



Process Development and Techno-Economic Analysis for Combined and Separated CO₂ Capture-Electrochemical Utilization

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ABSTRACT

Combining CO₂ capture and utilization into a single unit operation offers a feasible solution for converting a sustainable feedstock into marketable commodity chemicals, while reducing energy requirements from separated processes. In this research, we developed a process model and performed a techno-economic analysis (TEA) for point-source CO₂ capture and electrochemical-based utilization in light olefins production under both separated and integrated scenarios. CO₂ containing flue gas from a 500 MW power plant was utilized as a feed while CO₂ utilization involved electrochemical reduction reactions to produce light olefins directly from CO₂. A meticulous analysis was conducted, probing into the multifaceted impacts of various operating parameters, material properties, and downstream treatment units. Factors such as pressure, temperature, H₂O/CO₂ molar ratio, catalyst and adsorbent activities, deactivation rate, and heat integration were optimized to achieve 95 % CO₂ recovery and > 90 % conversion, and > 85 % ethylene yield. Through a comprehensive TEA, our findings unveiled that the combined process utilizing bifunctional adsorbent/catalyst materials (BFMs) incurs costs of approximately \$284/ton CO₂, whereas the separated process reported expenses of ~\$516/ton CO₂. This study, pivotal in its contributions, evaluated economic feasibility of combined capture-conversion method based on BFMs for CO₂ removal and subsequent utilization via a promising advanced process model for sustainable feedstocks conversion to commodity chemicals.

1. Introduction

The drive for sustainability is reshaping the chemical industry landscape, with a significant portion of Europe's largest chemical end users committing to substantial reductions in greenhouse gas emissions by 2030 and aiming for net-zero targets by 2050.[1] The escalating levels of atmospheric CO₂ necessitate innovative solutions for both its capture and sequestration. Despite ambitious goals, achieving these targets presents formidable challenges, particularly for an industry reliant on energy-intensive processes that produce substantial CO₂ emissions. While measures such as energy efficiency improvements, green energy adoption, CO₂ capture and storage, and advanced process technologies offer potential pathways to mitigate emissions while converting sustainable feedstocks with effective utilization to convert them to hydrocarbon chemicals and fuels where we require careful consideration of feedstock availability, technology maturity, and economic viability.[2].

Advanced processes that convert sustainable feedstocks to hydrocarbon chemicals and fuels represent a pivotal shift in various industries, aiming to address the significant environmental challenges posed by traditional production methods. In this regard, we can address, ethylene and propylene, known as light olefins, are key products of petrochemicals, accounting for a substantial carbon footprint exceeding 500 MT of CO₂ equivalent just for producing olefins.[3] Traditionally derived from fossil-based feedstocks such as oil and natural gas through thermal, catalytic, electrochemical processes like steam cracking, these chemical building blocks are indispensable in various industries, including polymer, plastics, and gasoline production.[4–7] However, with escalating demand and diminishing petroleum and gas reservoirs, the exploration of innovative and sustainable production techniques becomes imperative.[8–10] In response, pathways such as Fischer-Tropsch to olefin (FTO) and methanol to olefin (MTO), [11–14] present promising alternatives, directly synthesizing light olefins through catalytic upgrading of syngas.[15–17] This paradigm shift towards advanced process

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technologies not only addresses the pressing need for sustainability but also opens avenues for efficient and eco-friendly production of hydrocarbon chemicals and fuels.

The growing recognition of CO₂ emissions as a significant contributor to global warming has spurred regulatory action aimed at curbing these emissions. As a result, carbon capture and utilization (CCU) have emerged as promising strategies to mitigate the environmental impact of CO₂ emissions and move towards a net-zero economy.[18–20] Different pathways for net-zero emissions suggest permanent disposal of CO₂ via geological storage along with the ongoing progress in CCU technologies in search of an economically feasible route. In this regard, adsorption stands out as a particularly efficient and economically viable method for CO₂ capture, with the potential to convert captured CO₂ directly into valuable products such as light olefins through pathways like MTO or FTO.[21–24] Addressing the high energy intensity of the thermal conversion processes, electrochemical reduction of CO₂ (eCO₂R) appears to be a promising avenue for CO₂ utilization. By following reaction routes involving syngas and methanol (MeOH) intermediates, eCO₂R processes can produce specific light olefins at much lower operating temperatures and hence, energy consumption.[25–29].

Various materials, including zeolites, metal-organic frameworks (MOFs), and metal oxides, have shown promise as adsorbents for capturing CO₂ and catalysts for converting it into light olefins.[30–33] Among these, heterogeneous catalysts based on metal oxides and zeolites have demonstrated significant potential for CO₂ utilization in light olefins production[33–37] while transition metal-promoted calcium/magnesium oxides have exhibited excellent CO₂ adsorption performance at high temperatures.[38,39]

To sustain the robustness of an advanced technological advancement in CO₂ capture and conversion, techno-economic analysis (TEA) plays a crucial role in evaluating the economic feasibility of these processes. By estimating capital and operating costs per ton of olefin production and CCU cost per ton of captured CO₂, as well as revenue generation, TEA provides valuable insights into the economic performance of industrial processes.[41–43] In this study, we aimed at assessing the feasibility of an integrated CCU process to capture CO₂ and convert it in-situ to light olefins. The objective of this paper was twofold: (i) to develop a detailed process model for both separated and integrated CCU systems, and (ii) to conduct a comprehensive TEA to evaluate their feasibility and efficacy. The bifunctional material (BFM) considered in the combined process consisted of Na/CaO (at the weight ratio of 5:95 %), as the adsorbent, and Fe-K/ γ -Al₂O₃ (at the weight ratio of 15:2:83 %), as the catalyst constituents. The volume ratio of adsorbent to catalyst in the BFM was fixed at 60:40 %.The Fe-K/ γ -Al₂O₃ was selected on the basis of its demonstrated catalytic activity in the eCO₂R process.[40] Similarly, the Na/CaO was selected for its great CO₂ adsorption performance at high temperatures, attributed to its high surface area and optimized pore size, which facilitate efficient CO₂ capture even under varying pressure conditions.[54] The integrated CCU process proposed in this study offers a promising alternative to separated capture-conversion processes by potentially reducing energy consumption and overall costs. The analysis focused on optimizing the operating parameters such as pressure, temperature, and molar ratios, alongside catalyst and adsorbent performance, to achieve high CO₂ recovery and olefin conversion rates. Our findings indicated that the combined-intensified process is significantly more cost-effective compared to the separated process.

2. Process modeling

2.1. Simulation for separated and integrated processes

Previous studies have extensively investigated both technical and economic aspects of various CO₂ capture and utilization pathways, highlighting the profound influence of process parameters on both the efficacy and cost-effectiveness of CCU technologies.[25,44,45] Traditionally, CCU processes have been conducted in separate capture and

utilization units, typically employing pressure swing adsorption (PSA) or temperature swing adsorption (TSA) for cyclic adsorption and subsequent desorption of concentrated CO₂ molecules. The desorbed CO₂ is then utilized in a separate catalytic reactor for further reactions.[46,47] However, consolidating these processes into a single integrated system offers distinct advantages, including reduced thermal gradients and lower energy expenditures.[48–50] By intensifying the processes within an integrated system, captured CO₂ can be efficiently distributed over electrocatalytic active sites of electrodes without necessitating pressure or temperature adjustments. The integration of separate carbon capture and upgrading units through electrolytic reduction reactions into a single configuration promises reduced energy consumption, as well as diminished capital and operating costs.[51–53].

