

# Extending the application of bifunctional ionic liquid-based integrated capture and conversion of CO<sub>2</sub> to produce cyclic carbonates

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## ABSTRACT

Nowadays there is an urgent need for mitigating CO<sub>2</sub> emissions through clean energy and the development of new carbon capture and utilization (CCU) technologies. Among others, the use of bifunctional ionic liquids (ILs) addressed simultaneously CO<sub>2</sub> capture and conversion steps, having applied successfully to the propylene carbonate production case. In this work, a systematic evaluation of all representative cyclic carbonate literature was made, covering ethylene, propylene, butylene, hexylene, cyclohexene, and styrene cyclic carbonates, in order to guide the product role within the integrated CCU (ICCU) concept. The multiscale strategy combining molecular simulation (DFT -Density Functional Theory-, COSMO -Conductor-like Screening Model-), process simulation (COSMO/Aspen methodology), and life cycle assessment (LCA) was used to set up, simulate and evaluate the processes. ICCU configuration is the best approach when compared with sequential configuration for energy consumption analysis (reduction of 28, 28, 22, 11 and 6 %, respectively, for ethylene, propylene, butylene, hexylene, and cyclohexene cases) and CO<sub>2</sub> emissions associated (reduction of 38, 40, 31 and 14 %, respectively, for ethylene, propylene, butylene, and hexylene cases). The main variable of the results is the boiling point of the cyclic carbonate since heavy products impose technical limitations and even discard ICCU alternative. The ICCU concept works since all cyclic carbonates' reaction enthalpies are higher than that of the IL-CO<sub>2</sub> one, which reduces heating requirements. Finally, energy demand can be slightly further reduced, partially recycling the cyclic carbonate to the capture unit.

## 1. Introduction

Managing the rising carbon dioxide (CO<sub>2</sub>) emissions is imperative in the current fight against climate change [1]. Carbon capture assumes key strategy to mitigate the adverse impacts of global warming [2–4]. This practice not only implies the reduction of atmospheric CO<sub>2</sub> levels but also paves the way for reusing captured carbon to produce value-added commodities through post-capture processing rather than storage. The conversion of CO<sub>2</sub> into high-value products aligns with the principles of a circular economy [5,6], which not only contributes to environmental sustainability by reducing the carbon footprint [7], but also promotes resource efficiency and economic viability [8].

Currently, the production capacity of CO<sub>2</sub>-derived products represents a very low percentage of anthropogenic CO<sub>2</sub> emissions [9]. Now, there are approximately 40 operational carbon capture facilities worldwide, with a total annual capacity of over 45 million metric tons of CO<sub>2</sub> [10], covering mainly methanol, urea, formic acid, and cement or other construction materials [9]. Nevertheless, the production of

CO<sub>2</sub>-derived fuels has a scalable market that allows for the utilization of large quantities of CO<sub>2</sub>, yielding low-value products. On the other hand, the production of CO<sub>2</sub>-derived chemicals is an extensively evaluated strategy, despite the challenge of the profitability of the processes. In fact, given the urgent necessity to utilize CO<sub>2</sub>, exploring innovative approaches becomes crucial. Recently, the concept of a "carbon dioxide refinery" has been proposed to solve this urgency, where both fuels and chemicals are produced from CO<sub>2</sub>, with fuel production responsible for most of the CO<sub>2</sub> use, while chemical production generates most of the refinery's profits [11]. In this context, the possibility of combining methane dry reforming and cyclic carbonate production has recently been evaluated, which would potentially harness a quarter of annual global CO<sub>2</sub> emissions [12]. However, the design of the catalysts as well as the process scheme still needs to be further improved as it is hardly performed on a large scale [9]. Another option for improving these processes is their electrification, by replacing certain equipment that consumes fossil fuels with their electric equivalent, thus facilitating their supply with renewable energies [10].

