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Full Length Article

Analysis of new strategies integrating bipolar membrane electrodialysis and absorption systems in DAC applications

Grazia Leonzio [a,*], Lei Xing [b], Nilay Shah [c]

[a] Department of Mechanical, Chemical and Materials Engineering, University of Cagliari, via Marengo 2, 09123 Cagliari, Italy
[b] School of Chemistry and Chemical Engineering, Faculty of Engineering and Physical Sciences, University of Surrey, Guildford GU2 7XH, United Kingdom
[c] Sargent Centre for Process Systems Engineering, Department of Chemical Engineering, Imperial College London, London SW7 2AZ, UK

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ABSTRACT

Solvent-based carbon dioxide capture technologies remain among the most promising capture strategies but conventional thermal regeneration methods are hindered by significant drawbacks. In this context, electrochemical regeneration, particularly through the bipolar membrane electrodialysis, offers potential advantages. However, its application is challenged by carbon dioxide bubble formation in the acid compartment, which increases energy requirements. To address this issue, a novel process is proposed in which carbonates in the rich solvent react with weak organic acids to release carbon dioxide while forming acid salts treated in the electrodialysis unit, enabling simultaneous the regeneration of both acid and solvent. To date, comprehensive economic and environmental assessments of such approaches are lacking in the state-of-the-art. This study aims to fill that gap by simulating both the conventional process and alternative pathways based on formic acid and a formic/acetic acid mixtures. Comprehensive material and energy balances are established, alongside detailed evaluations of capital and operating expenditures, and the environmental impact are conducted through life cycle assessment implemented in OpenLCA. Although the alternative processes exhibit higher energy consumption (2314 kWh/tonCO_2 vs 1907 kWh/tonCO_2 with formic acid, and 1943 kWh/tonCO_2 with the acid mixture), the conventional route remains more favorable in terms of both overall cost and environmental impact. Specifically, the total cost and climate change impact of the conventional capture process are estimated to be 480 \$/tonCO_2 and –0.9593 kgCO_{2eq}/kgCO_2, respectively. On the other hand, the alternative process using formic acid and the mixture acid incur higher costs of 510 \$/tonCO_2 and 519 \$/tonCO_2 with corresponding environmental impacts of -0.9378 kgCO_{2eq}/kgCO_2 and 0.9238 kgCO_{2eq}/kgCO_2, respectively. Further optimization of the conventional process, particularly in mitigating carbon dioxide bubble formation, appears essential to fully exploit its economic and environmental potential.

1. Introduction

Since the industrial revolution, rising energy demand has been met largely by fossil fuels, which still account for about 85 % of global consumption despite growing environmental awareness (Karimi et al., 2023; Zhou et al., 2024). The resulting increase in carbon dioxide (CO_2) emissions has intensified global warming and heightened the urgency for effective mitigation strategies. International efforts, including the United Nations Framework Convention on Climate Change (UNFCCC) and the 2015 Paris Agreement, underscore the need to limit temperature rise to well below 2 °C above pre-industrial levels and a 75 % cut in CO_2 emissions by 2060 (Prado and MacDowell, 2023; Stankovic et al., 2023; IPCC, 2022). To meet global climate targets, large-scale carbon dioxide removal (CDR) technology is increasingly recognised as essential (Fuss et al., 2018; Leonzio et al., 2022a). Recent policy actions, e.g., the 2020 U.S. legislation supporting CDR deployment (Goll et al., 2021), indicate that CDR technologies may need to offset more than 100 billion tonnes of greenhouse gases this century to counter rising atmospheric CO_2 levels (Powis et al., 2023). Among CDR solutions, the research community has been focused and attracted for the most part on DAC, due to its advantages (Kiani et al., 2020¸ Bouaboula et al., 2024). DAC systems can incorporate different technologies such as absorption, adsorption, membrane, cryogenic separation, photocatalysis, ion-exchange resin and electrochemical approaches (Leonzio et al., 2022a; Leonzio and

* Corresponding author.
E-mail address: grazia.leonzio@unica.it (G. Leonzio).

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Shah, 2025; Song et al., 2019). Among them absorption and adsorption are currently the most mature and developed with the highest value of technology readiness level (TRL), high capture capacity, efficiency and versatility (Bisotti et al., 2024).

Adsorption-based DAC uses solid sorbents for CO_2 capture that undergo in several cycles changing temperature and/or pressure. On the other hand, absorption DAC using alkaline solutions leverages fast hydroxide-CO_2 reactions to form bicarbonate species into scalable contactors. Yet conventional regeneration typically relies on heat-intensive steps (e.g., steam or calcination with temperatures up to 900 °C), which inflate energy use and cost and complicate coupling to variable renewables. In fact, these conventional DAC systems based on the use of thermal energy for the regeneration of solvent or sorbent are said to have some difficulties with scalability, integration with renewable energy sources and process intensification (Hadi et al., 2025). For these reasons, in the last years, the attention of the research community has been focused on electrochemical based DAC processes due to their modularity and scalability, plug-and-play installation, lower energy requirements, higher sustainability and flexibility and improved CO_2 selectivity (Ganiyu et al., 2020; Kumar et al., 2023). It is evident that electrochemical based DAC might support a potential trajectory for significant CO_2 reduction and includes the following technologies: electrolysis and electrodialysis cell stacks, proton coupled electron transfer (PCET), electrochemically-mediated amine regeneration (EMAR), electro-swing adsorption (ESA), redox-active compounds and membrane capacitive deionization (Bouaboula et al., 2024).

In particular, recent overviews underline both the need for electrified regeneration and the opportunity space for alkaline DAC flowsheets (Khan et al., 2023; Wu et al., 2024; Jana et al., 2024). Hence, a bipolar membrane electrodialysis (BPMED) is linked to an absorption DAC for the regeneration of the solvent and release of captured CO_2, demonstrating potential for industrial application and it has been already tested in pilot projects (Liu et al., 2025).

BPMED applies an electrical potential across bipolar membranes (BPMs), inducing water dissociation at the membrane interface to generate protons (H^+) and hydroxide ions (OH^-), migrating toward the anode and cathode sides, respectively (Yan et al., 2025; Zhou et al., 2025). In bicarbonate-rich capture liquors, the H^+ stream acidifies the anode-side compartment to release high-purity CO_2, while the OH^- stream on the cathode side regenerates the alkaline absorbent, thus completing the closed chemical loop and exploiting the different solubility of carbonates with the pH (Sharifian et al., 2021). Several advantages are present in the literature for this technology and below discussed.

BPM-driven pH swings can potentially regenerate CO_2 from bicarbonate/carbonate solutions coming from an absorption column and even from brine with reasonable energy intensities, highlighting a credible pathway toward electrified solvent recycling (Cao et al., 2023; Aliaskari et al. 2024; Vallejo-Castaño et al., 2025; Khan et al., 2023; Wu et al., 2024; Mustafa et al., 2024). Bui et al. (2023) demonstrate that BPMED can attain energy intensities below 150 kJ/molCO_2 under optimised conditions, suggesting that electrochemical regeneration can rival or even surpass the energy efficiency of conventional thermal approaches while operating solely on electricity derived from intermittent renewable sources. Higher values of energy consumption for this DAC-BPMED process, but in the same order of magnitude, are reported by Sabatino et al. (2020), Sabatino et al. (2022) and Shu et al. (2020) showing respectively 236 kJ/molCO_2 (when operating at a low current density), 574 kJ/molCO_2 and 374 kJ/molCO_2.

BPMED also facilitates closed-loop solvent management via in-situ acid and base generation, allowing simultaneous CO_2 release and alkaline-solvent regeneration. This approach eliminates the need for external chemical reagents and significantly reduces waste, as its intrinsic electrochemical recycling mechanism enables continuous operation without solvent degradation or loss (Akhter et al., 2024). Vallejo-Castaño et al. (2025) further demonstrate that the electrochemically driven pH-swing in BPMED systems preserves the absorbent alkalinity and overall mass balance while achieving near-complete bicarbonate regeneration. Their findings highlight the BPMED capability to maintain continuous and reversible CO_2 capture-release cycles with minimal solvent degradation or loss. Another key advantage is that the electrochemical pH-swing in BPMED generates high-purity CO_2, which is readily suitable for downstream storage or utilisation. Akhter et al. (2024) report that the acidification step within BPMED selectively liberates CO_2 from bicarbonate solutions with purities exceeding 99 %, thereby eliminating the need for the energy-intensive gas-liquid separation stages typically required in amine- or carbonate-based systems.

One of the key benefits of DAC-BPMED lies in its modularity and operational flexibility, enabling deployment in distributed or load-following configurations (Chen et al., 2022). Unlike conventional thermally integrated capture plants that depend on continuous heat input, BPMED systems are purely electrochemical and can therefore respond dynamically to variable renewable power (Shen et al., 2026; Liu et al., 2022; Diederichsen et al., 2022).

Despite these technical advantages, several limitations remain, including higher costs and CO_2 bubble production inside the process, which reduce overall efficiency. These challenges have motivated the research community to seek new solutions, and the novelty of our work is directly addressing these critical limitations. In particular, the techno economic analysis (TEA) consistently shows that DAC-BPMED systems remain considerably more expensive than both thermal solvent regeneration and leading solid-sorbent DAC technologies. In the review of Bouaboula et al. (2024), a range for the cost between 200 \$/tonCO_2 and 1600 \$/tonCO_2 is reported for the DAC based on BPMED system. In particular, early BPMED analyses at lab and batch scale report the optimal CO_2 recovery costs of approximately 180 \$/tonCO_2, with sensitivity studies identifying the power cost and membranes as the dominant contributors to total plant cost (Iizuka et al., 2012). In addition to considering a higher lifetime for the membrane, both increasing the current efficiency to 90 % and decreasing the membrane cost at the 10 % of the base case help to reduce total costs to about 100 \$/tonCO_2.

Economic analysis for the absorption DAC combined with the BPMED are conducted at a larger scale by Sabatino et al. (2020), Young et al. (2023) and Leonzio and Shah (2025). In the work of Sabatino et al. (2020), the minimum capture cost for the DAC process using the BPMED for solvent regeneration is 773 \$/tonCO_2, higher than that of the equivalent thermal energy-based process used by the Carbon Engineering company. The optimal respective current density and energy consumption are 1000 A/m^2 and 957 kJ/molCO_2. The authors suggest the highest impact of membrane cost on the total capture cost as well as the importance of energy costs. Efforts should especially be made to increase the lifetime of the membranes and improve the energy efficiency of the whole process. The same result is reported in Sabatino et al. (2022), where more durable and cheaper membranes can ensure a cost below 250 \$/tonCO_2. Other factors can be significant on total costs: current density, cation concentration (K^+ or Na^+) in the rich solution and number of cells (Leonzio et al., 2025). In Young et al. (2023) a hybrid methodology is applied to find the net removed capture cost of the first-of-a-kind (FOAK) DAC-BPEMED plant and project this value at higher capture scales. Considering the US region and nuclear energy as the driving of the process, results show that the investigated technology can cost above 1000 \$/tonCO_2 at a lower scale (0.1 MtonCO_2/year) and between about 1400 \$/tonCO_2 and 500 \$/tonCO_2, at a higher scale (3 MtonCO_2/year). The same methodology is used in Leonzio and Shah (2025) comparing the considered DAC with other electrochemical capture solutions at different years, energy sources and geographic locations. Results show that the use of a BPMED stack for the regeneration of the rich solution can cost up to 537 \$/tonCO_2, 416 \$/tonCO_2, 386 \$/tonCO_2 respectively for the 2023, 2030 and 2050 using renewable solar energy and in the US region for 1 MtonCO_2/year as capture rate Moreover, it emerged that this technology has higher costs compared to the ESA and PCET based solution.