Fig. 1a presents the proposed process configuration for a separated CCU system. The process started by introducing flue gas at 1.1 bar, 40 °C, and a flow rate of 2,424 ton/h. The flue gas was compressed to 20 bar using a compressor and cooled down in a heat exchanger with water from the flash drum. The compressed flue gas then entered the PSA columns that adsorbed CO₂ at 20 bar and desorbed it at 1 bar. It was a 2-unit system with volume of 85 m³ (each), CO₂ recovery of 96 %, and adsorbent (Na/CaO) volume fraction of 75 %. Two PSA columns were considered here to ensure a continuous process. The CO₂-free stream left the PSA column during adsorption, while the purified CO₂ stream was released during desorption, then compressed to the reaction pressure of 20 bar, and heated to 400 °C for use in electrolyzer, which worked isothermally at 400 °C and 20 bar with a volume of 170 m³. The water was supplied as a stream with a H₂O/CO₂ molar ratio of 4, which was first compressed to 20 bar and then heated to 400 °C before entering the electrolyzer. The product stream was passed through heat exchangers, compressed to 30 bar, and sent to a flash drum at 30 bar and 30 °C to separate water and electrolyte from effluents and unreacted feed. The catalyst (Fe-K/ γ -Al₂O₃) volume fraction was 75 %. The water stream was recycled to the first heat exchanger, while the olefin-rich stream was further separated by being expanded to 15 bar, heated to 45 °C, and sent to four sets of membrane modules working at 45 °C and between 15 and 1 bar. The retentate stream was the final olefin-rich product, while the permeate stream, a mixture of CO₂, H₂O, and hydrocarbons, was sent to PSA unit, where the stream was compressed to 20 bar.

The choice of compressing the flue gas to 20 bar in the PSA configuration was made based on a balance between separation efficiency and energy consumption. Compressing to 20 bar facilitates a high CO₂ recovery (ca. 96 %), which is essential for effective CO₂ capture and subsequent utilization. Lower pressures may not achieve the same level of separation, potentially impacting the purity of the captured CO₂ for electrochemical conversion. The integration of CO₂ capture and utilization processes into a single system capitalizes on the efficiency of high-pressure operations. The elevated pressure supports optimal conditions for both adsorption and electrochemical reduction, reducing the need for additional processing steps that would otherwise increase overall energy consumption and operational complexity. While higher pressures do entail increased compression energy, the integrated process design—where captured CO₂ is directly utilized in electrochemical reactions—helps mitigate overall energy costs, essentially by reducing thermal gradients and capitalizing on waste heat recovery, thereby offsetting some of the additional energy requirements associated with high-pressure operations.

As stated earlier, the aim of the study was to assess the cost-effectiveness of the CCU process by combining the capture and utilization steps into a single process. Fig. 1b depicts the integrated CO₂ capture and electrocatalytic utilization process into a single unit, which shared similarities with the separated process in terms of downstream operational units. The difference lies in the fact that the adsorptive capture and eCO₂R reaction were carried out in a single unit. To ensure a continuous process, two adsorptive reactors were designed to work simultaneously, with CO₂ flowing into the first one during adsorption while H₂O flows to the other unit in the desorption state. The volume of

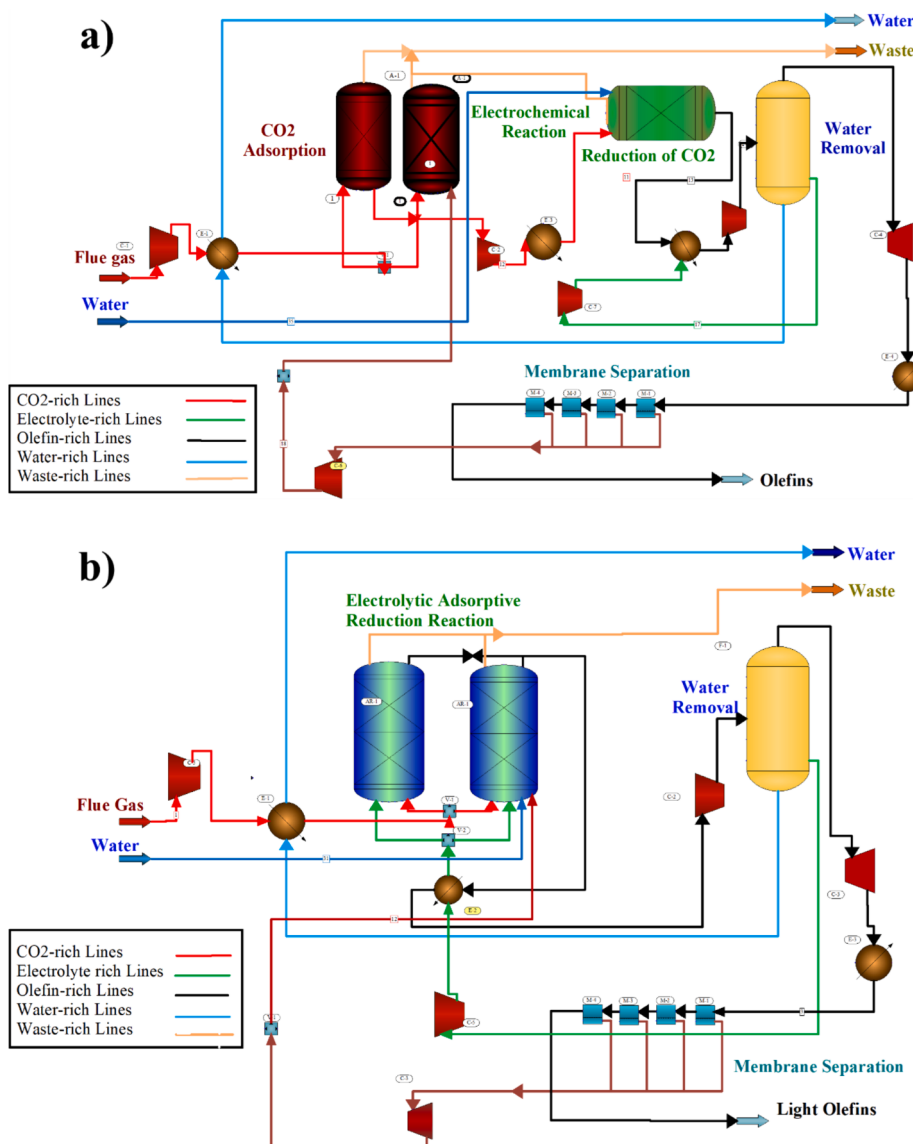


Fig. 1. Process flow diagram (PFD) of (a) separated and (b) integrated electrochemical CCU process.

each reactor was set at 165 m³ and the volume of the bed occupied by the BFM was assumed to be 75 %. In terms of olefin production and carbon efficiency, the increased reactor volumes provide more surface area for the adsorbent and catalyst, resulting in higher CO₂ conversion rates and olefin yields. The integrated design ensures better thermal and mass integration, optimizing reaction conditions and improving overall process stability, thereby maximizing resource utilization, and contributing to long-term sustainability and environmental benefits.

Similar to the separated system, flue gas from a coal-fired power plant was compressed and heated first. During in-situ adsorption-reaction, the waste stream, which contained N₂, O₂, H₂O, H₂S, NO_x, and SO_x, was vented from the top of the reactor, while the olefin product was sent to the downstream units including a flash drum for water and electrolyte separation, and membrane units, which operated under the same conditions as the process in separated system, for further separation. The purified olefin product stream left the process from the retentate side of the membrane units, while the individual CO₂ and H₂O streams were recycled to the adsorptive reactors for capture-eCO₂R, respectively to 20 bar and 400 °C before being sent to the reactor.

The membrane separation units selectively separated desired light olefins from by-products and unreacted gases, operating with lower energy consumption compared to traditional methods. Flash drum units

facilitated phase separation and efficient recovery of the light olefins, optimizing yield and minimizing energy requirements. These units significantly influence the techno-economic feasibility of the CCU processes by reducing operating costs and improving efficiency. Additionally, advancements in downstream technologies, such as enhanced membrane materials with higher selectivity and durability and advanced flash drum designs with better thermal integration, can further optimize CCU processes for commercial-scale deployment. [55–58]

Leveraging simulation and calculation techniques, we modeled the separation based on assumed feedstock compositions, operating conditions, and conversion yields derived from pertinent literature sources. CHEMCAD 8.1.1 software was used to simulate the above separated and integrated CCU processes.