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Within this framework, a recent work was developed regarding the production of propylene carbonate from CO<sub>2</sub>, integrating its capture and conversion in a pre-combustion scenario [13]. For this purpose, a bifunctional ionic liquid (IL) was employed, as it has advantages over conventional catalyst. The ILs are organic salts formed by cations and anions, with exceptional properties such as low volatility and corrosion resistance [14], which makes them a promising alternative. Additionally, ILs can offer the flexibility to tune both the cation and the anion to perform a specific task properly. This allows selecting an IL to adopt integrated product and process designs with optimal process performance on an industrial scale [15]. Specifically, [P<sub>66614</sub>][CNPyrr], as an aprotic heterocyclic anion-based (AHA) IL, can function either as an efficient chemical CO<sub>2</sub> absorbent [16,17] and as an active catalyst in the cycloaddition reaction of CO<sub>2</sub> to epoxides [18,19]. Moreover, [P<sub>66614</sub>][CNPyrr] demonstrated remarkably competitive energy and solvent demand values in previous CO<sub>2</sub> capture process simulations, superior to conventional amine-based processes in terms of techno-economic analysis [20,21]. ILs can boost the development of CCU technologies [22], which is exhibited even more potential through bifunctional ILs [15]. Two possibilities were studied in the literature: a separated capture and conversion (SCCU) or an integrated capture and conversion (ICCU) case. The integration of capture and conversion was found to be much more beneficial in terms of energy consumption, since the energy demand associated with IL sorbent regeneration was eliminated, and the demands in the CO<sub>2</sub> conversion reactor were reduced due to the synergy between desorption and cycloaddition processes [13]. Following the concept of the CO<sub>2</sub> biorefinery, the capture process involves a pre-combustion step for hydrogen production. Thus, with the integration of both processes, it could be possible to generate fuel (H<sub>2</sub>), power, and chemicals [13]. Therefore, in recent years, significant efforts have been directed towards investigating the viability of the ICCU for producing value-added chemicals such as methane [23], methanol [24], and cyclic carbonates [25].

The production of cyclic carbonates from CO<sub>2</sub> has been of notable interest due to their versatile applications as sustainable alternatives to traditional solvents in the industry. They serve as substitutes for toxic compounds in polymer synthesis [26], and as extractive solvents for fuel aromatic compounds [27,28]. These molecules exhibit considerable biological potential in pharmaceutical [29] and biomedical [30,31] applications. Therefore, the CO<sub>2</sub> conversion to cyclic carbonate is a valuable strategy to be explored from the necessity to offset gigatons of CO<sub>2</sub> emissions. The ILs have been demonstrated to be potential catalysts in the cycloaddition reaction towards different cyclic carbonates [32]. It was reported that IL regeneration and carbonate product purification are key stages in the process efficiency, determining the energy requirements of the global CO<sub>2</sub> conversion process. Distillation and liquid-liquid extraction have been evaluated as separation strategies with the purpose of decreasing energy demands, which become more relevant when increasing the cyclic carbonate boiling point [32]. However, to the best of our knowledge, an integrated capture and conversion approach has not been explored for multiple cyclic carbonates to evaluate the product impact on the CCU technology design.

On the other hand, despite the growing interest in CCU processes, there is a clear gap in assessing the CO<sub>2</sub> emissions and other environmental impacts related to these new processes [15]. Life-Cycle Assessments (LCA) tools are crucial for understanding environmental impacts across product lifecycle stages, aiding in informed decision-making [33]. Analyzing CO<sub>2</sub> capture and conversion processes highlights their importance in mitigating climate change [34,35]. In relation to the production of cyclic carbonates from CO<sub>2</sub>, there are only few studies assessing CO<sub>2</sub> emissions, devoted for the production of dimethyl or diethyl carbonates [36–38] and cyclic carbonates [13,39,40]. Remarkably, LCA analysis combined with COSMO-based/Aspen process simulation methodology was successfully applied to design new IL-based CO<sub>2</sub> conversion processes to produce propylene carbonate, which allows improving environmental impacts, energy consumption, and process

costs at the same time [36].