In recent years, an aqueous L-arginine amino acid solution has been used replacing the hydroxide solvent in the absorption DAC-BPMED system by Heß et al. (2025). Here, the conducted economic analysis further shows levelized capture costs between 350 €/tonCO_2 and 465 €/tonCO_2 largely due to high electricity demand, water loss, and the capital cost of BPMED stacks. These results show that the new proposed solution is competitive with other DAC technologies and more economically convenient with the process based on hydroxide solvent proposed by Sabatino et al. (2022), warranting further investigations and studies. Consequently, while BPMED presents an attractive pathway for electrified regeneration, its economic feasibility currently lags more mature DAC technologies. Regarding the environmental analysis of the absorption DAC combined with a BPMED stack, a complete analysis according to the principle of a life cycle assessment (LCA) is missing in the literature. The only work reported by Leonzio and Shah (2025) is conducted according to scope 1 and 2 quantifying the negative emissions for the investigated capture solution.

A further limitation and disadvantage of DAC-BPMED stems from CO_2 bubble formation within the acid compartment, which imposes additional energetic and operational penalties. Acidification of bicarbonate-rich streams leads to supersaturation and in-situ CO_2 nucleation, generating bubbles that obstruct flow channels, block active membrane area, increase local resistance, exacerbate mass-transport limitations, current crowding and local heating (Nagasawa et al., 2009). Experimental studies report that bubble accumulation can induce 20–30 % additional overpotential, particularly under high bicarbonate loading or elevated current densities, directly increasing electrical energy consumption and accelerating membrane aging. These bubble-induced resistances are intrinsic to conventional BPMED acid compartments and represent a fundamental constraint on energy efficiency (Eisaman et al., 2011; Sabatino et al., 2022).

In addition to the operation at a pressure higher than 6 bar ensuring 29 % of reduction in energy consumption (Eisaman et al., 2011; Sabatino et al., 2022), other alternative DAC-BPMED configurations designed to avoid in-cell CO_2 degassing, thereby mitigating bubble-related overpotentials must be explored inside the research community. A promising strategy involves first reacting bicarbonate/carbonate solutions with a weak organic acid, releasing CO_2 ex-situ while generating the corresponding acidified salt, which is subsequently regenerated via BPMED (Liu et al., 2025).

Even though the energy consumption of this alternative process is investigated by Valluri and Kawatra (2021), a detailed economic and environmental analysis is missing in the literature. Hence, our work aims to overcome this gap proposing a detailed economic and environmental analysis of alternative process solutions for CO_2 release and solvent regeneration by using a BPMED stack related to an absorption DAC system. This is the novelty of our work. In these alternative solutions, the rich solution coming from absorption is reacting with a weak acid solution producing a salt fed into the BPMED to regenerate both acid and basic solvent. In particular we want to compare from economic and environmental point of view the conventional DAC-BPMED system with the alternative processes using formic acid and a mixture of formic and acetic acid as solvents to release the CO_2 captured in the absorption column. Then, the use of different acid for CO_2 release, via chemical reaction, is another point of novelty of this work

2. Process description and methodology

2.1. Description of the capture plant

In this section a description of the considered CO_2 capture plant is provided according to three different scenarios: base case scenario with bicarbonates and carbonates coming from the DAC absorption column and that are sent directly to a BPMED stack, formic acid scenario with the reaction between bicarbonates and carbonates and formic acid producing the acid salt sent to the BPMED and formic/acetic acid mixture scenario with the reaction between bicarbonates and carbonates and formic/acetic acid mixture producing a new acid salt sent to the BPMED for the same acid recovery. A diagram block of these process schemes is reported in Fig. 1.

2.1.1. Description of the capture plant in the base case scenario

The overall "conventional" process consists of 6 DAC absorption columns and a BPMED stack unit for the release of CO_2. The overall plant is simulated in Aspen Plus software, as reported in Fig. 2a. The air contactor units are those described by Carbon Engineering company (Keith et al., 2018) and Sabatino et al. (2022; 2020). In particular, to simulate the cross-flow design (solvent solution trickles from top to bottom while air flows horizontally), the 6 DAC absorption columns are operated in parallel. This column configuration is used to reduce the DAC cost (Sabatino et al., 2020). An ambient air flow rate of 150 ton/h and a liquid flow rate according to a liquid to gas ratio equal to 0.6 are considered in the feed (Sabatino et al., 2020). The liquid flow rate is based on a mixture of an aqueous solution of potassium hydroxide (KOH) (1 M) and potassium carbonate (K_2CO_3) (0.01 M), the latter added with the aim to reduce toxicity and corrosivity (Keith et al., 2018; Rouxhet et al., 2022). CO_2 is absorbed into the aqueous KOH/K_2CO_3 solution, generating potassium carbonate (K_2CO_3) and potassium bicarbonate ($KHCO_3$) which are fed into the BPMED unit. RadFrac absorption columns are used in Aspen Plus for the simulation of air contactors: each column is characterized by a height of 7 m, packed internal type with Mallapak typology, Sulzer as vendor and with a dimension of 250Y (Keith et al., 2018), 20 stages (Sabatino et al., 2020) and a diameter of 3.2 m to avoid flooding phenomena inside. Moreover, their chemistry (with chemical equilibrium and kinetic reactions) is modelled for the rate-based calculations as reported in Aspen Plus documentation (Aspen Technology, 2013).

For the BPMED unit, a cation-exchange membrane cell configuration is taken into account to release CO_2 from the rich solution and regenerate the alkaline solvent sent back to the absorption column. The operating principle is reported in Fig. 2b The electrochemical cell consists of two compartments: an acidifying and alkaline compartment divided by a cation exchange membrane. A bipolar membrane ensures the pH swing via water electrolysis and drives the overall process. At the two ends of the electrochemical stacks, an anode and cathode are present. In the system the CO_2-rich stream is fed into the acid compartment where protons (H^+) from water dissociations inside the bipolar membrane can reduce the pH of the rich solution, allowing the conversion of carbonate and bicarbonate ions to the dissolved CO_2. At the same time, K^+ cations cross the membrane towards the basic compartment where are combined with the OH^- from the water dissociation in the bipolar membrane to regenerate the alkaline solvent sent back to the absorption column. After the separation of CO_2, at the outlet of the acid compartment, the liquid stream, which is significantly diluted in KOH and CO_2, is fed to the base compartment where with the produced KOH is recycled to the absorption column.

The BPMED unit is modelled in Aspen Plus by using the Matlab Cape Unit Operation, considering a model based on equilibrium, electroneutrality and mass balance equations. An equation system consisting of chemical equilibrium equations, electroneutrality (sum of anionic charges equals the sum of cationic charges) and mass balance to keep constant the dissolved inorganic carbon (DIC) (as the total amount of carbon as CO_2, HCO_3^-, CO_3^{2-} and H_2CO_3 all taken from the simulation) concentration between the rich and acid solution is taken into account. The chemical equilibrium equations are related to the following reactions (see Eq. (1)–(3)) (Wang and He, 2025):

$$CO_{2\ (aq)} + H_2O \leftrightarrow H_2CO_3 \tag{1}$$

$$H_2CO_3 + H_2O \leftrightarrow H_3O^+ + HCO_3^- \tag{2}$$

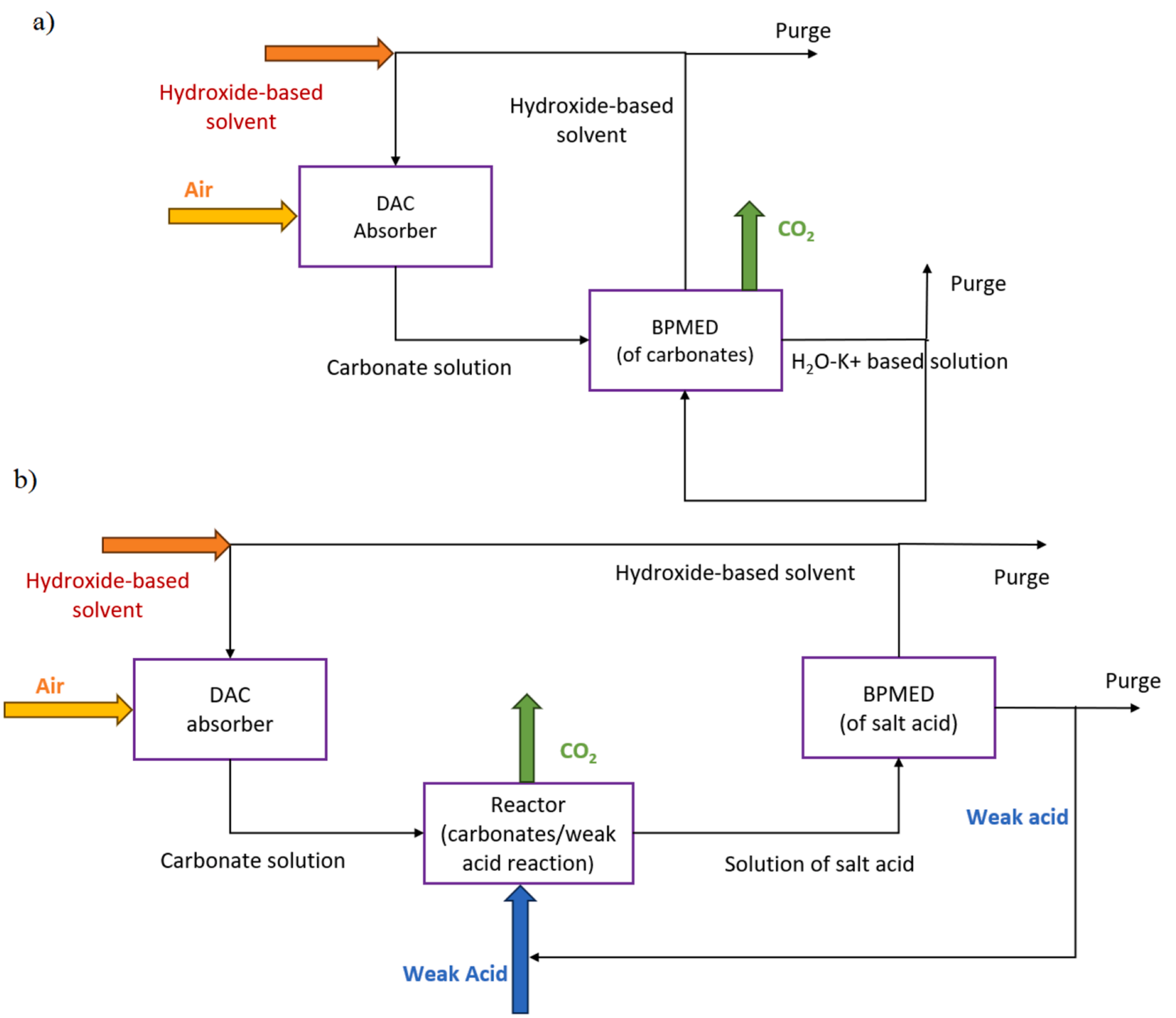

Fig. 1. Diagram block of the investigated processes: a) BPMED is used for the rich solution coming from the absorption column; b) BPMED is used for the solution of salt acid coming from the reactor.

$$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-} \quad (3)$$

Values of equilibrium constants for Eq. (1), Eq. (2), Eq. (3) are respectively 1.7×10^{-4} M, 4.5×10^{-7} M, 4.7×10^{-11} M (Vallejo-Castaño et al., 2025; Emerson and Hedges, 2008). In practice, in this model, the concentrations of dissolved CO_2 gas and hydrated dissolved CO_2 (the carbonic acid H_2CO_3) are lumped together (Emerson and Hedges, 2008). To solve the above equation system, the concentration of K^+ (K^+_{acid}) and H^+ in the acid solution must be found. To this aim, the total flux of cations (K^+, protons are neglected) that across the membrane is determined by the applied current density (Vallejo-Castaño et al., 2025) (See Eq. (4)):

$$J_{tot} = J_{K^+} = \frac{i \cdot A \cdot n}{F} \quad (4)$$

where i the current density (A/m^2) and F the Faraday constant (96,485 C/mol), A the membrane area (m^2) and n the number of cells. Setting the previous parameter, i, it is possible to evaluate the K^+_{acid} from the following equation related to the flux of K^+ (J_{K+} in mol/s) across the membrane (Vallejo-Castaño et al., 2025) (See Eq. (5)):

$$J_{K^+} = V_{rich} \cdot \left(K^+_{rich} - K^+_{acid}\right) \quad (5)$$

where the concentration of K^+in the rich solution (K^+_{rich}) entering the acid compartment is known as well as the volume of rich solution (V_{rich} in L/s). The value of pH (H^+ concentration) in the acid compartment is evaluated from the amount of H^+ generated by the bipolar membrane, as in Eq. (6), as well as from that present in the solution (Sharifian et al., 2021) (See Eq. (6)).

$$H^+_{produced\ from\ BPMED} = \frac{i \cdot A \cdot n}{F} \quad (6)$$

where $H^+_{produced\ from\ BPMED}$ the amount of protons produced from BPMED (mol/s), A the membrane area in (m^2), i the current density (A/m^2), F the Faraday constant (96,485 C/mol), n the number of cells. By adding this amount of moles with that already present in the solution and dividing by the volumetric flow rate (L/s), the value of pH can be obtained for the acid compartment.