2.2. Process description

This study examined the flue gas stream of a coal-fired power plant with a 500 MW capacity as the input for the CCU plant. [59].

Table 1 presents the composition and conditions of the flue gas used for the plant design and necessary calculations. Based on this information, the software utilized built-in equations and algorithms to execute

mass, energy, and momentum balance equations within the process. The system offered customizable unit operation models, electrolyte-thermodynamic models, and equations of state, allowing to tailor the simulation to our specific needs. The applicable equations for mass, energy, and momentum balances during the simulation are presented in the [supporting information](#).

The simulation employed the Soave-Redlich-Kwong (SRK) thermodynamic model, while the kinetic model for the $e\text{CO}_2\text{R}$ reaction was adopted from the literature.[24,58] Specifically, the electrochemical reaction route considered in the simulation was the MTO process followed by syngas to MtOH (STM) to yield the desired olefins (pathway 3 in Fig. 2).[25,60–63].

The software's membrane module was utilized to model the membrane separation unit, which consisted of four cellulose acetate (CA) hollow fiber membranes for CO and CO_2 separation from product olefins.[64,65] The permeability values for all gases, obtained from the literature, are listed in Table 2. The operating temperature was set to 45 °C where the retentate and permeate sides' pressure were fixed at 15 and 1 bar, respectively. The total area for the membrane was set 160000 m^2 for both processes.

3. Methodologies for process analyses

3.1. Analysis of technical aspects for CCU process

To assess the process efficiency in terms of captured and utilized CO_2 , as well as the energy requirements, we defined two metrics: energy efficiency (η_E) and carbon efficiency (η_C). These metrics were calculated using equations (1) and (2), respectively, which were derived from previous studies.[66,67]

$$\eta_E = \frac{H_{HC}}{H_{H_2O} + U_0} (\%) \quad (1)$$

$$\eta_C = \frac{C_{HC}}{C_{CO_2}} \times 100(\%) \quad (2)$$

Specific heat values (MJ/kg) of the input water and product hydrocarbons/olefins were denoted by H_{H_2O} and H_{HC} , respectively, and U_0 represented the consumed utilities in kWh. Additionally, the total carbon molar flow rate of the final hydrocarbons stream in the outlet of the membrane unit and inlet CO_2 of the process were represented by C_{HC} and C_{CO_2} , respectively.

The CO_2 conversion and product selectivities were estimated from equations 3–4:[65]

$$\text{CO}_2 \text{ conversion} = \frac{\text{CO}_{2\text{in}} - \text{CO}_{2\text{out}}}{\text{CO}_{2\text{in}}} \times 100 \quad (3)$$

$$\text{HC selectivity} (\%) = \frac{HC_{\text{out}}}{\sum HC_{\text{out}}} \quad (4)$$

Table 1
Model flue gas stream composition and conditions.[59].

Parameter	Value
Power plant size (MW)	500
Flue gas flow rate (ton/h)	2424
Temperature (°C)	40
Pressure (bar)	1.1
Composition	
H_2O (mol %)	8.18
N_2 (mol %)	72.86
CO_2 (mol %)	13.58
O_2 (mol %)	3.54
H_2S (mol %)	0.05
SO_x (mol %)	0.00015
NO_x (mol %)	0.0001

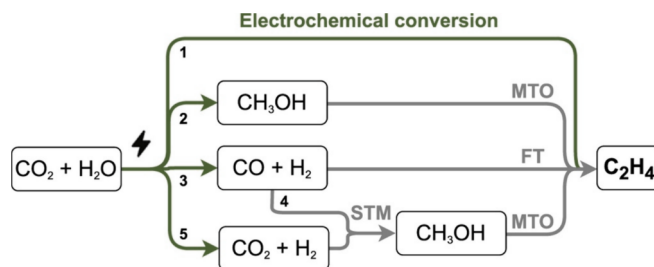


Fig. 2. Overview of reaction pathways. (Abbreviations: Methanol-to-Olefins [MTO], Fischer-Tropsch [FT], Syngas-to-Methanol [STM]).[25] Published 2022 by Elsevier under a Creative Commons CC BY 4.0 license (<http://creativecommons.org/licenses/by/4.0>).

Table 2
Permeability of the compounds in the membrane unit.[8].

	Membrane permeability (Barrer)
Carbon dioxide (CO_2)	6.3
Carbon monoxide (CO)	0.26
Methane (CH_4)	0.21
Ethane (C_2H_6)	0.21
Ethylene (C_2H_4)	0.45
Propane (C_3H_8)	0.18
Propylene (C_3H_6)	0.46

where HC_{out} is the target hydrocarbon molar flow in the outlet stream and $\sum HC_{\text{out}}$ refers to the sum of all hydrocarbons' molar flows in the outlet stream.

3.2. Analysis of economic aspects for CCU process

Table 3 presents all the assumptions made for the economic analysis of the designed plants. To calculate and estimate the costs, CAPCOST version 2017 software was utilized, which can calculate all the capital and operating costs in a plant. The capital cost of the CCU process was analyzed by considering the operational units' purchased cost and relating them to the global cost, and all other direct and indirect costs were included in the total module cost of the equipment.[68] To adjust the reference equipment costs to the 2019 price level, the chemical engineering plant cost index (CEPCI) of 607.5 was used, as the economic analysis was based on 2019 costs. Moreover, the capital costs were

Table 3
Assumptions for economic analysis of the designed plant.

Parameter	Value
Year of analysis	2019
CEPCI	607.5
Construction period	2 years
Finance distribution	60 % in first year and 40 % in second year
Annual operating hours	8760 h
Number of operating labor	10
Number of shifts per day	3
Operating labor salary	\$65,000/y
Land cost	\$10,000,000
Maintenance and repair	0.06 C_{GR}
Insurances and taxes	0.032 C_{GR}
Contingency	0.15 C_{BM}
Auxiliary facility	0.35 C_{BM}
Catalyst price	\$2,092/ton
Adsorbent price	\$5,726/ton
Membrane price	\$100/ m^2
Catalyst replacement rate	20 % /y
Adsorbent replacement rate	15 % /y
Membrane replacement rate	25 % /y
Electricity price	\$0.06 /kW
Cooling water price	\$0.03 / m^3
Medium-pressure steam price	\$3.19 /GJ

estimated for constructing a new plant, and grassroots design was considered.

It was also assumed that the plant's construction period would be two years, with 60 % of the finance allocated during the first year and the remaining 40 % distributed during the second year. The modules' bare cost (C_{BM}), which is the sum of the equipment's capital and installation costs, was calculated using equation (5):

$$C_{BM} = C_p^0 F_{BM} \quad (5)$$

where the equipment bare module cost factor, F_{BM} , and the reference equipment cost, C_p^0 , were used to calculate the total bare module cost of all the equipment, $\sum_i C_{BM,i}$. Here, the installed costs of the electrochemical adsorptive reactor were assumed to be \$848 million, based on the electrode area required for the process, with adjustments made to reflect 2019 costs using a CEPCI of 607.5. [25] The capital cost for the compressor was also adjusted for 2019 prices, resulting in a final cost of approximately \$200 million. The operating costs for the electrolyzer included a catalyst replacement rate of 20 % per year, which accounted for the typical degradation of the catalyst over time. This resulted in an annual catalyst cost of approximately \$50 million, based on the catalyst price of \$2,092 per ton. The expected lifetime of the electrolyzer was assumed to be around 10 years, which influences both the maintenance costs and the overall economic analysis. The operating costs for the compressor included regular maintenance and energy consumption. With an expected lifetime of 15 years, the annual maintenance costs were estimated to be 6 % of the compressor's capital cost, which translates to \$12 million per year. The energy cost for operating the compressor was calculated using an electricity price of \$0.06 per kWh, leading to an additional annual operating cost of \$5 million. The expected lifetimes of the electrolyzer (10 years) and compressor (15 years) significantly impacted the total operating costs over the plant's lifespan. The need for periodic replacement of the electrolyzer's catalyst and regular compressor maintenance are key contributors to the operating expenses, directly affecting the cost per ton of CO₂ captured and the overall feasibility of the process. The compressors are designed to handle significant pressure increases for compressing the entire flue gas, which requires advanced materials and robust engineering to ensure reliable operation under high pressures. This contributed to their high cost. Besides, compressors for high-pressure applications are complex and often need to be scaled to handle large volumes, adding to their capital cost. In contrast, the reactor, while critical, has a more standardized design and is less expensive per unit compared to high-pressure compressors. Conducting the separation process at ambient pressures could potentially reduce the cost of compressors as operating at ambient pressures decreases the energy required for compression, which could also lead to operating cost savings over time but it could impact the overall efficiency and effectiveness of the process optimization addressing the values of key performance indicators.