According to this background, this work deals with an extension of the integration of carbon capture and conversion using the [P<sub>66614</sub>][CNPyrr] bifunctional IL for the production of several cyclic carbonates, namely ethylene carbonate (Eth-C), butylene carbonate (But-C), hexylene carbonate (Hex-C), cyclohexene carbonate (Cyc-C), and styrene carbonate (Sty-C). The aim of this work is to analyze product impact on the integrability of capture and conversion following the approach of using bifunctional ILs. The change of the product is modifying reaction enthalpies, boiling points of reactants and products, and hybrid absorbents in the capture unit, since the nature of the cyclic carbonate recycled to the capture unit changes. The idea is to establish whether it is more advantageous to conduct these processes in an integrated (ICCU) or sequential (SCCU) process scheme, finding what are the main features of the products that allow to integrate capture and conversion steps satisfactorily. To achieve this, reaction enthalpies were estimated by DFT calculations [41], the COSMO-based/Aspen methodology [15,42,43] has been employed to simulate these CCU processes and determine their energy consumption and, finally, an estimation of the environmental impacts associated with utility consumption, including a CO<sub>2</sub> balance, has been conducted through LCA methodology, enabling the comparison of said processes in environmental terms as well.

## 2. Process simulation details

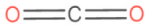

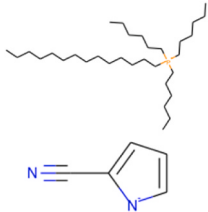

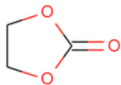
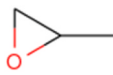
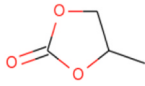
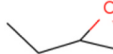
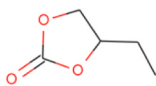
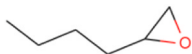
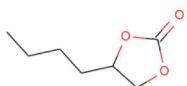

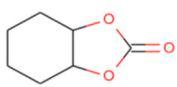
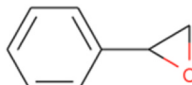
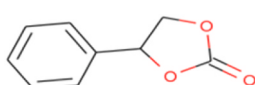
### 2.1. Component definition and property method specification

The simulation of SCCU and ICCU processes based on [P<sub>66614</sub>][CNPyrr] was conducted using Aspen Plus v12, employing a well-known COSMO-based/Aspen Plus methodology. This methodology, validated in previous studies involving ILs [44–47], has also been applied with [P<sub>66614</sub>][CNPyrr] and cyclic carbonates [13,32]. In brief, quantum chemical structure optimizations of all compounds were performed using Turbomole 7.5 software [48] using the computational BP86/TZVP level and using the COSMO continuum solvation method, to ensure minimum energy levels. The ion-pairing model of the CA molecule was used for the IL description. Subsequently, the COSMOTermX version 19.0.4 software was employed to predict various thermodynamic properties by using the COSMO-RS method. This involved specific calculations for boiling points,  $\sigma$ -profiles, viscosities, and COSMO volumes of all the compounds that are not included in Aspen Plus' databanks. These parameters, essential for the COSMO-SAC, property method introduced by Lin and Sandler [49] (code 1), were employed to represent the compounds as pseudo-components following the methodology based on COSMO/Aspen reported elsewhere [50]. It is worth mentioning that COSMO/Aspen predictions on cyclic carbonate's properties were quantitatively validated in a previous work [42]. Table 1 compiles information on the main compounds used, their abbreviations, and whether they have been used as conventional compounds or as pseudo-components in Aspen Plus. The incorporation of experimentally derived temperature-dependent viscosity data for [P<sub>66614</sub>][CNPyrr] [51] was achieved using the Andrade equation to account for mass transfer kinetics during absorption. The viscosity of cyclic carbonates was determined using COMOSTermX software. This methodology has been previously validated for the viscosity of these compounds in a previous work [42]. All those parameters calculated for the epoxides and cyclic carbonates examined in this research and incorporated in Aspen Plus are collected in Table S1 of the Supplementary Material.