The electrical conductivity (σ^*_{acid} in µS/cm) of the acid solution is calculated by the following correlations (Aqion, 2025; Vadakkepatt et al., 2015; Taqieddin et al., 2018) (See Eq. (7)–(10)):

$$I = \frac{1}{2} \cdot \sum_i z_i^2 \cdot c_i \quad (7)$$

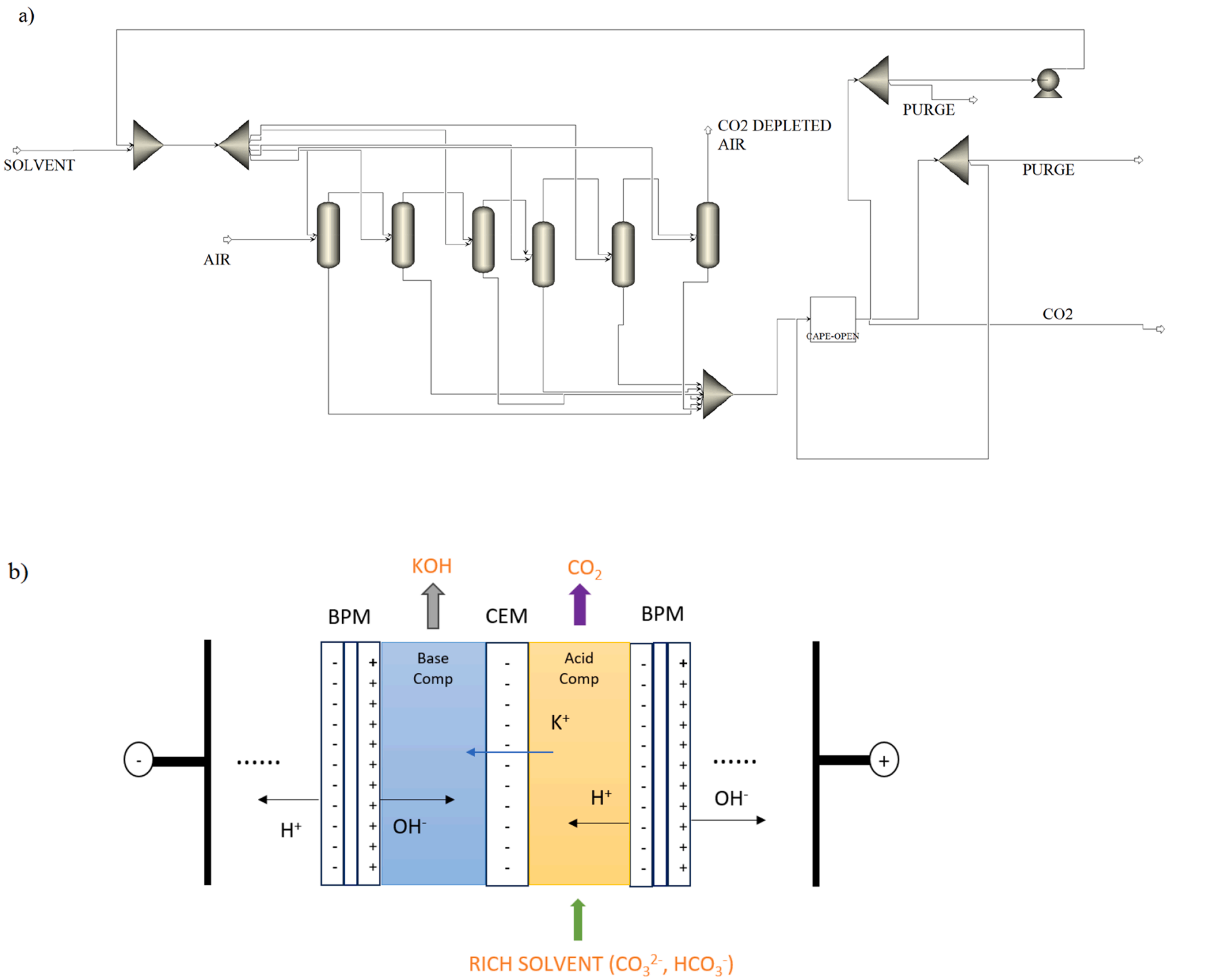

Fig. 2. a) Process flow of the process in the base case scenario developed in Aspen Plus software; b) Operating principle of the BPMED cell for the process in the base case scenario.

$$\sigma_{acid} = 6.2 \cdot 10^4 \cdot I \quad (8)$$

$$\varepsilon = \frac{V_g}{V_g + V_l} \quad (9)$$

$$\sigma^*_{acid} = \sigma_{acid} \cdot (1-\varepsilon)^{2.5} \quad (10)$$

where I the ionic strength in mol/L, z_i and c_i respectively the charge number and molar concentration of ion species i, σ_{acid} the electrical conductivity of solution without considering CO_2 bubbles (μS/cm), ε the gas void fraction of CO_2 gas bubbles in the acidic solution, V_g the CO_2 gas volume in the acidic compartment V_l the liquid volume in the compartment. Values of these parameters are taken from the simulation. The correction on electrical conductivity calculation is because CO_2 bubbles are perfect insulators increasing the overall resistance of the acid compartment due to a reduction of the effective membrane area (Sabatino et al., 2022). Bubbles are generated due to the extremely low solubility of CO_2 in the acid solution (Sabatino et al., 2020).

The alkaline compartment is modelled considering equilibrium, mass balance and electroneutrality equations. Equilibrium equations are related to the following reactions (See Eq. (11)–(13)) (Rouxhet et al., 2022):

$$CO_{2\ (aq)} + H_2O \leftrightarrow H_2CO_3 \quad (11)$$

$$H_2CO_3 + OH^- \leftrightarrow HCO_3^- + H_2O \quad (12)$$

$$HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O \quad (13)$$

where values of the equilibrium constant for Eq. (11), (12) and (13) are respectively 1.7×10^{-4} M, 4.25×10^7 M, $1 \times 10^{3.75}$ M (Rouxhet et al., 2022). For the mass balance, the total carbon concentration inside the alkaline compartment is fixed to be equal to that of the feed into it. The electroneutrality equation is considered in order to have a neutrally charged solution. The equation system can be solved by fixing the concentration of H^+ and K^+ in the alkaline solution. The K^+ concentration in the basic solution can be found considering the quantity of cations crossing the membrane from Eq. (5). On the other hand, the pH is evaluated by evaluating the amount of moles of OH^- ($OH^-_{produced\ from\ BPMED}$ (mol/s)) produced from the bipolar membrane by the following correlation (Sharifian et al., 2021) (See Eq. (14)):

$$OH^-_{produced\ from\ BPMED} = \frac{i \cdot A \cdot n}{F} \quad (14)$$

where i being the current density (A/m^2), F the Faraday constant and A the membrane area (m^2), n the number of cells. The value is added to the amount of OH^- present in the basic solution so that, after the evaluation of OH^- concentration, from the water dissociation constant (1×10^{-14})

the pH and then the concentration of H^+ in the solution is established.

The conductivity of the aqueous solution in the alkaline compartment is found according to Eq. (7) and (8), because no CO_2 bubbles are present here.

Overall, for the above model the following assumptions are considered: well mixed compartments (concentration gradients are not present inside the cell), ideal membrane behavior, no transport of neutral species through the membrane, equilibrium chemistry (chemical reactions are modelled as equilibrium reactions neglecting mass transfer limitations), isothermal conditions (a constant temperature is considered neglecting conductive heating effects), ideal gas assumption and steady state conditions (Vallejo-Castaño et al., 2025; Shaahmadi et al., 2025).

For the BPMED the following parameters are defined: membrane area equal to 1.785 m^2 and current density equal to 800 A/cm^2 (selected because it means fast reaction rates with a high product yield and a benefit of lower total costs as reported in Sabatino et al. (2020), number of cells equal to 105 to have 90 % of CO_2 recovered from the air stream at a fixed membrane area and current density. The liquid flow rate in the basic compartment is fixed with the aim to have a velocity in the range between 0.5–5 cm/s (Culcasi et al., 2021). The BPMED unit operates at ambient pressure. The electrolyte Non-Random Two-Liquid (e-NRTL) thermodynamic model is used for the simulation in Aspen Plus of the overall capture plant (Sabatino et al., 2022, 2021). The e-NRTL model is chosen based on its capability to accurately represent the interactions between CO_2, KOH, water, and the resulting ionic species in aqueous solutions (Shaahmadi et al., 2025).

2.1.2. Description of the capture plant with the reaction between bicarbonates/carbonates and formic acid

The capture plant in the formic acid scenario is characterized by the DAC absorption column section, a reactor and a BPMED stack unit, as reported in Fig. 3a. The formic acid is selected as an organic weak acid as suggested in the literature for carbonate stimulation (Alhamad et al., 2020a, 2020b). A reactor for the reaction among carbonates, coming from the absorption column, and formic acid is present to produce the potassium formate salt that is sent to the BPMED stack for the regeneration of the organic weak acid and alkaline solvent both recycled respectively to the reactor and absorption columns. Its operating principle is illustrated in Fig. 3b The potassium formate solution is sent to the acid compartment for the regeneration of acid and basic solution with the same principle as described for the conventional based process.