Contingency costs, C_C , were also considered to cover any uncertainties, unexpected expenses, and potential gaps in the flowsheet design. The contingency costs were estimated to be 15 % of the total bare module cost or $0.15 \sum_i C_{BM,i}$. [69] The total module cost, C_{TM} , was then calculated as the sum of the bare module cost and the contingency costs, $C_{TM} = \sum_i C_{BM,i} + C_C$. Additionally, the auxiliary facility costs (C_{AF}), which include site developments, utility systems, construction overheads, and off-sites, were estimated to be 35 % of the total bare module cost and calculated using [70]

$$C_{AF} = 0.35 \sum_i C_{BM,i} \quad (6)$$

Finally, the overall grassroots cost, C_{GR} , was calculated by adding the total direct and indirect costs,

$$C_{GR} = C_{TM} + C_{AF} \quad (7)$$

The operating costs of the process included several factors such as

raw materials, operating labor, maintenance, utilities, insurance, taxes, and manufacturing. These costs were classified into two categories: direct or variable costs and indirect or fixed costs. Variable costs consisted of raw materials, utilities, maintenance, and labor fees, while indirect costs included insurance, tax, storage, and other plant overheads. The cost of raw materials (C_{RM}) was estimated based on market prices of chemicals. The amount of catalyst, adsorbent, and membrane required for the process was determined based on balance equations and simulation results, assuming replacement rates of 15, 20, and 25 % per year, respectively.

The utility costs (C_U) were determined based on literature-reported prices of grid electricity and cooling water. Operating labor costs (C_{OL}) were estimated using a method that correlates labor costs to the number of processing units and operators per shift, assuming a salary rate of \$65,000 per year and 24/7 operation. The plant overhead costs were estimated as the sum of 70.8 % of C_{OL} and 3.6 % of the fixed capital cost (C_{GR}). Insurance and taxes were estimated to be 3.2 % of C_{GR} , while maintenance and repair costs were estimated to be 6 % of C_{GR} . Finally, the total operating cost (C_{TO}) was calculated by

$$C_{TO} = C_{RM} + C_U + C_{OL} + 0.13 C_{GR} \quad (8)$$

where 0.13 represents the contingency cost factor for unexpected costs and probable completeness of the flowsheet design. Based on the used method and assumed salary rate, operating labor cost was calculated by [70]

$$C_{OL} = 65000 \times (6.29 + 0.23 N_{NP}) N_{OP} \quad (9)$$

where N_{NP} is the number of operational processing units and N_{OP} is the number of operators in a shift. To estimate the working capital cost, 0.1 times the sum of fixed capital cost, raw material cost, and operating labor cost was used, i.e.,

$$C_{work} = 0.1 (C_{RG} + C_{RM} + C_{OL}) \quad (10)$$

The land cost was assumed to be \$10,000,000. The total capital cost was calculated by adding up the grassroots cost, land cost, and working capital cost.

$$C_{TC} = C_{GR} + C_{land} + C_{work} \quad (11)$$

Finally, the overall plant cost, including operating costs was estimated by [68]

$$C_{overall} = C_{TC} + C_{TO} \quad (12)$$

To determine the cost of CCU and light olefin productions, the overall plant cost was divided by the total mass of CO₂ captured and utilized, and the total mass of light olefins produced, respectively. For the carbon capture alone process, the overall plant cost was calculated by considering only the units and equipment required for CO₂ capture and then divided by the mass of CO₂ captured and recovered.

4. Results and discussions

4.1. Techno-Economic analysis

In this study, the technical efficiency of CO₂ capture and utilization plants were analyzed both for separated and integrated processes of simultaneous adsorption and electrochemical reaction. Both configurations achieved a CO₂ conversion of ~90–95 % under optimal conditions, which included a pressure of 20 bar, a temperature of 400 °C, and a H₂O/CO₂ ratio of 4. Additionally, both processes showed a light olefin selectivity when the integrated process emerged as economically more feasible pathway. The downstream treatment units were also evaluated, and the flash drum removed 95 % of the water from the hydrocarbon stream used for cooling purposes. Moreover, the membrane separation unit separated 90–95 % of the unreacted CO₂ from the hydrocarbons.

The separated system had a carbon efficiency of 92 %, while the integrated process showed a value of approximately 98 %, demonstrating the advantage of integrating both capture and utilization steps into one unit. Similarly, the energy efficiency of the integrated process was estimated to be approximately 50 %, compared to the energy efficiency of the separated CCU system, which was only about 40.5 %. This difference was primarily due to the integration strategy, which reduced the number of compressors, heat exchangers, and reactor required. Additionally, the heat integration strategy to use the energy of streams inside the plant to heat or cool down other streams contributed the energy efficiency for both processes. Fig. 3 displays the distribution and relative contributions of various costs to the overall cost of the two different CCU processes. It provides insight into how different cost components, such as equipment, labor, materials, and other expenses, impact the overall cost structure of these two process configurations.

It is clear from this figure that the integrated configuration exhibited a higher contribution (13.89 %) from the total annual raw materials cost than the separated process (8.45 %). This increase could be attributed to the synergistic effects of co-locating gas streams and water in a single unit. Integrating processes often allows for larger-scale operations, which can sometimes lead to lower costs per unit of production with efficiency gains, reduced transportation costs, or optimized resource utilization. However, in this case, the increased efficiency or productivity gains from integration may not fully offset the higher raw materials costs associated with supplying multiple streams to a single unit.

By combining CO₂ capture and utilization into a single unit operation, the integrated process reduces the overall energy demand, leading to lower greenhouse gas emissions associated with energy production. This reduction in energy consumption directly translates to a smaller carbon footprint for the entire operation. Moreover, the integrated process promotes the efficient use of CO₂ as a feedstock, turning a waste product into valuable light olefins, which can reduce reliance on fossil-based raw materials. In the long term, this approach supports the circular carbon economy, enhances resource efficiency, and contributes to the mitigation of climate change. Furthermore, the cost savings associated with the integrated process can incentivize broader adoption of CCU technologies in various industries, fostering widespread environmental benefits and advancing sustainable industrial practices.

While both configurations exhibited similar percentages of cost contribution across various sectors, discrepancies arose due to few fixed values and assumptions. For instance, the total annual operating labor cost, derived from a fixed labor cost of \$65,000/operator/year, yielded same totals for both processes (\$4,387,500). However, their

contribution percentages differed; in the integrated process, it was at 0.28, whereas in the separated process, it was 0.42 which signified the interdependent managements of intensified combined equipment and simplicity of individual operations in separated systems requiring less oversight and specialized skills, reduced maintenance needs leading to fewer labor hours.