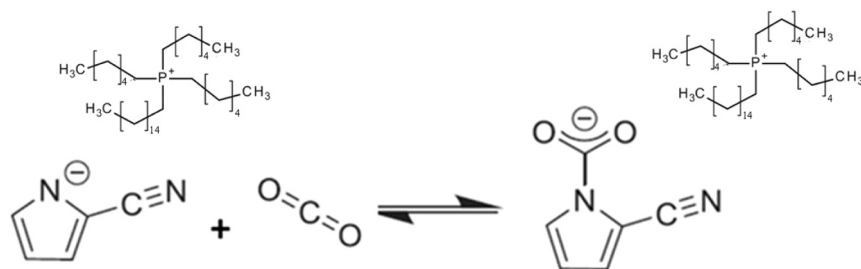
In order to describe the physical and chemical absorption of CO<sub>2</sub> in [P<sub>66614</sub>][CNPyrr] (Scheme 1), Aspen Plus built-in temperature dependence expressions for Henry's Law and chemical equilibrium reaction constants (specifically, Aspen Plus's Reactive-Distillation equilibrium reaction) were used, as detailed in previous works [13,52]. Additionally, considering the cyclic carbonate also physically capture CO<sub>2</sub>, the temperature dependence expression for Henry's Law was predicted using the

**Table 1**

Compounds used in the simulations, type of description in Aspen Plus, molecular weights, and boiling points.

Name	Abbreviation	Aspen Plus description	Structure	Molecular weight (g/mol)	Normal boiling point (°C)
Carbon dioxide	CO <sub>2</sub>	Conventional		44.0	−78
Hydrogen	H <sub>2</sub>	Conventional		2.0	−253
Trihexyl(tetradecyl)-phosphonium 2-cyanopyrrolide	[P <sub>66614</sub> ] [CNPyr]	Pseudocomponent		575.0	974*
Ethylene oxide	Eth-E	Conventional		44.1	10
Ethylene carbonate	Eth-C	Conventional		88.1	248
Propylene oxide	Pro-E	Conventional		58.1	35
Propylene carbonate	Pro-C	Conventional		102.1	242
1,2-Epoxybutane	But-E	Pseudocomponent		72.1	63
Butylene carbonate	But-C	Pseudocomponent		116.1	251*
1,2-Epoxyhexane	Hex-E	Pseudocomponent		100.2	119
Hexylene carbonate	Hex-C	Pseudocomponent		144.2	262*
Cyclohexene oxide	Cyc-E	Pseudocomponent		98.1	130
Cyclohexene carbonate	Cyc-C	Pseudocomponent		142.2	354*
Styrene oxide	Sty-E	Pseudocomponent		120.2	194
Styrene carbonate	Sty-C	Pseudocomponent		164.2	402*

\* Data obtained by COSMO-RS method.



**Scheme 1.** Reaction scheme of CO<sub>2</sub> chemical absorption, forming carbamate product.

COSMOThermX software.

Subsequently, the reaction of the CO<sub>2</sub> cycloaddition for the formation of the cyclic carbonates (**Scheme 2**) must be conveniently described in Aspen Plus simulations. In this respect, the enthalpy reaction of CO<sub>2</sub> conversion was crucial as a critical parameter in the reactor's energy consumption. This reaction's enthalpy was incorporated into the Aspen Plus software in terms of the gas-phase enthalpy formation of the compound involved in the reaction. As the formation enthalpy data for most compounds were unavailable, the Turbomole software was employed to predict the respective reaction enthalpies via DFT calculations, employing the BP86/TZVP computational level in the gas phase. This methodology has been previously validated for predicting the reaction enthalpy of CO<sub>2</sub> chemical absorption with ILs [41]. To quantitatively improve the reaction enthalpy values used in Aspen Plus process simulations, the DFT reaction enthalpy values were corrected by fitting to available experimental data. Thus, the experimental enthalpy of formation in the gas phase for epoxide/cyclic carbonate pairs (only available for three systems: propylene, ethylene, and glycol) and CO<sub>2</sub> were collected from the NIST database in Aspen Plus [53]. These enthalpies were used to calculate the experimental standard reaction enthalpy using the equations:

$$\Delta H_{\text{reaction}} = \sum m \Delta H_f(\text{products}) - \sum n \Delta H_f(\text{reactants}) \quad (1)$$