In the simulated plant, the characteristics of the 6 absorption columns are those defined in the base case scenario. A stoichiometric reactor, at 1 bar and 25 °C, is used to simulate the occurring reactions converting carbonates and bicarbonates, coming from the absorption section, into salt acid via reaction with an aqueous solution of formic acid (50 % w/w) (See Eq. (15)–(16)):

$$2{\cdot}CH_2O_2 + CO_3^{2-} \rightarrow 2{\cdot}CHO^{2-} + H_2O + CO_2 \tag{15}$$

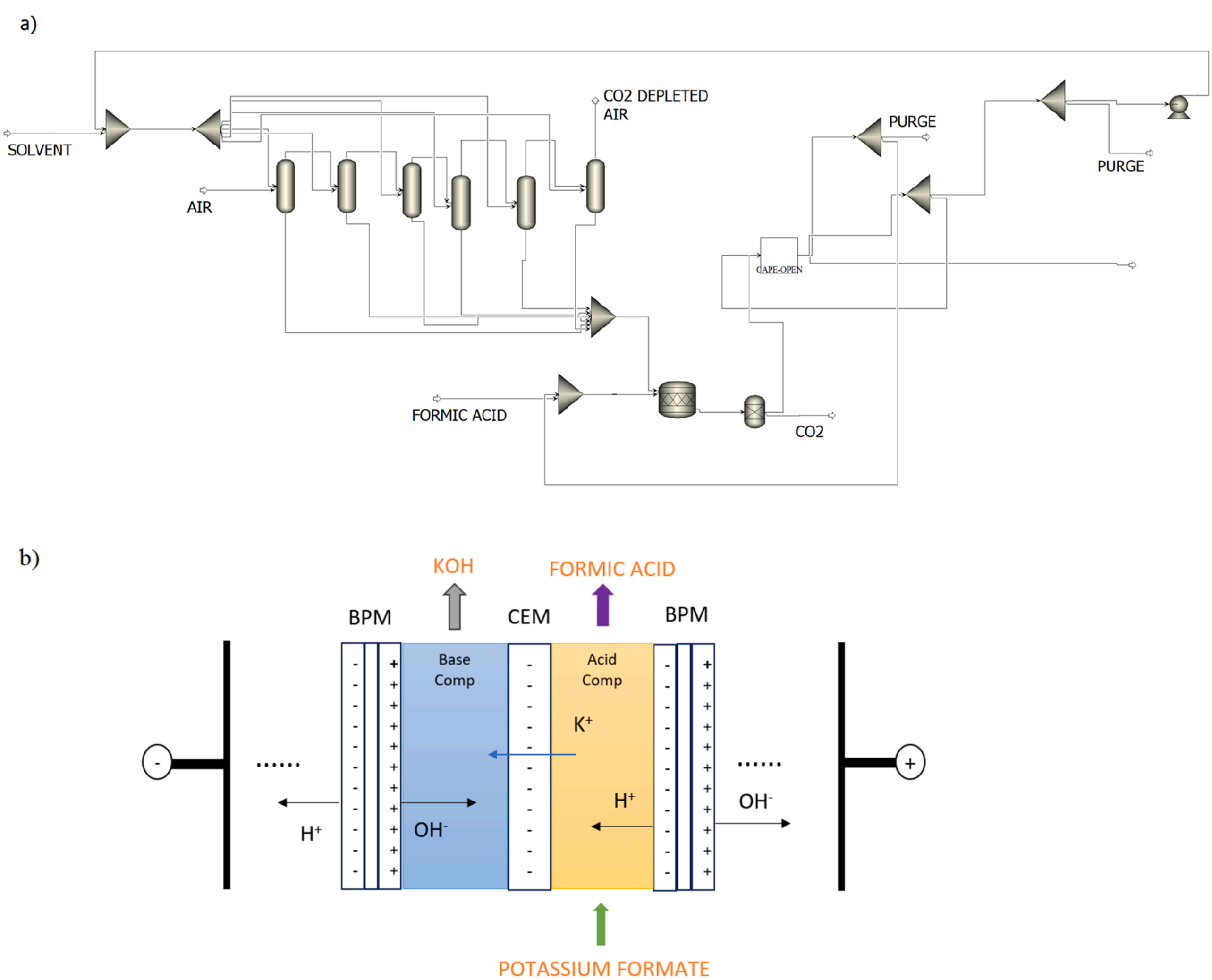

Fig. 3. a) Process flow of the process in the formic acid scenario developed in Aspen Plus software; b) Operating principle of the BPMED cell for the process in the formic acid scenario.

$$CH_2O_2 + HCO_3^- \rightarrow CHO^{2-} + H_2O + CO_2 \quad (16)$$

where a conversion fraction (based on feed of carbonate and bicarbonate) of 99 % is fixed in both reactions using a stoichiometric amount of acid.

The BPMED stack is modelled using the MATLAB Cape Unit Operation framework defining an acid and alkaline compartment both divided by a cation exchange membrane. In the first chamber, an equation system consisting of chemical equilibrium equations, electroneutrality and mass balance to keep constant the carbonate and formate concentration between the rich and acid solution is considered. The chemical equilibrium equations are related to the following reactions (see Eq. (17)–(20)) (Wang and He, 2025):

$$CO_{2\ (aq)} + H_2O \leftrightarrow H_2CO_3 \quad (17)$$

$$H_2CO_3 + H_2O \leftrightarrow H_3O^+ + HCO_3^- \quad (18)$$

$$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-} \quad (19)$$

$$HCOOH + H_2O \leftrightarrow HCOO^- + H_3O^+ \quad (20)$$

with values of equilibrium constants for Eq. (17), Eq. (18), Eq. (19) and Eq. (20) respectively 1.7×10^{-4} M, 4.5×10^{-7} M, 4.7×10^{-11} M and 1.8×10^{-4} M (Vallejo-Castaño et al., 2025; Emerson and Hedges, 2008; Chem, 2025). Considering, in addition, equations for electroneutrality and mass balances the overall model is solved evaluating at first the pH (H^+ concentration) and K_{acid}^+, as done for the previous base case scenario.

The conductivity of the aqueous solution in the acid chamber is evaluated by using Eq. (7) and (8) of Section 2.1.1, because in this case there are not CO_2 bubbles.

The basic compartment is modelled in the same way as for the base case scenario, described in Section 2.1.1. In order to have a fair comparison among the proposed process schemes, the same membrane area (1.785 m^2) and current density (800 A/cm^2) of the previous case study are set for the BPMED stack. Also in this case, the e-NRTL thermodynamic model is used for the simulation in Aspen Plus of the overall capture plant (Sabatino et al., 2022).

2.1.3. *Description of the capture plant with the reaction between bicarbonates/carbonates and formic/acetic acid mixture*

In this case study, the CO_2 capture plant scheme is the same as that described in Section 2.1.2, however, an aqueous mixture of formic/acetic acid (25 % w/w of formic acid and 25 % w/w of acetic acid) is used. Formic and acetic acids are, in fact, usually blended together (acetic provides retardation, formic increases blend strength) providing better results in carbonate stimulation (Alhamad et al., 2020a). The plant is simulated in Aspen Plus as in Fig. 4a.

The chemical reactions related to acetic acid are added in the reactor model and in the acid compartment of the BPMED stack. In fact, in the

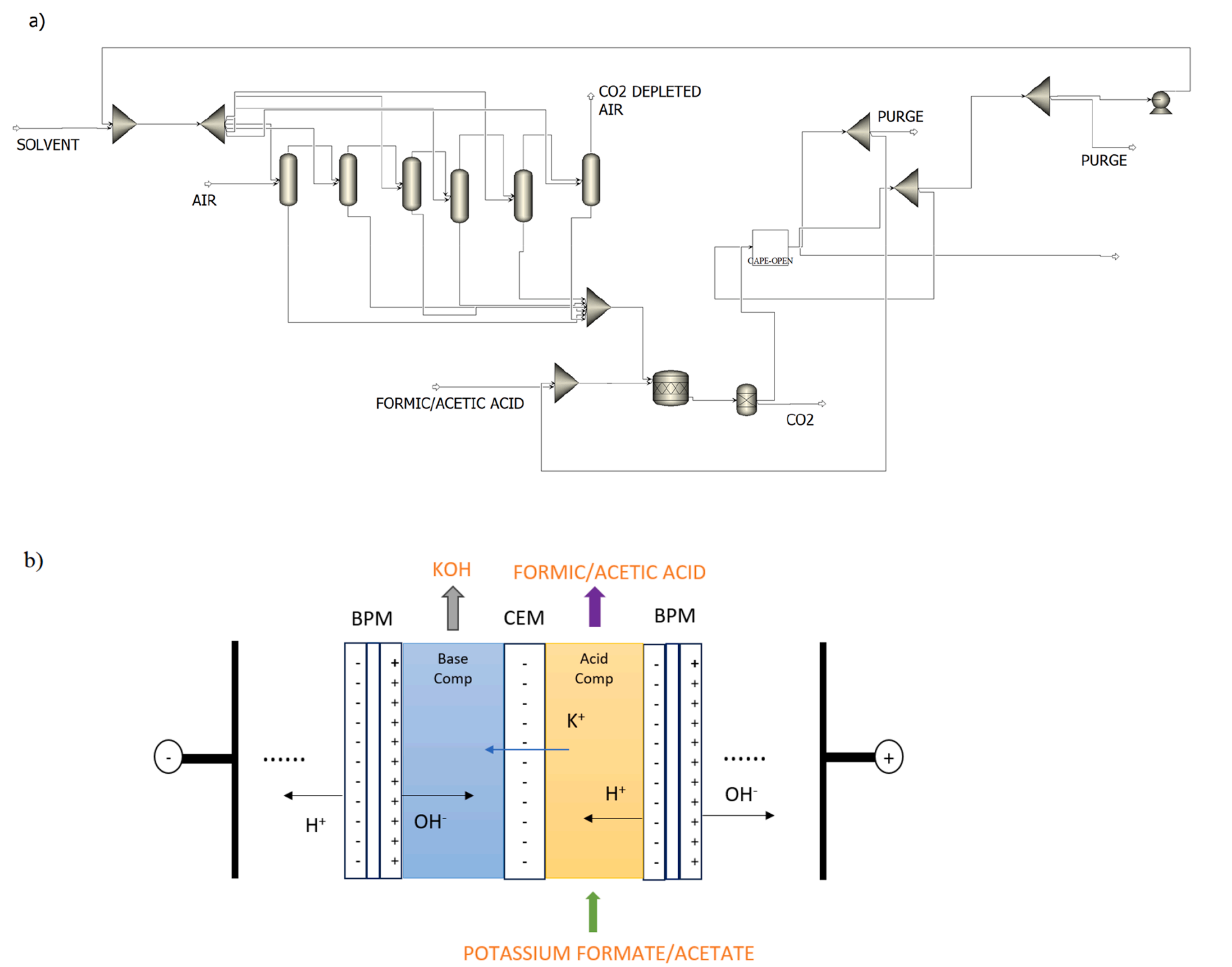

Fig. 4. a) Process flow of the process in the formic/acetic acid scenario developed in Aspen Plus software; b) Operating principle of the BPMED cell for the process in the formic/acetic acid scenario.

stoichiometric reactor, at 1 bar and 25 °C, the following reactions are involved (See Eq. (21)–(24)):

$$2\cdot CH_2O_2 + CO_3^{2-} \rightarrow 2\cdot CHO^{2-} + H_2O + CO_2 \tag{21}$$

$$CH_2O_2 + HCO_3^- \rightarrow CHO^{2-} + H_2O + CO_2 \tag{22}$$

$$2\cdot CH_3COOH + CO_3^{2-} \rightarrow 2\cdot CH_3O^{2-} + H_2O + CO_2 \tag{23}$$

$$CH_3COOH + HCO_3^- \rightarrow CH_3O^{2-} + H_2O + CO_2 \tag{24}$$

with an overall fraction conversion for carbonates and bicarbonates of 99 %. The amount of acid fed into the reactor is stoichiometric.