The bare module costs contributing more than other expenses in both processes could stem from the fundamental infrastructure and equipment required for the process, often constituting a significant portion of the initial investment. In the integrated process, this contribution (45.5 %) was lower than the bare module cost contribution in separated process (50.7 %) due to economies of scale, shared infrastructure, or streamlined design, resulting in efficiencies that drive down overall module expense contribution percentage compared to the separated process, where each unit requires standalone infrastructure and equipment, potentially leading to higher individual module costs comparing to other elements of expense. The integrated process demonstrates a significant reduction in capital costs primarily due to streamlined equipment requirements. By consolidating CO₂ capture and utilization into a single unit, the integrated system reduces the number of necessary compressors, heat exchangers, and reactors. This integration translates to a decrease in bare module costs, which are a substantial portion of capital expenditure. Specifically, the integrated process showed a 5.2 % reduction in equipment installation costs compared to the separated process. While the integrated process incurred higher raw materials costs due to co-locating multiple streams, it compensated by lowering operational labor and utility costs. The integrated configuration's reduced need for separate unit operations translated to a 0.3 % decrease in labor costs and an 8.2 % reduction in utility costs per ton of CO₂ captured and utilized. This reduction was achieved through fewer operational units and enhanced efficiency in energy use.

Electrolyzer and compressors were the major cost drivers for the capital costs,[69,70] with the inlet compressor alone accounting for about 25–30 % of the total grassroots cost. This was primarily due to the large amount of power required to compress a significant volume of inlet flue gas to 20 bar. Fig. 3 also presented the utility cost contribution disparity between separated (6.09 %) and integrated (8.2 %) systems, which attributed to factors like independent process units optimization, fewer utility requirements per production unit, potential economies of scale in smaller operations, differences in infrastructure design, and better suitability for energy recovery in separated process. Although compressing the entire flue gas to 20 bar imposed significant energy penalties, the overall electricity consumption relative to other costs was mitigated in the integrated process. This is due to improved energy efficiency and heat integration strategies that reduce the net electricity demand. For instance, the integrated system's optimized heat recovery systems lowered the effective energy consumption, demonstrating a 10 % reduction in relative electricity costs compared to the separated process. The integrated process achieved a 9.5 % higher energy efficiency due to the reduced number of heat exchangers and compressors, which optimized the overall energy utilization. This improvement is attributed to the effective integration of heat recovery and reduced thermal gradients, contributing to a more efficient energy profile. The relatively lower share of electricity consumption, despite the significant energy penalty from compressing the entire flue gas, can be attributed to the integration of capture and utilization processes into a single system. Although compression is energy-intensive, the overall process benefits from reduced thermal gradients and improved energy recovery, which helps mitigate the relative impact of compression on total electricity consumption. The integrated design incorporates waste heat recovery and heat integration measures that offset some of the energy required for compression. This integration reduced the net electricity demand by utilizing recovered heat effectively. The process's operational efficiency, including optimization of compressor performance and integration with other units, contributed to a lower relative share of electricity consumption compared to what might be expected from the standalone

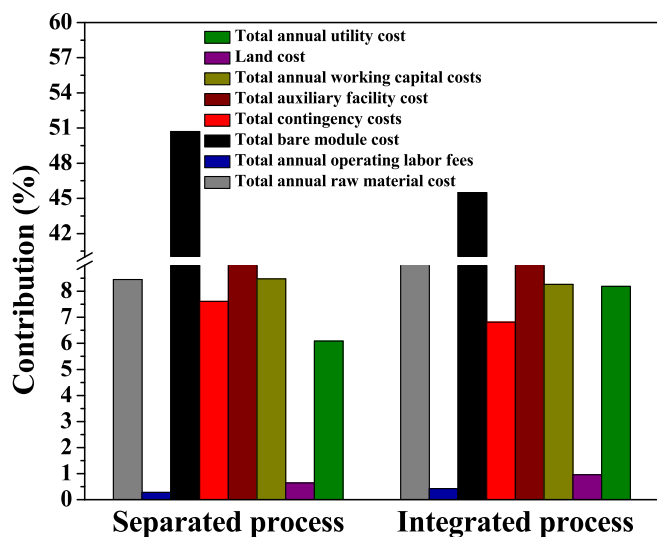


Fig. 3. Contribution of different costs to the overall plant cost in separated and integrated CCU processes.

energy requirements of compression.

Equipment installation costs made up the largest portion of the overall plant cost at 50.7 %, while utilities and labor costs contributed only 6.09 % and 0.28 % to the operating costs. In the case of integrated process, equipment installations contributed 45.5 % to the overall plant costs, while utilities and labor costs contributed only 8.2 % and 0.42 % to the operating costs. The values demonstrated that integrating the process made the investment more affordable, even without considering the increase in final product rate. In the separated process, 26.8 % of the overall costs were related to capital costs and 73.2 % to operating costs, while in the integrated, capital and operating costs contributed 22.06 % and 77.94 %, respectively. The integration of two PSA columns and an electrolytic reactor in two adsorptive reactors, using one less compressor and one less heat exchanger primarily made integrated process more cost-effective. The separated process required ~\$1403 and ~\$516 for producing 1 ton of light olefins and capturing and utilizing 1 ton of CO₂, respectively, while the integrated process cost ~\$1004 and ~\$284 for the same purposes. However, the cost of the plant per ton of CO₂ captured (and utilized) was sensibly comparable to that reported in the literature.

4.2. Sensitivity analyses

This study conducted a sensitivity analysis to investigate the impact of operating parameters and uncertainties on the technical and economic aspects of both separated and integrated CCU processes. Specifically, the effects of temperature, pressure, and H₂O/CO₂ molar ratio on conversion, selectivity, and overall cost were examined from a thermodynamic perspective. The study also evaluated the impact of material properties, including adsorbent capacity, catalyst conversion capability, and material deactivation rate, on the associated costs. Furthermore, the analysis assessed how the presence of downstream units and heat integration influenced the final costs of carbon capture and utilization and olefin production.

4.2.1. Effect of thermodynamical parameters

To investigate the effect of pressure, the pressure was varied between 1 and 20 bar at a constant H₂O/CO₂ molar ratio of 4 and a temperature of 400 °C. As presented in Fig. 4, increasing the pressure led to an increase in CCU cost/ton of captured CO₂ and a decrease in the cost of light olefins production for both integrated and separated processes. However, the increased pressure also incurred additional costs due to the need for a bigger compressor that consumes more utility, leading to an increase in the CCU cost/ton of captured CO₂. This was observed as an increase in the cost of CCU from \$327 to \$490 and \$313 to \$449/ton of captured CO₂ for separated and integrated processes, respectively.

Nevertheless, the conversion of feed increased dramatically,

resulting in a significant increase in light olefins' conversion and productivity, as seen in Figure S1-S2. As a result, the cost of olefin production decreased from \$2,250 to \$250 and \$1,375 to \$375 in separated and integrated processes, respectively, upon increasing the pressure from 1 to 20 bar. The most significant effect was observed by changing the pressure from 5 to 15 bar while the optimum pressure for olefin production cost was found to be 20 bar.

The effect of reaction temperature on the process was evaluated by changing it from 300 to 400 °C at 20 bar and H₂O/CO₂ molar ratio of 4. As shown in Fig. 5, increasing the temperature smoothly increased both CCU cost/ton of captured CO₂ and cost of olefin production, but had a negligible effect on conversion, except for a slight increase in olefin productivity, as shown in Figure S2-S4. The temperature of 350–400 °C was found to be the optimal temperature for the reaction, resulting in only a marginal increase in the costs of separated and integrated process.

The impact of H₂O/CO₂ molar ratio in the feed composition on the process was investigated by varying it between 2 and 4 at 20 bar and 400 °C. Fig. 6 shows that increasing the molar ratio from 2 to 4 resulted in an increase in CCU cost for both separated and integrated process. This was expected since water does not affect the amount of captured CO₂, and its impact is on the electrolysis step and olefin production. The trend for olefin production cost was different, however, increasing the ratio from 2 to 3 lowered the cost, while further increasing the molar ratio to 4 significantly raised the olefin production cost by over 10 % for both processes. This was due to the effect H₂O/CO₂ molar ratio, where a value of 3 resulted in the best olefin yield, as demonstrated in Figures S5 and S6. Furthermore, increasing the ratio to 4 necessitated a larger compressor with more power, as well as the cost of water, resulting in a significant increase in costs. Consequently, the H₂O/CO₂ molar ratio of 3 was determined to be the optimal ratio for a CCU plant.