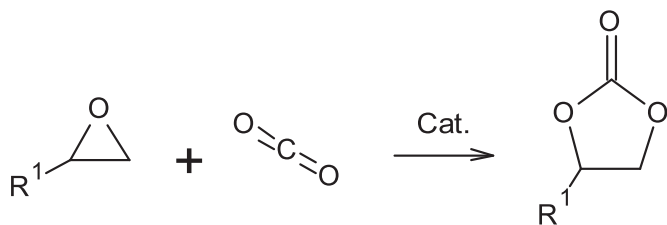
where  $\Delta H_{\text{reaction}}$  denotes the standard enthalpy reaction, and  $\Delta H_f$  represents the standard enthalpy formation for both products and reactants, and 'm' and 'n' correspond to the stoichiometric coefficients of the products and reactants, respectively. **Figure S3** of the **Supplementary Material** shows the linear relationship ( $R^2 = 0.99$ ) between available experimental and calculated reaction enthalpy. Then, the DFT predicted values of reaction enthalpy were corrected by using the obtained linear regression equation in **Figure S1**. **Table S1** of the **Supplementary Material** collected the estimated standard enthalpy reactions to produce butylene, hexylene, cyclohexene, and styrene carbonates included in the Aspen Plus properties for process simulations.

## 2.2. SCCU process description and simulation procedure

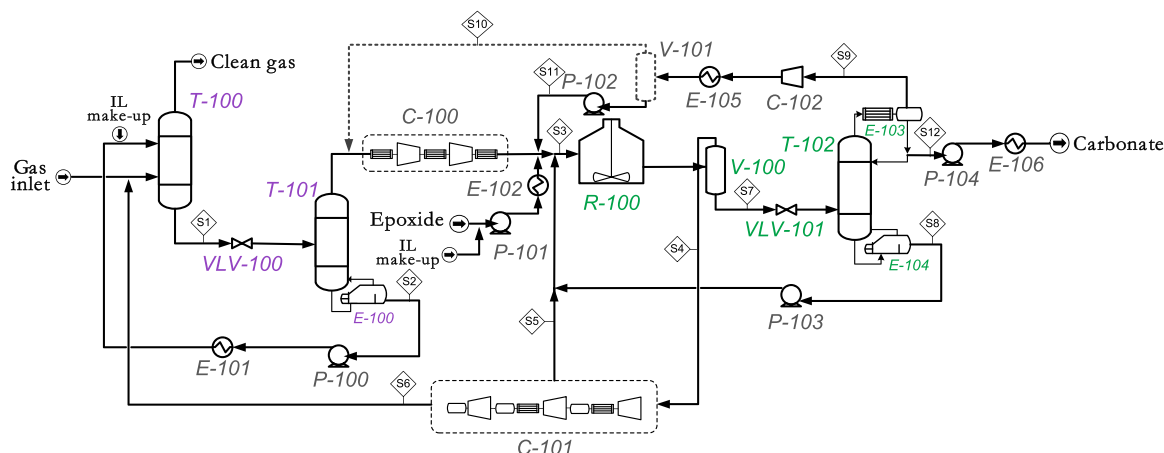
The SCCU process developed in Aspen Plus v. 12 is illustrated in **Fig. 1**, this process scheme is based on that of a previous work for the production of propylene carbonate [13], but slight changes have been made to it. To compare the production of all selected carbonates under

the same conditions, the production of propylene carbonate has been modeled again following the new diagram (**Fig. 1**). The process can be categorized into two distinct zones: the first involves the chemical capture of CO<sub>2</sub> using ILs from an industrial stream, while the second focuses on the conversion of the captured CO<sub>2</sub> into cyclic carbonates using ILs as catalysts in the cycloaddition reactions. In this process, an inlet gas stream (S1) with a flow rate of 250 kmol/h is treated. This stream comprises 40 % mol of CO<sub>2</sub> and 60 % mol of H<sub>2</sub>, as a simplified coal gasification effluent [52]. S1 enters the absorption column (T-100) at 40°C, simulated in Aspen Plus as a packed column using the RADFRAC rigorous model with rate-based calculations to account for mass transfer kinetics. The column operates with Flexipac 700Y structured packing for the internal components and has a packing height of 15 m. The column operates at 32.7 bar and is supplied with sufficient ionic liquid (IL) to achieve 90 % CO<sub>2</sub> absorption in the IL phase, operating under adiabatic conditions.