The BPMED stack is modelled according to the same principles described in Section 2.1.2 and as in Fig. 4b, however, the chemical equilibrium equations are updated to include acetic acid as follows (see Eq. (17)–20) (Wang and He, 2025):

$$CO_{2\ (aq)} + H_2O \leftrightarrow H_2CO_3 \tag{25}$$

$$H_2CO_3 + H_2O \leftrightarrow H_3O^+ + HCO_3^- \tag{26}$$

$$HCO_3^- + H_2O \leftrightarrow H_3O^+ + CO_3^{2-} \tag{27}$$

$$HCOOH + H_2O \leftrightarrow HCOO^- + H_3O^+ \tag{28}$$

$$CH_3COOH + H_2O \leftrightarrow CH_3O^{2-} + H_3O^+ \tag{29}$$

with values of equilibrium constants for Eq. (25), Eq. (26), Eq. (27), Eq. (28) and (29) respectively 1.7×10^{-4} M, 4.5×10^{-7} M, 4.7×10^{-11} M, 1.8×10^{-4} M and 1.75×10^{-5} M (Vallejo-Castaño et al., 2025; Emerson and Hedge, 2008; Chem, 2025). The conductivities of aqueous solutions with ions are evaluated as in the case study related to the reaction between carbonates and formic acid. Moreover, for a consistent comparison, dimensions and current density of the BPMED stack are defined in the formic acid scenario. Also in this case, the e-NRTL thermodynamic model is selected to simulate the process in Aspen Plus software.

2.2. Energetic and economic analysis modelling

Regarding the energetic analysis, the needed electric power for the BPMED is evaluated with the following correlations (See Eq. (30)–(33)) (Sabatino et al., 2020; 2022):

$$E_{cell} = i\cdot R_{cell} + E_{BP} \tag{30}$$

$$R_{cell} = R_{base} + R_{CEM} + R_{acid} + R_{BP} \tag{31}$$

$$R_{base/acid} = \frac{\delta}{\sigma_{base/acid}} \tag{32}$$

$$P_{cell} = i\cdot A\cdot N_{cell}\cdot E_{cell} \tag{33}$$

where E_{cell} the voltage drop across the BPMED cell, E_{BP} the water-splitting potential of the BPM (equal to 0.829 V for ΔpH of 14 (Sabatino et al., 2022)) (V), R_{cell} the electrical resistance of a unit area of a single cell (Ωm^2), i the current density (A/m^2), R_{base}, R_{acid}, R_{CEM} and R_{BP} respectively the resistance of basic and acid solution and cation and bipolar membrane (these two last are respectively equal to 1.5×10^{-4} Ωm^2 and 5.2×10^{-4} Ωm^2 (Sabatino et al., 2022)) (Ωm^2), $\sigma_{base/acid}$ the electrical conductivity of acid and base solutions, δ the distance between the BPM and cation membrane (1.5 mm (Sabatino et al., 2020)) (m), A the membrane area (m^2), N_{cell} the number of cells, P_{cell} the power of the BPMED unit (W).

In the economic analysis the CO_2 capture cost is evaluated from the sum of capital (CAPEX) and operating (OPEX) costs. The CAPEX in the form of total overnight capital (TOC) ($) is evaluated on the basis of the bare erected cost (BEC), as the sum of the purchase cost of all plant components, taken from the literature and from Aspen Plus Economic Analyzer (APEA): absorption columns from Sabatino et al. (2022, 2020), reactor and pump from APEA, BPMED stack from Virruso et al. (2024). For the total cost of membranes, an ion exchange membrane cost and bipolar membrane cost respectively are assumed at 145 \$/m^2 and 1300 \$/m^2 (Ankoliya et al., 2023). In particular, the total overnight capital (TOC) is evaluated in accordance with NETL guidelines (Spallina et al., 2016), as the sum of engineering, procurement and construction (EPC) ($) and total contingencies and owner's cost (C&OC) ($). The EPC is the sum of total direct plant cost (TDPC) ($) and indirect cost (IC) ($). TDPC is the sum of total installation cost (TIC) (evaluated as 80 % of BEC) ($) and bare erected cost (BEC) ($). The C&OC is found to be 15 % of EPC (10 % for contingency cost and 5 % for owner's cost). To have the annualized TOC ($/year), the above value is multiplied by a capital recovery factor using an interest rate of 8 % and plant lifetime of 25 years.

OPEX is evaluated as the sum of fixed and variable operating and maintenance cost (O&M) ($/year). In the fixed O&M there are labor, maintenance, insurance and membrane replacement costs. Labor costs ($/year) are scaled to that reported by Sabatino et (2022), claiming 1.5 M$/year for a capture capacity plant of 1 Mton$_{CO2}$/year. Maintenance costs ($/year) are 2.5 % of TOC. The insurance cost ($/year) is assumed to be 2 % of TOC while membrane replacement costs are found as the cost of membrane divided the replacement year (5 years for the scenarios with acid reaction (Virruso et al., 2024) and 3 years for the base case scenario (Sabatino et al., 2022, 2020)). In the variable O&M cost, the cost of raw materials and utilities is taken into account assuming a price for aqueous hydroxide solvent of 580 $/ton (Intratec, 2025), potassium carbonate of 600 $/ton, sustainable formic acid from CO_2 of 1738 $/ton (Cuevas-Castillo et al., 2025), sustainable acetic acid from CO_2 of 1170 $/ton (Regis et al., 2025) and renewable electricity from wind onshore in the UK of 0.05 $/kWh (OurWorldInData, 2025). The specific CO_2 capture cost is the sum TOC and OPEC divided the amount of captured CO_2.

To consider the volatility of electricity and raw material costs inside the market, a Monte Carlo analysis is carried out considering a variation of these parameters of ± 20 % of the nominal case study according to a uniform distribution.

2.3. Environmental analysis modelling

The LCA is conducted with OpenLCA software (version 1.11) and Ecoinvent database 3.9 accordingly with ISO 14040–14044 (ISO 14040, 2009; ISO 14044, 2006). This methodology includes four phases (goal and scope definition, life cycle inventory, life cycle impact assessment (LCIA) and life cycle interpretation). The goal of the study is the comparison of the three investigated processes from an environmental point of view with the scope to understand which of them is the most favorable. To this aim the functional unit is 1 ton$_{CO2}$ that is captured with cradle-to-gate system boundary (the end use of captured CO_2 is not considered in the analysis). In the inventory phase, inventory data (e.g. material and energy balances) for the processes are defined as taken from the simulation in Aspen Plus. For formic acid and acetic acid, a sustainable production process from CO_2 is considered as that reported in Cuevas-Castillo et al. (2025) and Regis et al. (2025). After these stages, the LCI results are organized into the usual LCA impact categories and then into the impact indicators at the midpoint level. The life cycle impact assessment is performed with the ReCiPe Midpoint (H) 2016 to obtain a general overview of the impact of the studied process on the different impact categories (climate change, terrestrial acidification, freshwater eutrophication, marine eutrophication, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, ionizing radiation and agricultural land occupation (Eke et al., 2025). In the interpretation phase, a comparison of the obtained results is carried out suggesting hot spots and with also a comparison with the literature, in addition to the sensitivity analysis evaluating the variability of impact categories at the operating parameters. In fact, a Monte Carlo analysis is developed to see how the considered impact categories are affected by the uncertainty of all inputs. To this scope an uniform distribution with a variation of ± 20 % of the nominal value is taken into account for all inputs to the system.

2.4. Marginal abatement cost equation

The formula for the evaluation of the marginal abatement cost (MAC in $/ton$CO_{2eq}$) is reported in the following equation (See Eq. (34)) (Huang et al., 2022; Misconel et al., 2022):

$$MAC = \frac{\Delta TC}{\Delta CO_2} = \frac{\left(Cost_{Tech,2} - Cost_{Tech,ref}\right) - B}{CO_{2\ emission\ in\ tech,\ ref} - CO_{2\ emission\ in\ tech,\ 2}} \tag{34}$$

where the $Cost_{Tech,2}$ is the CO_2 capture cost for the considered technology ($/ton$CO_2$ captured), $Cost_{Tech,ref}$ is the CO_2 capture cost for the reference technology, B benefit/economic incentives for the captured CO_2 ($/ton$CO_2$ captured) (set at 100 $/ton$CO_2$ captured (Catf, 2025)), $CO_{2,emission\ in\ tech,ref}$ the CO_2 emitted in the capture reference technology (tonCO_{2eq}/tonCO_2 captured) and $CO_{2,emission\ in\ tech,2}$ the CO_2 emitted in the considered technology (tonCO_{2eq}/tonCO_2 captured). While the absolute cost ($/ton$CO_2$ captured) analyzes the engineering cost of the capture unit, the marginal abatement cost ($/ton$CO_{2eq}$) compares mitigation strategies or informs climate policy. In the above formula, only positive values of ΔCO_2 are considered (the alternative system has lower net CO_2 emissions compared to the reference system). In these conditions, if ΔTC is positive means that the investigated CO_2 reduction technology has higher costs compared to the reference one, while if ΔTC is negative means that the considered technology is profitable compared to the reference one (Huang et al., 2022).

The reference technologies that are considered in this analysis are the adsorption DAC process based on 3-aminopropylmethyldiethoxysilane (APDES) grafted onto nano-fibrillated cellulose (NFC) sorbent (Leonzio et al., 2022a) and the absorption DAC process using thermal energy as in the Carbon Engineering plant (Keith et al., 2018; Eke et al., 2025).

The MAC is used to generate the marginal abatement cost curve (MACC) as a method to assess the economy of measures to reduce greenhouse gases emissions such as CO_2. The MACC shows the MAC on the y-axis associated with the cumulative CO_2 emission reduction on the x-axis over 15 years (until 2040).

3. Results and discussion

3.1. Results of process modelling

In all simulations, the kinetic model of the absorption column is validated with the experimental data of Keith et al. (2018): a CO_2 recovery of 76 % is obtained as that reported in the literature. Moreover, it is ensured that no flooding conditions occur inside the columns. The BPMED stack is validated with data reported by in Sabatino et al. (2020): with a flow rate of the rich solution (2500 kmol/h) and a KOH, K_2CO_3, $KHCO_3$ compositions equal to 0.0053 M, 0.217 M and 0.0014 M, the KOH composition in the lean flow rate has a difference compared to that in Sabatino et al. (2020) of about 3 %. Moreover, as the stack unit is modelled with a MATLAB code, all material balances (inputs less outputs) for the three scenarios are verified as reported in the Supplementary Materials (Tables S1-S3).

Table 1 reports the overall material and energy balances (classified as air fed into the absorption columns, solvents such as that used in the absorption columns and acids fed into the reactor, energy requirement, emissions, wastewater and captured CO_2). It is possible to see that the process without acid reaction has a higher efficiency in terms of CO_2 capture rate at 1142 tonCO_2/year are captured against 959 tonCO_2/year and 949 tonCO_2/year respectively for the formic acid and formic/acetic acid scenario. In all case studies, the feed flow rate of air and alkaline solvent to the absorption column is kept the same and equal to 5229 kmol/h and 3137 kmol/h respectively (L/G is 0.6). The higher efficiency of the system regenerating CO_2 from the electrodialysis of carbonates and bicarbonates is due the fact that in this system the total dissolved organic carbon is conserved while in the acid reaction-based process CO_2 is produced not after a redistribution of carbonates because it is a chemical transformation.

Regarding energy consumption, the process with the highest electricity demand is that without the reaction between the weak organic acid and bicarbonates and carbonates coming from the absorption columns (2314 kWh/tonCO_2 are needed) while the system involving the formic acid reaction requires the lowest energy consumption (1907 kWh/tonCO_2). 18 % of reduction in energy requirement is measured compared to the previous process. On the other hand, the process with the rection between formic/acetic acid mixture and carbonates and bicarbonates requires 1943 kWh/tonCO_2 (16 % lower compared to the process releasing CO_2 in the BPMED stack). In any case, these values are

Table 1
Material and energy balances for the three investigated processes.