In the case of separated process, the impact of pressure and temperature on CO₂ recovery and capture cost was analyzed, as presented in Fig. 7. As shown in the figure, increasing the capture pressure from 5 to 20 bar resulted in an increase in CO₂ recovery from 73 % to 90 %. These results were expected as increasing the pressure enhances adsorption capacity at the expense of greater cost due to the requirement of a compressor with higher power. Furthermore, raising the temperature from 300 °C to 400 °C led to an increase in CO₂ recovery as a result of greater adsorption capability. Therefore, the condition of 20 bar and 400 °C was determined to be the optimal conditions for achieving over 90 % CO₂ recovery with reduced cost and in both cases, integrated process provided higher CO₂ recovery.

4.2.2. Effect of materials properties

The impact of using catalysts with varying degrees of activity on the overall cost of the CCU process was assessed and is presented in Fig. 8 for both the separated and integrated processes. Catalysts with conversion

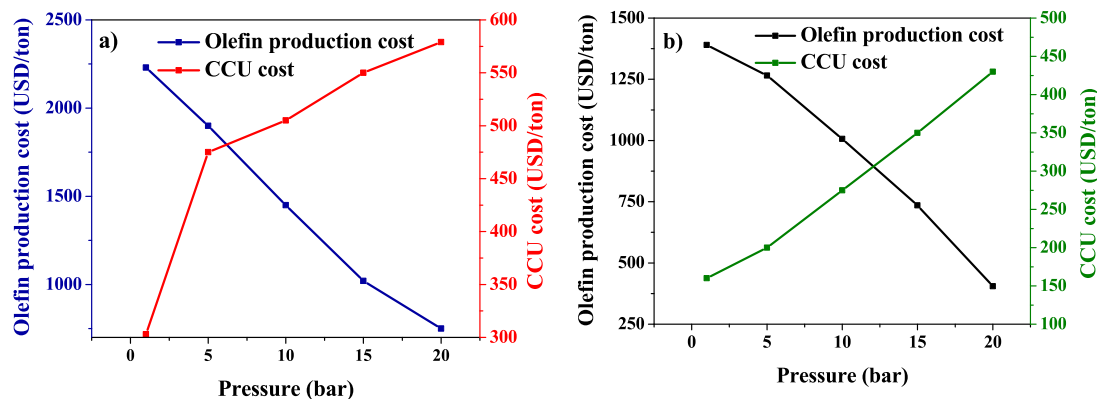


Fig. 4. Effect of pressure on olefin production cost and CCU cost/ton of captured CO₂ at 400 °C and H₂O/CO₂ molar ratio of 4 for a) separated and b) integrated CCU processes.

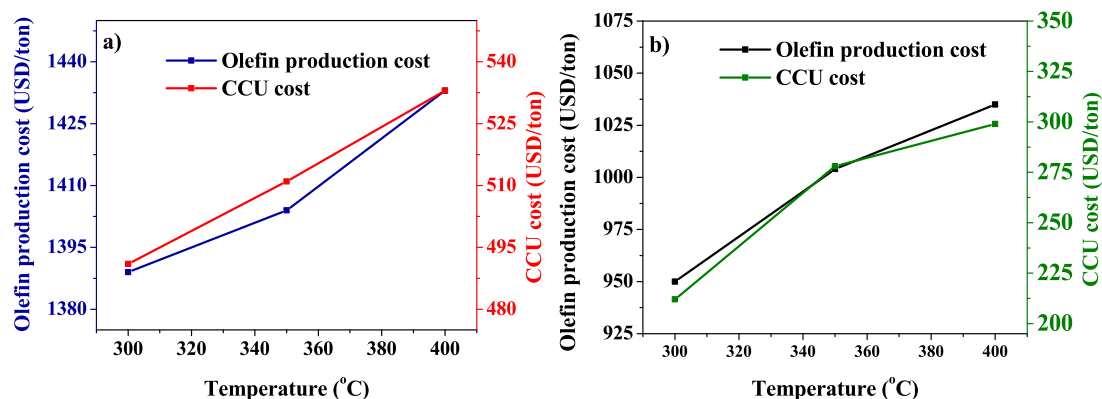


Fig. 5. Effect of temperature on olefin production cost and CCU cost/ton of captured CO₂ at 20 bar and H₂O/CO₂ molar ratio of 4 for a) separated and b) integrated CCU processes.

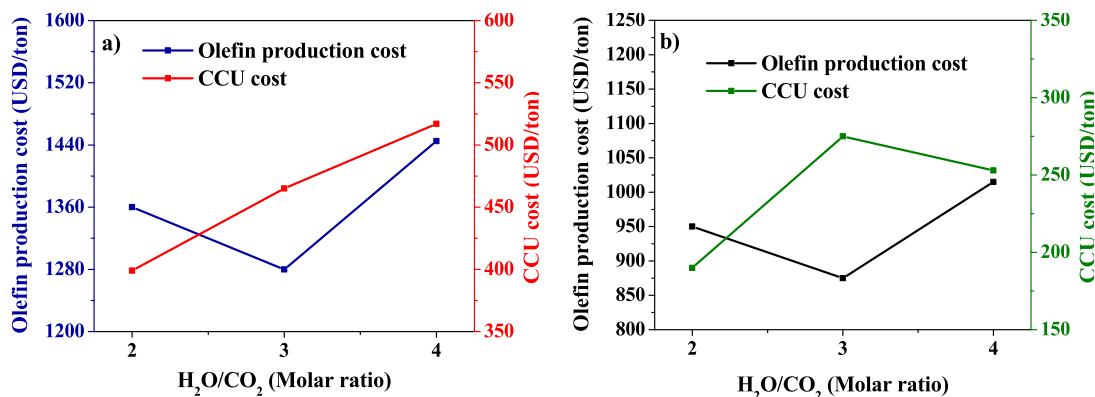


Fig. 6. Effect of H₂O/CO₂ molar ratio on the olefin production cost and CCU cost/ton of captured CO₂ at 400 °C and 20 bar for a) separated and b) integrated CCU processes.

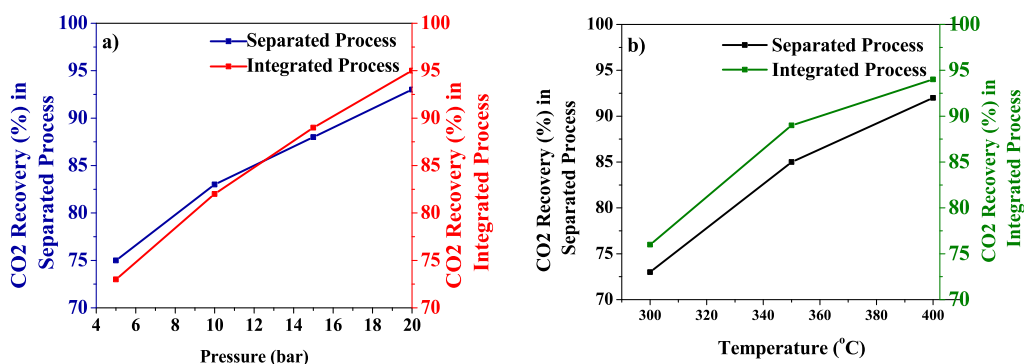


Fig. 7. CO₂ recovery as a function of a) pressure at 400 °C and b) temperature at 20 bar, for separated and integrated CCU processes.

capabilities ranging from 50 to 75 % were assumed. The results showed that as the catalyst activity increased, the costs of both CCU and olefin production decreased in both configurations. For instance, a catalyst with a conversion capability of 50 % incurred \$190 and \$102 more costs per ton of olefin produced and captured CO₂, respectively, compared to a catalyst with a potential conversion capability of 75 %. The corresponding values for the integrated process were estimated to be \$80 and \$35, respectively. Therefore, the use of more efficient catalysts that gives rise to higher CO₂ conversion and olefin yield could lower the costs. Consequently, by maintaining catalyst activity over long periods (i.e., catalyst durability), less catalyst would be required, leading to a lower overall cost.