The top of T-100 yields a H<sub>2</sub>-rich stream with a purity of 94 % mol (depicted as clean gas in **Fig. 1**), while the bottom stream contains the spent IL. The exhausted IL is regenerated in a stripping column (T-101) operating at 0.1 bar, using the RADFRAC model in rate-based mode. The column operates with Flexipac 700Y structured packing for the internal components and has a packing height of 8.5 m. For both columns, T-100 and T-101, the Interactive sizing tool was used to determine the appropriate diameter to maintain an 80 % fractional capacity in all instances. The regenerated IL (S2) exits the bottom of the stripper, undergoes pressurization (P-100), and cooling (E-101) to reach the absorption column's inlet conditions (pre-combustion, 32.7 bar and 40 °C) [20]. Conversely, the captured CO<sub>2</sub> (S3) undergoes conditioning to 15 bar and 60°C in C-100 before entering the isothermal reactor (R-100). The reactor is modeled as an RStoic conversion reactor, operating at 120°C and 15 bar [13,18,54]. Additionally, an epoxide stream, pre-pressurized to 15 bar in P-101, is introduced into the reactor. As stated in **Table 1**, six different epoxides can be fed in order to obtain the corresponding different cyclic carbonates. The specified conversion for the CO<sub>2</sub> cycloaddition is 80 % mol of epoxide, as reference per literature values [18,32,54]. The conversion value is dependent on temperature, pressure, and reaction volume, so as a first approach, a reasonable value was chosen to fairly compare all cyclic carbonates for the same effectiveness in the reactor, since the enthalpy balance is close to the specified mass balance in the reactor. The molar flow of the epoxide stream is adjusted to achieve equimolar conditions with CO<sub>2</sub> in the reactor. The epoxides are at 25 °C and 1 bar at battery limit, except for ethylene oxide, which, due to its higher volatility, is pressurized to 3 bar. Simultaneously, the molar proportion of epoxide to IL in the reactor is maintained at 200:1 -ensured by means of an IL make-up-, a ratio based on insights from CO<sub>2</sub> conversion experimental assays and process designs utilizing ILs [44,55,56]. Subsequently, the effluent from the reactor is directed to a flash unit (V-100) operating at 5 bar. In this unit, the gas phase (S4) is separated and compressed to 32.7 bar in a 3-stage compression with intermediate cooling (in C-101). This allows phase separation and S5 (mixture of liquid phases) is recirculated to fed into the reactor since it contains mainly CO<sub>2</sub> and the corresponding epoxide. The resulting gas phase (S6) contains mainly CO<sub>2</sub> and H<sub>2</sub> and is



**Scheme 2.** Reaction scheme of CO<sub>2</sub> cycloaddition to epoxide to produce cyclic carbonate.



**Fig. 1.** Separated capture and conversion (SCCU) process flow diagram.

recirculated back to the absorption column.