Inputs		Base case scenario	Formic acid scenario	Formic/acetic acid scenario
Air				
N_2	ton/tonCO_2	889	1042	1053
H_2O	ton/tonCO_2	11	13	14
CO_2	ton/tonCO_2	0.69	0.81	0.818
O_2	ton/tonCO_2	269	315	319
H_2CO_3	ton/tonCO_2	0.017	0.0196	0.02
Solvent				
KOH	ton/tonCO_2	0.05	0.022	0.025
Formic acid	ton/tonCO_2		0.012	0.008
Acetic acid	ton/tonCO_2			0.008
K_2CO_3	ton/tonCO_3	0.018	0.068	0.068
Energy consumption				
Electricity	kWh/tonCO_2	2314	1907	1943
Outputs				
Captured CO_2				
CO_2	ton	1	1	1
CO_2	ton/year	1142	959	949
Emissions				
N_2	ton/tonCO_2	889	1042	1053
H_2O	ton/tonCO_2	16	21	21
CO_2	ton/tonCO_2	0.03	0.028	0.04
O_2	ton/tonCO_2	269	315	319
Waste water				
Purge	ton/tonCO_2	0.31	0.53	0.556

higher compared to the similar thermal process developed by Carbon Engineering suggesting an energy demand of 1726 kWh/tonCO_2 (Sabatino et al., 2022). The lower energy consumption for the system using formic acid is due to a very low specific energy required to regenerate this acid from its salt: 2.6 kWh/kg of formic acid (Handojo et al., 2019; Ferrer et al., 2006). On the other hand, energy consumption for recovery of acetic acid from its salt can be up to 15.7 kWh/kg of acetic acid (Wang et al., 2011). Then the presence of acetic acid in the mixture increases the energy demand for CO_2 capture.

The highest energy demand, for the process releasing CO_2 without a chemical reaction, is due to the CO_2 bubble formation inside the cells that causes a reduction of electrical conductivity of the acid solution, and hence an increase of resistance of the same solution that increases at the same time the cell voltage and as well as the overall power. Values of this electrical consumption agree with that reported in the literature by Sabatino et al. (2020; 2022) and Eisaman et al. (2011) where energy consumption up to 3789 kWh/tonCO_2 are reported when varying current density and composition of the rich solution. Similar values are reported by Vallejo-Castaño et al. (2025), Shu et al. (2023) analyzing the same process under different sensitivity analyses. For the other two processes, a direct comparison with literature cannot be conducted because a similar process has not been considered for CO_2 capture yet before. The only similar process that is reported in the state-of-the art is using an aqueous solution of sodium hydroxide (NaOH) for the absorption column and sulfuric acid for the reaction with bicarbonates and carbonates: here a consumption of 328 kWh/tonCO_2 is reported (Valluri and Kawatra, 2021). However, this process is proposed for the post-combustion CO_2 capture and not for DAC application as in this research. Overall, these results show that more efforts are directed toward reducing these energy requirements and optimizing BPM for more efficient and largescale CO_2 recovery thanks to other research suggesting the potentiality of BPED stack to recover acids (Zhou et al., 2025; Yan et al., 2025). This includes developing a continuum model for multi-ion transport in BPM, focusing on internal concentration polarization and ion crossover, key factors in determining ion transport modes (Khoiruddin et al., 2024). The future target is energy consumption below 947 kWh/tonCO_2 (Bui et al., 2023).

Regarding the alkaline solvent used to absorb CO_2 from the air, a higher specific amount of aqueous KOH is needed in the base case scenario (0.05 tonKOH/tonCO_2) compared to the other case studies where 0.022 tonKOH/tonCO_2 and 0.025 tonKOH/tonCO_2 are required respectively for the case with formic acid and formic/acetic acid mixture. This means that a lower regeneration of KOH is present in the base scenario, compared to the other two processes. On the other hand, an opposite picture is present for the K_2CO_3: a specific consumption of 0.018 tonK_2CO_3/tonCO_2 and 0.068 tonK_2CO_3/tonCO_2 are needed for the case without and with acid reaction.

For acid consumption, the minimum amount required ensures the desired conversion is evaluated in Aspen Plus and equal respectively to 0.012 ton/tonCO_2 for formic acid in the formic acid scenario and 0.008 ton/tonCO_2 for formic and acetic acid in the respective scenario.

Another input in the process is the air fed to the absorption column train. Even though the absolute amount of air is the same in all case studies, the specific requirement is different due to the different amounts of CO_2 being captured. Hence higher specific amounts of N_2, humidity, CO_2, O_2 and carbonic acid are present in processes with acid reaction.

Regarding the outputs, emissions, waste waters and captured CO_2 are considered. The process with the reaction of carbonates/bicarbonates with the acid mixture has higher wastewater production (0.556 ton/tonCO_2) followed by other processes using acid (0.53 ton/tonCO_2) and the base case scenario (0.31 ton/tonCO_2). Regarding emissions from the last final column to (e.g. depleted CO_2 air), higher specific values are for the process using the acid mixture followed by the formic acid scenario and then by the base case scenario (but for CO_2 emission into the air the lowest value is for the process using formic acid to react with carbonates and bicarbonates).

In all three investigated processes, the velocity of alkaline solution in the base compartment is found to be lower than 5 cm/s: 4.42 cm/s for the process with formic/acetic acid mixture scenario, 4.7 cm/s for the process with formic acid scenario and 4.9 cm/s for the process in the base case scenario. These values are in agreement with those in the literature (0.5–5 cm/s) (Culcasi et al., 2021). This ensures good performance of the cell. For the acid compartment, slightly higher values are obtained for the acid solution: 7.1 cm/s for processes involving acid reaction and 7 cm/s for the process without acid reaction. These values are still acceptable as reported in Merkel et al. (2024).

The K^+ transport efficiency parameter is evaluated too, according to Liu et al. (2024b). Results show that an efficiency of 100 % is present for all proposed processes. In fact, it is assumed that other ions are not crossing the membrane so that competitive transport is not present.

It is interesting to compare the energy consumption of the closed-loop BPMED system with the ex-situ BPMED one recovering formic acid and acetic acid from its salt. The ex-situ process recovering formic acid and acetic acid requires respectively 2.6 kWh/kg of formic acid produced (Ferrer et al., 2006) and 5.1 kWh/kg of acetic acid produced (Zhou et al., 2025). In our closed loop process, we have 0.89 kWh/kg of formic acid (in the process using only formic acid as reactant) and 1.39 kWh/kg of acetic acid (in the process using the mixture formic/acetic acid as reactant) saving respectively 65 % and 72 % of energy demand compared to the ex-situ configuration. Results show that the alternative process for CO_2 capture has energetic advantages compared to the conventional one based on BPMED stack, but also better performances compared to ex situ processes for acid recovery from the respective salt.

3.2. Results of economic analysis

Table 2 shows the results for the economic analysis of the three processes investigated in terms of TOC, total fixed O&M, total variable O&M and total capture cost. It is possible to see that the process with the highest CO_2 capture cost is the recovery of the formic and acetic acid mixture in a BPMED, at 519 \$/tonCO_2. The lowest cost is for the process without involving acid (base case scenario) with 480 \$/tonCO_2. This last value is in line (e.g. the same order of magnitude) with studies reported in the literature from Sabatino et al. (2020; 2022), Iizuka et al. (2012). On the other hand, the process recovering formic acid has a cost of 510 \$/tonCO_2. For processes based on reaction between the weak organic acid and carbonates and bicarbonates coming from the absorption section, an economic comparison with the literature is not available. The total CO_2 capture cost of these electrified processes is higher compared to that reported by Carbon Engineering developing an equivalent thermal process for which Keith et al. (2018) estimate a capture cost of 232 \$/tonCO_2. The reason of that is due to the worse air contactor performance and a more expensive energy source (Sabatino et al., 2022). In addition to working on these two aspects, reducing membrane resistivity

Table 2
Results of the economic analysis for the investigated processes.

	Base case scenario	Formic acid scenario	Formic/acetic acid scenario
Total overnight cost (TOC) (\$/tonCO_2)	165	229	231
Total fixed O&M (\$/tonCO_2)	161	111	112
Total variable O&M cost (\$/tonCO_2)	153	170	176
Total cost (\$/tonCO_2)	480	510	519

Table 3
Detailed economic results for the investigated processes.

		Base case scenario	Formic acid scenario	Formic/acetic acid scenario
BEC	$	852,349	992,049	990,149
Total installation cost (TIC)	$	681,879	793,639	792,119
Total direct plant cost (TDPC)	$	1534,228	1785,688	1782,268
Indirect cost (IC)	$	214,792	249,996	249,517
Engineering, procurement and construction (EPC)	$	1749,020	2035,684	2031,785
Contingencies and owner’s cost				
Contingency	$	174,902	203,568	203,179
Owner’s cost	$	87,451	101,784	101,589
Total contingencies and owner’s cost (C&OC)	$	262,353	305,353	304,768
Total overnight cost (TOC)	$	2011,373	2341,037	2336,553
Total overnight cost (TOC)	$/year	188,423	219,305	218,885
Labor	$/year	1713	1438	1423
Maintenance	$/year	50,284	58,526	58,414
Insurance	$/year	40,227	46,821	46,731
Membrane replacement	$/year	91,823	55,094	55,094
Total fixed O&M	$/year	184,048	106,785	106,568
Electricity	$/year	129,980	91,410	92,177
KOH	$/year	32,832	12,347	13,648
K_2CO_3	$/year	12,277	38,970	38,970
Formic acid	$/year		20,376	13,169
Acetic acid				8609
Total variable O&M cost	$/year	175,089	163,104	166,572
Total capture cost	$/ton$CO_2$	480	510	519

could help to reduce specific energy consumption (SEC) and therefore specific capture costs (Sabatino et al., 2022).

Regarding the TOC, total fixed O&M and total variable O&M, their value is equal to 165 \$/tonCO_2, 161 \$/tonCO_2 and 153 \$/tonCO_2 respectively for the process in the base case scenario. For the process using formic acid, their value is respectively equal to 229 \$/tonCO_2, 111 \$/tonCO_2 and 170 \$/tonCO_2. On the other hand, for the process involving the mixture acid, TOC, total fixed O&M and total variable O&M are respectively of 231 \$/tonCO_2, 112 \$/tonCO_2 and 176 \$/tonCO_2. Overall, the processes using the weak organic acid have a higher TOC and total variable O&M but a lower total fixed O&M compared to the process in the base case scenario. The lower total fixed O&M is due to a lower membrane replacement cost (the membrane replacement occurs in fact every 5 years). The influence of membrane lifetime on total costs is also reported in Sabatino et al. (2020). The higher TOC is due to a more complex process with more equipment while, the higher total variable O&M is due to a higher consumption of raw materials (acid is used in comparison with the base case scenario). Moreover, OPEX costs have a higher impact on total costs in all processes investigated (66 % for the base case scenario, 55 % for the other systems). This agrees with works from Sabatino et al. (2022, 2020).

Detailed results of the economic analysis are reported in Table 3. Considering the total variable O&M costs, it results that electricity consumption has the highest contribution at 74 % for the process in the base case scenario, 56 % for the process with formic acid scenario and 55 % for the process involving the acid mixture. This is in line with the literature of Sabatino et al. (2022; 2020) and Wang and He (2025). Moreover, it suggests that by reducing the renewable electricity price, the total capture cost of the process could be decreased, allowing operation at higher current density able to ensure a higher capture rate or capital productivity. For the first above-mentioned process, hydroxide solvent and potassium bicarbonate influence the total variable O&M at 19 % and 7 % respectively. For the other processes recovering acid from their salt, potassium bicarbonate has a higher impact with about 24 % while the hydroxide solvent impact only for about 8 %. On the other hand, in the process based on formic acid recovery, the cost of this acid influences the total variable O&M at 12 %, while the impact of formic acid and acetic acid on the other process is respectively 8 % and 5 %.