The study also evaluated the impact of using different adsorbents

with varying adsorption capacities (ranging from 1.5 to 14 mmol/g) for the separated and integrated processes. Similar to the catalyst efficiency, increasing the adsorption capacity led to a decrease in olefin production and CCU costs for both processes, as illustrated in Fig. 9. The effect of adsorbent efficiency was more pronounced in the processes due to the presence of two distinct adsorption columns, where the efficiency of the adsorbent directly affected the size of both units. In contrast, the integrated processes had two electrolytic adsorptive reactor units filled with BFM and changing the amount of adsorbent constituent was less pronounced on the size. Increasing the adsorption capacity from 1.5 to 14 mmole/g resulted in a decrease in olefin production cost and CCU cost/ton of captured CO₂ by \$115 and \$36, respectively for the separated process and the corresponding changes in the integrated process were

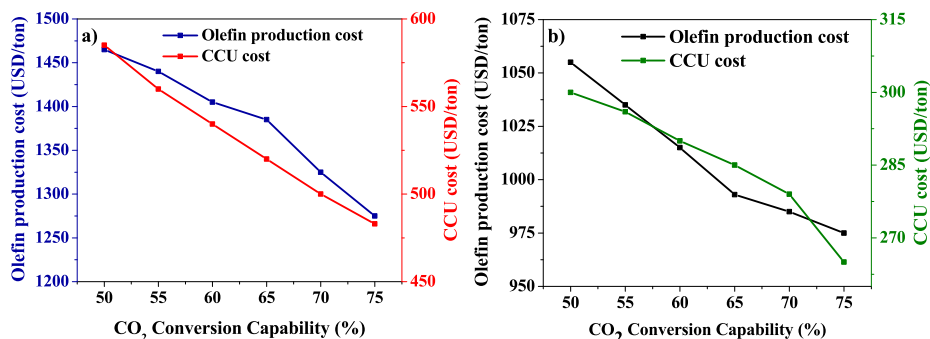


Fig. 8. Effect of catalyst performance (CO₂ conversion capability) on olefin production cost and CCU cost/ton of captured CO₂ at 400 °C and H₂O/CO₂ molar ratio of 4 for a) separated and b) integrated CCU processes.

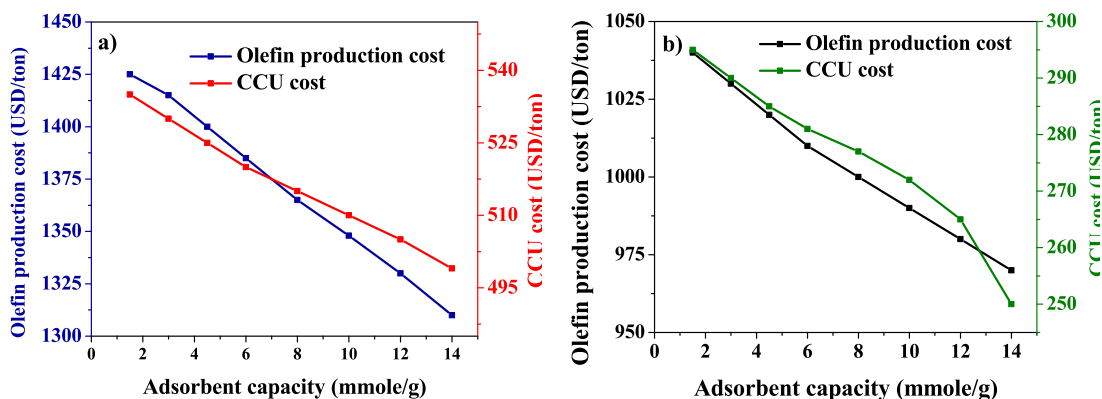


Fig. 9. Effect of adsorbent capacity on olefin production cost and CCU cost/ton of captured CO₂ at 400 °C and H₂O/CO₂ molar ratio of 4 for a) separated and b) integrated CCU processes.

\$70 and \$45, respectively.

Therefore, employing potential adsorbents with higher efficiency could lead to lower expenses for carbon capture and utilization to produce light olefins. However, the effect of catalyst efficiency on the light olefins production cost was more significant than that of adsorbent efficiency. On the other hand, adsorbent efficiency had a greater impact on the CCU cost. As expected, increasing the adsorbent capacity led to an increase in CO₂ recovery, resulting in a decrease in capture cost. The results indicated that to achieve a recovery of greater than 90 %, adsorbents with a capacity of at least 5–6 mmole/g should be employed.

The impact of material deactivation rate on process costs was also analyzed. Deactivation of catalyst and adsorbent, caused by coke formation, reduced efficiency and necessitated replacement, thereby

increasing operating costs. To assess the effect of deactivation rate, replacement rates were varied between 10 to 30 % for catalyst and 5 % to 20 % for adsorbent. Fig. 10 indicates that as catalyst replacement rate increased, costs for both CCU and olefin production in both processes increased.

When catalyst replacement rate was increased from 10 to 30 % per year, the olefin production cost and CCU cost/ton of captured CO₂ were increased by \$90 and \$46, respectively for separated process. In the case of the integrated process, the values were increased by \$75 and \$35 respectively, which were less than those of the separated process.

Similarly, Fig. 11 showed that increasing the adsorbent replacement rate from 5 to 20 % per year increased olefin production cost by \$74 and \$50 for separated and integrated processes respectively. In addition,

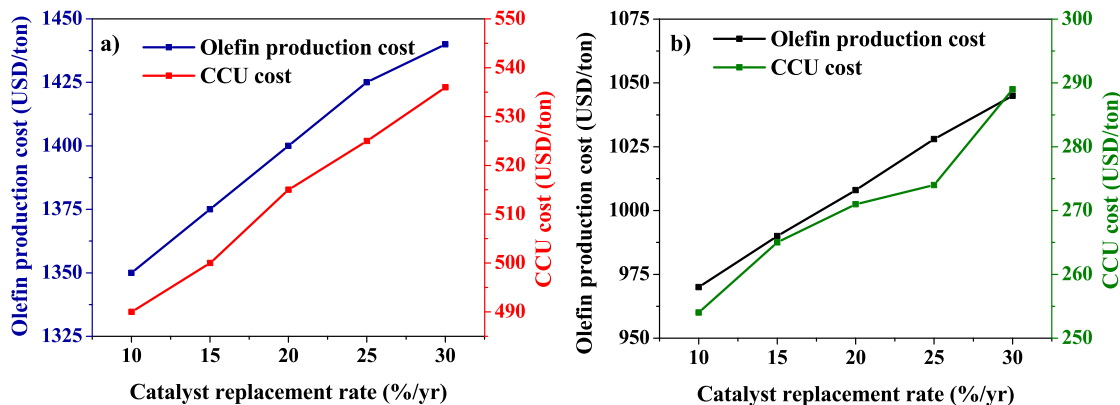


Fig. 10. Effect of catalyst replacement rate on olefin production cost and CCU cost/ton of captured CO₂ at 400 °C and H₂O/CO₂ molar ratio of 4 for a) separated and b) integrated CCU processes.

CCU cost/ton of captured CO₂ also increased by \$68 and \$44, respectively for these processes. Hence, the durability of the materials can significantly affect the cost-effectiveness of both separated and integrated CCU processes.

