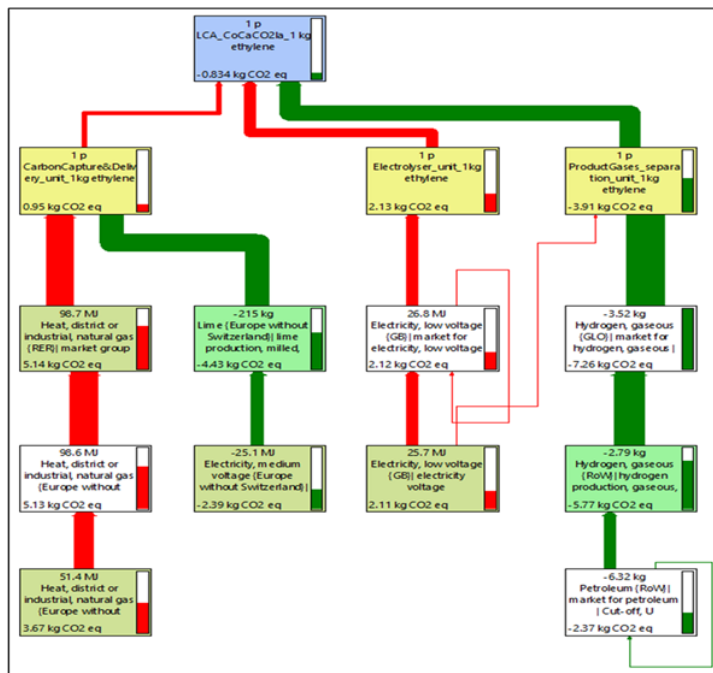


Figure 3: Network model of long-term climate change for the production of 1 kg ethylene

It is evident from Figure 2 that the separation and electrolyser units contribute positive and negative environmental impacts in most of the midpoint impact categories, respectively, whereas the carbon capture unit contributes positive and negative environmental impacts in 10 and 8 impact categories, respectively.

In this study, the results of long-term climate change impact categories for these three units have been analysed only. The network model of long-term climate change (carbon footprint) in units of kg CO₂ eq of three units and the total system for the production of 1 kg ethylene from captured CO₂ from a quicklime plant is presented in Figure 3. It is seen from Figure 3 that the electrolyser, carbon capture and separation units showed the carbon footprints of 2.13, 0.95 and - 3.91 kg CO₂ eq / kg ethylene production, respectively. The positive contribution of environmental impact of separation unit is mainly occurred due to the avoided products of hydrogen gases as a by-product. The environmental impact of carbon capture unit is much lower than that as compared with the electrolyser unit due to by-product quicklime production is given credit using system expansion through the substitution process. The overall climate change footprint of these processes is about - 0.834 kg CO₂ eq for the production of 1 kg of ethylene. Figure 4a presents the comparative studies of climate change footprints of the conventional and CO₂ captured processes for the production of 1 kg ethylene.

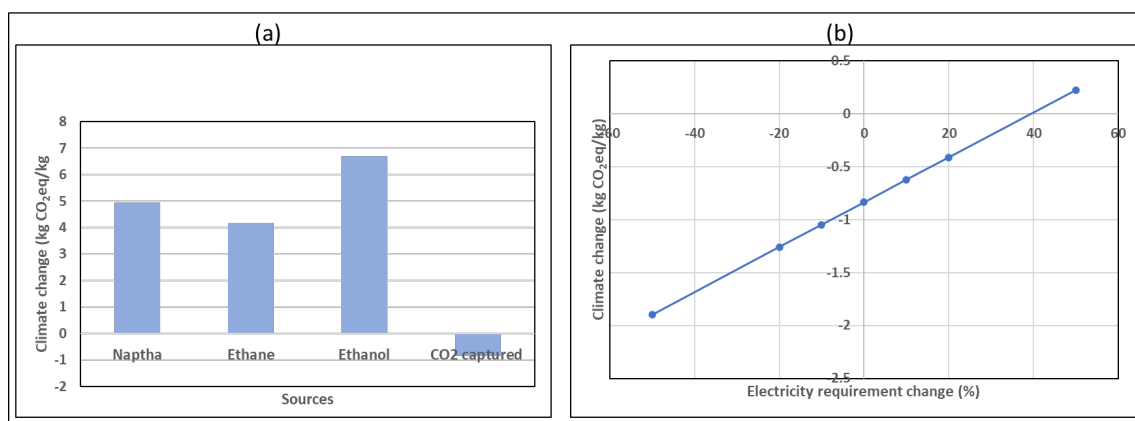


Figure 4: (a) Contributions of climate change footprints of conventional and CO₂ captured processes (b) sensitivity analysis of electricity requirement in the electrolyser unit with overall climate change footprint.

It has been demonstrated that the production of ethylene from captured CO₂ in these processes has shown much better results than those of conventional production processes. For the impact category climate change footprint, CO₂ captured processes reduce the climate change impact by 116.87 %, 120 %, and 112.46 % from conventional ethylene production using Naphtha, Ethane, and Ethanol as resources respectively. Similar results were obtained for other midpoint impact categories.

The amount of electricity needed for pressurising and operating the electrolyser system has been identified as the hot spot for the climate change footprint because it contributed more than 99 % to that footprint. For that reason, a sensitivity analysis was conducted to show the variations of climate change footprints due to the change of electricity requirements. It has been found that the climate change footprint changes by ± 1.068 kg CO₂ eq with the change of electricity requirements by ± 50 % (Figure 4b).

4. Conclusions

The environmental footprints of the three processes (carbon capture, electrolyser and separation systems) for ethylene production using CO₂ as resource from a quicklime plant have been evaluated. The environmental impact results of the conventional methods of ethylene production using naphtha, ethane, and ethanol as resources have been reviewed from the literature. A comparative result of environmental impacts of these processes and conventional methods have been analysed in context of climate change footprint. A sensitivity analysis of the electricity requirements for electrolyser system has been carried out in context of climate change footprint impacts. The key findings of this study as follows:

- The overall climate change footprint of the CO₂ captured processes is about - 0.834 kg CO₂ eq/kg ethylene.
- The climate change footprint savings of 116.87 %, 120 %, and 112.46 % occurred due to the adoption of the CO₂ captured processes as compared with conventional ethylene production processes using naphtha, thane, and Ethanol as resources, respectively.
- The climate change footprint result changes by almost ± 128 % with the change of electricity requirements for the electrolyser system by ± 50 %.

A systematic investigation of technology gaps in CCU technology is needed to develop a low-temperature intensified CCU system to produce ethylene that improves further environmental footprint.

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