Regarding the total fixed O&M, in all investigated processes, the highest impact is from the membrane replacement, contributing to almost 50 %. However, for the process in the base case scenario, a higher cost for this term is obtained (91,823 \$/year compared to 55,094 \$/year of the process using weak organic acids). More research and efforts must be made to improving the membrane lifetime to reduce total fixed O&M and therefore the overall CO_2 capture cost. It is also reasonable to assume that by 2050 cheaper and more resistant membranes (e.g. in addition to functional inorganic particles to the polymer phase to improve the thermal and mechanical stability) would be produced. Due to a higher TOC, the processes involving acid have a greater value for maintenance and insurance cost respectively about 58 k\$/year and 46 k \$/year. In the base case scenario, the maintenance costs 50,284 \$/year while the insurance costs 40,227 \$/year. The labor cost is impacting about 1 % of the total fixed O&M in all case studies.

For the TOC, the term with the highest contribution (87 %) is the that related to engineering, procurement and construction, in all case investigated processes. Total contingencies and owner’s cost influence the TOC for 13 %. For the BEC, the highest cost is for the process with formic acid with a value of 992,000 \$, followed by the other process involving the acid mixture with a value of 990,000 \$ and the base case scenario with a value of 852,000 \$. In the system recovering both acetic and formic acids in the BPMED stack, absorption columns cost 433,000 \$

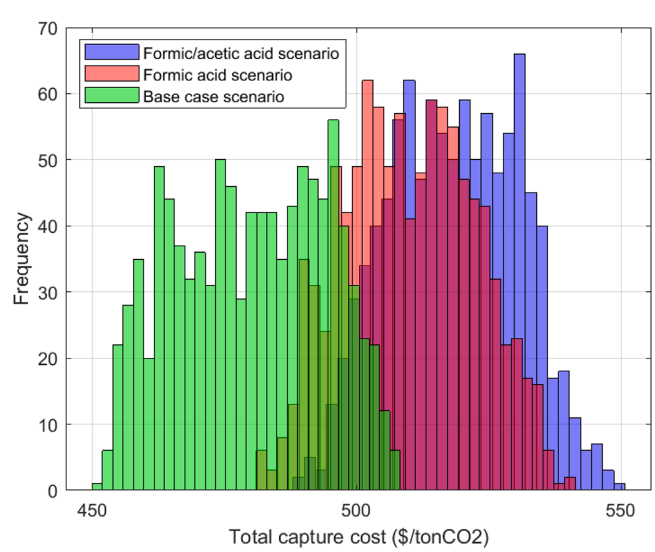

Fig. 5. Results of Monte Carlo sensitivity analysis for CO_2 capture cost for all investigated processes (number of points=1000).

Table 4
Results of LCA for the investigated processes.

	Base case scenario	Formic acid scenario	Formic/acetic acid scenario
Climate change ($kgCO_{2eq}/kgCO_2$)	−0.9593	−0.9378	−0.9238
Terrestrial acidification ($kgSO_{2eq}/kgCO_2$)	0.0001929	0.00025789	0.00031829
Freshwater eutrophication ($kgP_{eq}/kgCO_2$)	0.00002179	0.00002791	0.00003436
Marine eutrophication ($kgN_{eq}/kgCO_2$)	0.000015	0.00001964	0.00002275
Terrestrial ecotoxicity ($kg1–4DB_{eq}/kgCO_2$)	0.0000104	0.0000153	0.0115744
Freshwater ecotoxicity ($kg1–4DB_{eq}/kgCO_2$)	0.0139623	0.0139719	0.0175396
Marine ecotoxicity ($kg1–4DB_{eq}/kgCO_2$)	0.0121855	0.01222136	0.0154165
Ionising radiation ($kgU235_{eq}/kgCO_2$)	0.002614	0.0039173	0.0052471
Agricultural land occupation ($m^2a/kgCO_2$)	0.0026163	0.00420663	0.0047891

as from the literature in Sabatino et al. (2022; 2020), pump cost 4300 $ and reactor cost 139,600 $ from APEA and the BPMED stack costs 413, 205 $ as from Virruso et al. (2024). For the process recovering only formic acid in the BPMED stack, the absorption columns cost 433,043 $ (Sabatino et al., 2022; 2020), pump and reactor cost respectively 4300 $ and 141,500 $ from the APEA while the BPMED stack costs 413,205 $ (Virruso et al., 2024). In the other process recovering CO_2 directly from the BPMED, the absorption column train and BPMED stack cost as in the previous schemes (e.g. 433,043 $ and 413,205 $ respectively) while the recycling pump has a cost of 6100 $. Inside the TOC analysis, total installation cost, total direct plant cost and indirect cost for the process in the base case scenario are respectively 681,880 $, 1534,200 $, 214, 800 $. For the system using formic acid to release CO_2, total installation cost, total direct plant cost and indirect cost are respectively 793,639 $, 1785,688 $ and 249,996 $. On the other hand, for the process recovering CO_2 through the mixture between formic and acetic acid these values are respectively 792,100 $, 1782,300 $ and 249,500 $. Contingency cost for the process in the base case scenario, formic acid scenario and formic/acetic acid scenario are respectively 174,900 $, 203,600 $ and 203, 200 $. On the other hand, owner's cost for these processes is respectively 87,500 $, 10,200 $, 101,600 $.

A Monte Carlo sensitivity analysis is carried out changing the cost of utilities and raw materials inside the range equal to ± 20 % of the nominal case, described above. Results are reported in Fig. 5. Despite the uncertainty analysis, the process with the release of CO_2 from the BPMED is that with the lowest capture cost, even though it can have higher costs compared to the process releasing CO_2 via formic acid reaction. The highest costs are obtained with the process based on the formic acetic acid mixture, as in the nominal case study.

Overall, this economic analysis shows that despite the higher energy consumption, the process in the base case scenario has a slightly lower capture cost compared to those involving reaction of carbonates and bicarbonates with a weak acid to release CO_2. This result is due to the lower TOC and higher CO_2 capture rate occurring in the conventional process. We note that, working at high operating pressure of 20–30 bar can partially overcome the CO_2 bubble problem even though the CO_2 solubility in water is still limited (Sabatino et al., 2022).

Also for the economic analysis it is interesting to compare the cost of the closed loop BPMED process for acid recovery with the ex-situ configuration. For this last one option, 4.6 $/kg of formic acid and 8.65 $/kg of acetic acid are needed according to the literature (Zhou et al., 2025). Our alternative processes cost 0.22 $/kg of formic acid and 0.34 $/kg of acetic acid respectively for the system with formic acid as reactant and mixture acetic/formic acid as reactant, saving about 95 % of money in both cases.

3.3. Results of environmental analysis

Results of the LCA, in terms of climate change, terrestrial acidification, freshwater eutrophication, marine eutrophication, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, ionizing radiation and agricultural land occupation are reported in Table 4. The inventory data are those reported in Table 1.

It is possible to see that values of climate change for the process in the base case scenario, formic acid scenario and formic/acetic acid scenario are respectively equal to −0.9593 $kgCO_{2eq}/kgCO_2$, −0.9378 $kgCO_{2eq}/kgCO_2$ and −0.9238 $kgCO_{2eq}/kgCO_2$. Then, recovering CO_2 from carbonates via BPMED ensures the lowest environmental burden in terms of climate change, followed by the process whit a reaction between bicarbonates/carbonates and formic acid and then followed by the process with a reaction between bicarbonates/carbonates with the acetic/formic acid mixture. Results for the system based on electrodialysis of carbonates are in agreement with the literature (Leonzio and Shah, 2025). For the other systems, a direct comparison with the state-of-the-art is not possible.

For the process based on CO_2 recovery by using a BPMED the highest contribution to climate change is electricity consumption (0.02852 $kgCO_{2eq}/kgCO_2$), followed by the potassium carbonate production (0.00935 $kgCO_{2eq}/kgCO_2$) and potassium hydroxide production

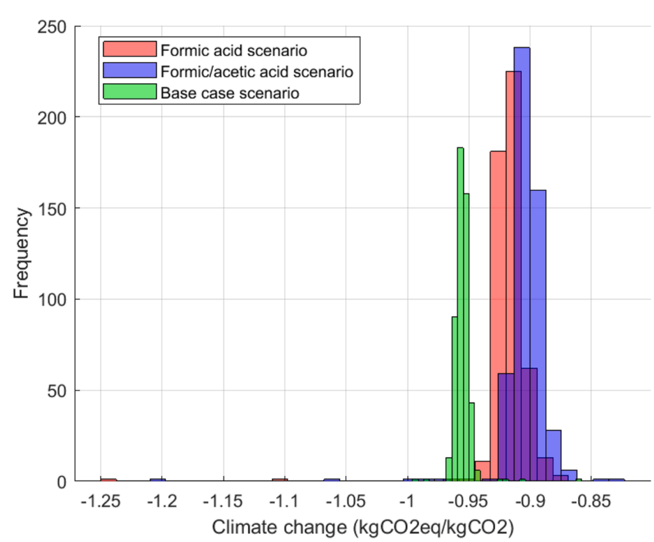

Fig. 6. Results of Monte Carlo sensitivity analysis for climate change impact for all investigated processes (number of points=500).

(0.00285 $kgCO_{2eq}/kgCO_2$). For the process scheme based on the regeneration of formic acid from its salt, potassium carbonate production is the highest hotspot (0.03514 $kgCO_{2eq}/kgCO_2$), followed by electricity production by wind energy (0.02351 $kgCO_{2eq}/kgCO_2$), formic acid production (0.00232 $kgCO_{2eq}/kgCO_2$) and potassium hydroxide production (0.00125 $kgCO_{2eq}/kgCO_2$). On the other hand, for the process based on the reaction between bicarbonates and carbonates with the formic/acetic acid mixture, the main hotspot is the potassium carbonate production (0.03551 $kgCO_{2eq}/kgCO_2$), followed by electricity generation via wind energy (0.0309 $kgCO_{2eq}/kgCO_2$), acetic acid production (0.00685 $kgCO_{2eq}/kgCO_2$), formic acid production (0.00151 $kgCO_{2eq}/kgCO_2$) and potassium hydroxide production (0.0014 $kgCO_{2eq}/kgCO_2$).

Considering other impact categories, it emerges that the process using the BPMED stack unit to release CO_2 has the lowest environmental impact. In fact, terrestrial acidification, freshwater eutrophication, marine eutrophication, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, ionizing radiation and agricultural land occupation are respectively 0.0001929 $kgSO_{2eq}/kgCO_2$, 0.00002179 $kgP_{eq}/kgCO_2$, 0.000015 $kgN_{eq}/kgCO_2$, 0.0000104 $kg1{-}4DB_{eq}/kgCO_2$, 0.0139623 $kg1{-}4DB_{eq}/kgCO_2$, 0.0121855 $kg1{-}4DB_{eq}/kgCO_2$, 0.002614 $kgU235_{eq}/kgCO_2$ and 0.0026163 $m^2a/kgCO_2$. This process ensures the lowest environmental burden not only for climate change but also for other considered impact categories.

The highest environmental impact for all impact categories is for the process recovering CO_2 via a reaction between carbonates and formic/acetic acid mixture. In fact, the value of terrestrial acidification is 0.00031829 $kgSO_{2eq}/kgCO_2$, freshwater eutrophication is 0.00003436 $kgP_{eq}/kgCO_2$, marine eutrophication is 0.00002275 $kgN_{eq}/kgCO_2$, terrestrial ecotoxicity is 0.0115744 $kg1{-}4DB_{eq}/kgCO_2$, freshwater ecotoxicity is 0.0175396 $kg1{-}4DB_{eq}/kgCO_2$, marine ecotoxicity is 0.0154165 $kg1{-}4DB_{eq}/kgCO_2$, ionizing radiation is 0.0052471 $kgU235_{eq}/kgCO_2$ and agricultural land occupation is 0.0047891 $m^2a/kgCO_2$.