4.2.3. Effect of heat integration and downstream units

As discussed earlier, this study examined the use of stream recycling to simplify heating and cooling processes and integrated available energy within the plant as a way to reduce the demand for utilities. To support this claim, the impact of heat integration on overall costs was investigated. Fig. 12 displayed the olefin production and CCU costs with and without heat integration for both separated and integrated CCU processes. The results indicated that heat integration led to a reduction in olefin production and CCU costs by \$70 and \$45, respectively for the separated process and \$90 and \$60, respectively for the integrated process. Since the separated process had one more heat exchanger than the integrated system, the impact of the heat integration was more pronounced.

We modeled an integrated network of heat exchangers designed to recover and reuse the waste heat from high-temperature process streams within the plant. Each process stream was analyzed to identify potential heat sources and sinks. Waste heat from processes such as CO₂ capture and electrochemical reactions, which typically operate at high temperatures, was routed through heat exchangers to preheat feed streams, thereby lowering the energy required for heating. The efficiency of the heat recovery system was analyzed based on the temperature differences between streams and the heat exchanger effectiveness. The overall energy recovered was used to reduce the energy requirements of the heating system, quantified as a reduction in utility costs. The recovered waste heat was used to preheat feed streams entering various units e.g. incoming cold streams. This reduced the need for additional external heating, which was modeled using heat transfer equations and efficiency factors. In addition to heat recovery, the cooling system was optimized by using energy-efficient cooling methods and minimizing the need for external cooling utilities. This included the use of cooling water and heat exchangers to manage process temperatures more effectively. For the integrated process, the design inherently included a fewer heat exchangers and more efficient heat integration due to the consolidation of CO₂ capture and utilization units. This reduced the overall energy demand and improved process efficiency. The implementation of heat recovery measures reduced the total demand for external utilities by effectively reusing waste heat within the plant. This was modeled by calculating the reduction in energy consumption based on the recovered heat's contribution to preheating and other energy-saving measures. The overall process efficiency improved as a result of effective waste heat utilization and optimized cooling systems. The energy savings from these measures were incorporated into the process simulation, showing a lower total energy consumption and better process stability. We benchmarked the model parameters against reported values in the literature, such as reaction kinetics, heat transfer coefficients, and

material properties including previous studies on CCU technologies, electrochemical processes, and TEA studies. While literature data provided a robust foundation for the model, we acknowledge that there are inherent limitations such as variations in feedstock compositions, operating conditions, and equipment efficiencies. Differences in scale, equipment design, and operating conditions between reported studies and our modeled process could affect the accuracy of the predictions. We performed sensitivity analyses to assess the impact of varying key parameters on the model outcomes. This approach helps to identify how changes in input data affect the results and provides insight into the robustness of the model predictions. Although exact experimental validation was not conducted, this comparative approach ensured that our model predictions are aligned with known data trends.

5. Conclusion

Direct electrochemical conversion of CO₂ captured from flue gas stream into light olefins, utilizing STM-MTO processes in both separated and integrated configurations, was demonstrated in this study. Our process simulations and TEA indicated that the integrated process offers significant cost benefits, with reductions of approximately \$400/ton for olefins production and \$232/ton for CO₂ capture. A detailed sensitivity analysis was also conducted to assess the impact of various operating parameters, materials properties, and process configuration on the costs of light olefins production and CO₂ capture-utilization. Although the integrated process demonstrated cost benefits, the total capital and operating costs were higher than anticipated when compared to an ideal integrated process, primarily due to the significant expenses associated with the adsorptive reactors. However, these higher initial costs may be offset by long-term savings through enhanced efficiency, reduced energy consumption, and lower waste production. Additionally, the process could offer higher throughput, create synergies with existing systems, and provide better scalability—where, as production scales up, the per-unit costs decrease more rapidly. This underscores the inspiration for future scopes and research on more cost-effective technologies to fully capitalize on the potential advantages of the intensification and integration approaches. Overall, our findings demonstrated the advantages of the combined-intensified single unit CCU process in real industrial applications. Future research should focus on developing and designing more cost-effective electrolyzer (i.e., adsorptive reactor) technologies and other key components or unit operations to reduce overall plant costs. Advances in material science and engineering could substantially contribute to this goal. Furthermore, conducting experimental studies to validate the simulation results will enhance the credibility of the model and provide more accurate data on cost and performance. Further TEA studies are needed to explore additional optimization strategies, including advanced heat integration, waste heat recovery, and process intensification, to achieve greater efficiency and cost-effectiveness. Investigating the scalability of the integrated process and its practical implementation in industrial settings will be crucial for assessing its

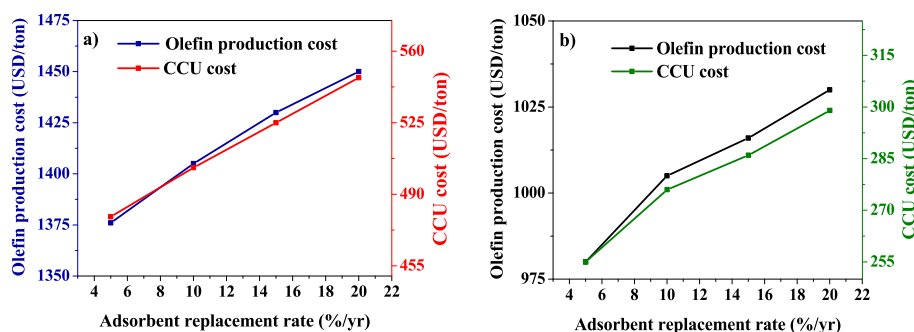


Fig. 11. Effect of adsorbent replacement rate on olefin production cost and CCU cost/ton of captured CO₂ at 400 °C and H₂O/CO₂ molar ratio of 4 for a) separated and b) integrated CCU processes.

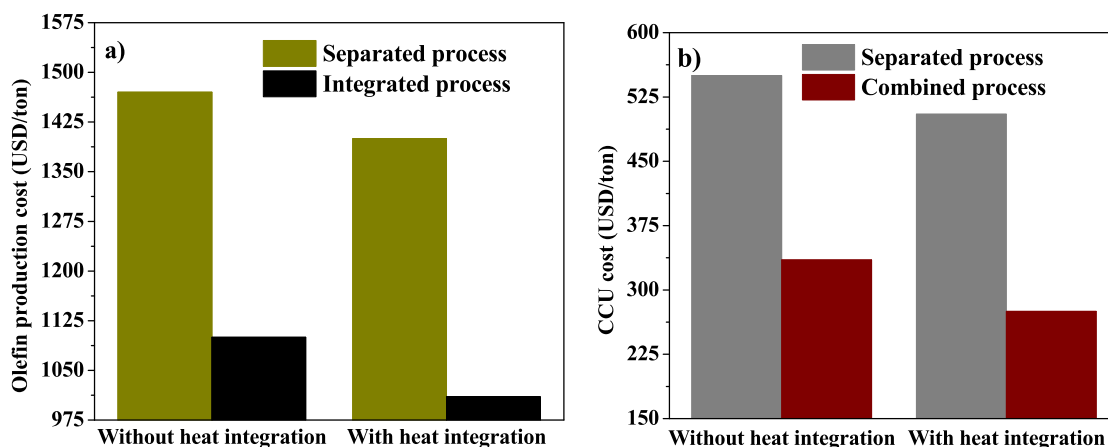


Fig. 12. Effect of heat integration for separated and integrated CCU processes on a) olefin production cost and b) CCU cost/ton of captured CO₂ at 400 °C and H₂O/CO₂ molar ratio of 4.

viability for widespread application.

CRedit authorship contribution statement

Abdullah Al Moinee: Writing – original draft, Software, Methodology, Formal analysis, Data curation. **Ali A. Rownaghi:** Writing – review & editing, Validation, Project administration, Conceptualization. **Fateme Rezaei:** Writing – review & editing, Validation, Supervision, Funding acquisition, Conceptualization.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2024.155909>.

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