The other process releasing CO_2 via a formic acid reaction has a lower environmental impact compared to the above system. In particular, terrestrial acidification, freshwater eutrophication, marine eutrophication, terrestrial ecotoxicity, freshwater ecotoxicity, marine ecotoxicity, ionizing radiation and agricultural land occupation are respectively 18.9 %, 18.8 %, 13.6 %, 99.8 %, 20.3 %, 20.7 %, 25.3 % and 12 % lower compared to the respective value in the system using a mixture of formic and acetic acid reacting with carbonates in the rich solution.

The Monte Carlo analysis is conducted for the climate change impact category, as reported in Fig. 6.

Results show that even with uncertainty conditions, the process with release of CO_2 via carbonate electrodialysis has the lowest impact in terms of climate change. Despite the lower impact for the process using formic acid, both processes using a weak organic acid are comparable in variability of all inputs. These results show the stronger potential of base case scenario process to be marginally more environmentally friendly compared to the other solutions.

Table 5 shows the values of correlation factors between the changed inputs and capture cost and climate change impact. For the economic aspect the electricity price has the highest impact on total cost; on the other hand, for the environmental impact, the electricity consumption has the highest impact in the base case scenario while the potassium carbonate production dominates the variance in the alternative capture processes.

3.4. Results of MACC

Marginal abatement cost curves are presented here to show the convenience of the proposed processes compared to the absorption DAC technology based on thermal energy (as in the Carbon Engineering plant) (as shown in Fig. 7) and compared to the adsorption DAC technology based on APDES-NFC-FD sorbent (like Climeworks plant) (as shown in Fig. 8). The abatement cost ($\$/tonCO_{2eq}$) as a function of the amount of CO_2 reduced during the 2025–2040 period is reported. In this analysis other DAC systems based on the use of electricity, as studied in Leonzio and Shah (2025) are also considered and compared to have a fully picture of several electrochemical DAC technologies. These systems are the electrolysis, electro-swing adsorption (ESA), proton coupled electron transfer (PCET) based processes located in the European Union (EU), in 2023 year, using electricity from nuclear, solar (PV), wind on-shore and wind off-shore energy. All of these are baselined to capture 1 $MtonCO_2$/year.

From Fig. 7 it is possible to see that the bar of processes investigated in this research is above the x-axis: these CO_2 reduction technologies have higher costs compared to the DAC absorption using thermal energy for solvent regeneration and CO_2 release. These results are clearly demonstrated by the above analyses showing a higher cost and energy consumption of the proposed solutions compared to that of Carbon Engineering, despite their lower environmental climate change (for the Carbon Engineering process 0.38 $kgCO_{2eq}/kgCO_2$ are assumed as in Eke et al., (2025). Processes using weak acids for CO_2 reaction are less economically favorable. Compared to the classic thermal-based absorption DAC, the investigated solutions have an additional implementation cost of about 4 M€ (e.g., the product between the height representing the marginal abatement cost and width of the bar representing the abatement potential of the measure).

From Fig. 8 it is possible to see that the bar of processes investigated in this research is below the x-axis: these CO_2 reduction technologies are more convenient compared to the DAC adsorption using APDES-NFC-FD sorbent, characterized by a cost of 600 $\$/tonCO_2$ and a climate change of -0.116 $kgCO_{2eq}/kgCO_2$ (Leonzio et al., 2022b, 2022c). By installing a DAC process using an absorption column with the regeneration of the solvent via BPMED, reaction with formic acid and reaction with formic/acetic mixture acid can enable have a saving respectively equal to 15 M$, 12 M$ and 11 M$. Electrodialysis regeneration offers several additional advantages, including the potential for complete process electrification, rapid ramp-up capability, and the elimination of solids

Table 5
Values of correlation factors between inputs and CO_2 capture cost/climate change impact.

	Base case scenario	Formic acid scenario	Formic/acetic acid scenario
CO_2 capture cost			
Electricity cost	0.966	0.891	0.897
KOH cost	0.254	0.111	0.156
K_2CO_3 cost	0.089	0.357	0.367
Formic acid cost		0.259	0.116
Acetic acid cost			0.079
Climate change impact			
Electricity consumption	1	0.672	0.872
KOH consumption	0.121	0.031	0.041
K_2CO_3 consumption	0.332	1	1
Formic acid consumption		0.072	0.042
Acetic acid consumption			0.193

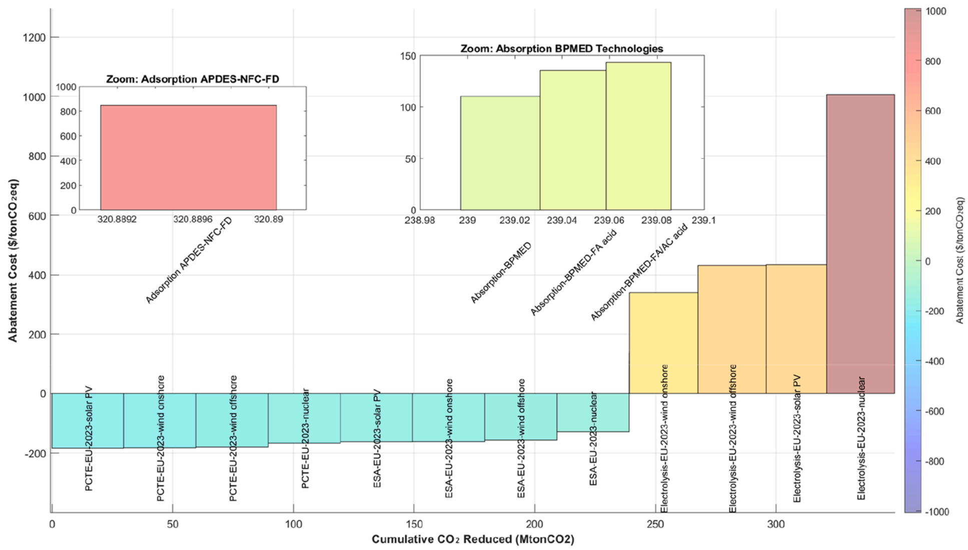

Fig. 7. Marginal abatement cost curve (2025–2040) of e-DAC technologies considering the absorption DAC process (based on thermal energy) as the reference technology.

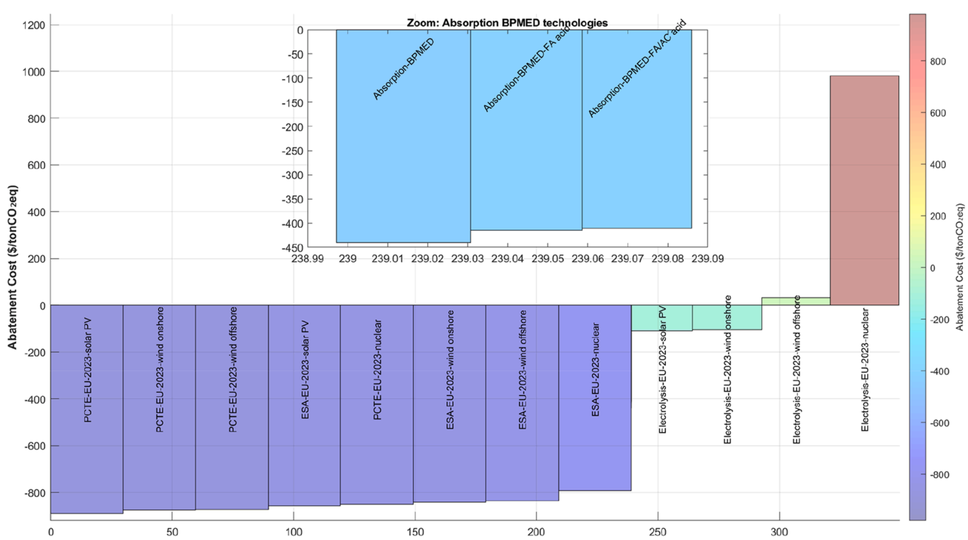

Fig. 8. Marginal abatement cost curve (2025–2040) of e-DAC technologies considering the adsorption DAC process (based on APDES-NFC-FD sorbent) as the reference technology.

handling. These attributes may represent critical enablers for deployment at the gigaton scale. Furthermore, BPMED is an inherently flexible technology that can be efficiently implemented across a broad range of operational scales.

From both Fig. 7 and 8, it is interesting to see that currently the most attractive DAC technologies in terms of abatement cost are ESA and PCET as also reported in Leonzio and Shah (2025). All of them, in fact, have a bar below the x-axis. On the other hand, electrolysis-based capture technology is favorable compared to the adsorption DAC process when not driven by nuclear energy. However, compared to the thermal absorption DAC system, the electrolysis-based process has higher costs in all cases. An electrolysis process powered by nuclear energy has the highest cost compared to all technologies (1600 \$/tonCO_2) (Leonzio and Shah, 2025).

4. Conclusions

With the aim of reducing energy consumption and in line with the electrification of chemical processes, the integration of absorption DAC systems with BPMED stack for solvent regeneration has been explored in the past. However, BPMED processes are characterized by CO_2 bubble formation reducing efficiency, hence new solutions are suggested in this work. CO_2 can be released from the rich solvent leaving the absorption column through the reaction with weak acids (formic acid and formic/acetic acid mixture) where the salt acid is produced and sent to the BPMED stack for the regeneration of acid and alkaline solvent both recycled into the process. A similar process has not been investigated in the literature for DAC applications yet, then the novelty of the work is underlined. In particular, a comparison of the two solutions for recovery of the captured CO_2 is conducted.

To this aim, the investigated and proposed processes are simulated in Aspen Plus and Matlab software generating material and energy balances useful to carry out economic and environmental analyses. Results show that:

- despite a higher energy consumption of the cell stack (2314 kWh/tonCO_2 vs 1907 kWh/tonCO_2 and 1943 kWh/tonCO_2 respectively for the process involving formic acid and formic/acetic acid mixture), the process without acid reaction has the lowest capture cost (480 \$/tonCO_2) while the process releasing CO_2 via formic acid reaction and formic/acetic acid mixture reaction cost respectively 510 \$/tonCO_2 and 519 \$/tonCO_2. This is due to a higher CAPEX and lower amount of captured CO_2;
- better performances of the process in the base case scenario are also provided for the environmental point of view in all investigated impact categories. Values of climate change for all three processes are equal to -0.9593 kgCO_{2eq}/kgCO_2, -0.9378 kgCO_{2eq}/kgCO_2 and -0.9238 kgCO_{2eq}/kgCO_2 respectively for the process without acid reaction, with reaction between carbonates and formic acid and with reaction between carbonates and formic/acetic acid mixture;
- more efforts and research must be carried out and developed to improve the efficiency of alternative processes in order to have lower costs and environmental burden.

As another innovative point of this research, the marginal abatement cost curve of electrochemical DAC technologies is reported in this study considering the adsorption DAC with APDES-NFC-FD sorbent and absorption DAC with high temperature regeneration as the reference technologies. Results show that the BPMED based processes may not be currently attractive compared to the conventional DAC absorption process but they are favorable compared to the adsorption DAC system.

For future research it is recommended to consider different aspects, such as experimental validation, system integration and optimization, or membrane material improvement. Moreover, in the future, other applications of the BPMED must be analyzed and in particular the potential scalability of BPMED to treat seawater and environmental implications of discharging treated seawater must be considered in future research too.

CRediT authorship contribution statement

Grazia Leonzio: Writing – review & editing, Writing – original draft, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Lei Xing:** Writing – review & editing, Writing – original draft. **Nilay Shah:** Writing – review & editing, Methodology, 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.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccst.2026.100579.

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