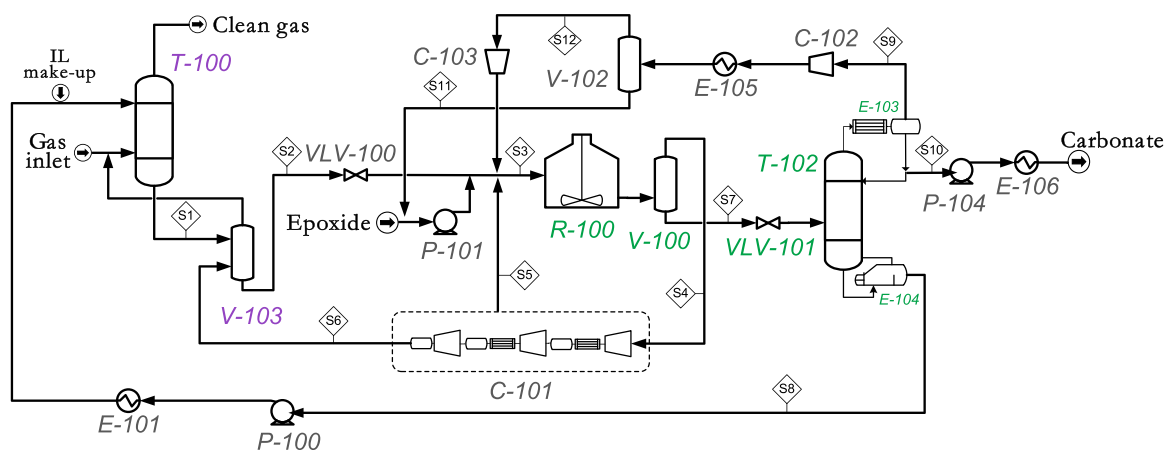
The liquid stream exiting V-100 (S7) is then introduced into the downstream rectification column (T-102), which operates at vacuum conditions. This low pressure is maintained to facilitate the evaporation of propylene carbonate while preventing the reboiler temperature from exceeding 120 °C. This is crucial for ensuring the thermal stability of [P<sub>66614</sub>][CNPyr] is not compromised [18]. This column is simulated using the RADFRAC model under equilibrium conditions, leveraging its capability to mitigate mass transfer issues related to viscosity at elevated temperatures. The column incorporates a partial condenser (E-103). In the bottom stream of T-102 (S8), the ionic liquid (IL) is recovered and subsequently pressurized to 15 bar using P-103 before being recirculated back to the reactor. The vapor phase in E-103 (S9) mainly contains the epoxide and CO<sub>2</sub>. This vapor stream is pressurized in C-102 and cooled in E-105, and thereafter, in the cases of Eth-C and Pro-C production, since they are more volatile, a flash separator (V-101) is used to separate the liquid and vapor phases. In those two cases, the vapor phase (S10) is recirculated just before C-100 for conditioning to the reaction conditions, and the liquid phase (S11) is pressurized in P-103 and recirculated to the reactor. In the case of other carbonate production (But-C, Hex-C, Cyc-C, and Sty-C), phase separation is not necessary. Thus, for these cases, after cooling in E-105 the mixture is pressurized in P-102 up to 15 bar and fed into the reactor. In other words, V-101, and S10 are not simulated for But-C, Hex-C, Cyc-C, and Sty-C. On the other hand, the liquid distillate of T-102 (S10) is subject to a specified 95 % recovery carbonate and a mass purity >99 % This cyclic carbonate phase-rich stream is pressurized and cooled to 1 bar and 30 °C through P-104 and E-106, respectively. For a comprehensive overview of the

main process equipment specifications see [Table S2](#) in Supplementary Material.

### 2.3. ICCU process description and simulation procedure

As before, the ICCU process is based on that of a previous publication [13], follows a similar approach to the SCCU and is illustrated in Fig. 2. In contrast to the SCCU process, ICCU eliminates the need to regenerate the IL after CO<sub>2</sub> capture by employing the same IL to capture and conversion of CO<sub>2</sub>. The initial gas stream, identical to that in SCCU (S1, 250 kmol/h, comprising 40 %mol CO<sub>2</sub> and 60 %mol H<sub>2</sub>), is treated in the absorption column (T-100, RADFRAC model with rate-based calculations). The T-100 column operates with Flexipac 700Y structured packing for internal comments and has a packing height of 15 m. This process yields a stream with 90 % CO<sub>2</sub> absorption in the IL phase. The absorbent is a mixture of IL and cyclic carbonate recycled from T-102. The IL proportion is adjusted to achieve the desired CO<sub>2</sub> capture percentage. Following T-100, the exhausted absorbent is directed to a flash unit (V-103, operating at 32.7 bar). Here, most of the H<sub>2</sub> is recovered in the gas phase to prevent downstream accumulation. The resulting gas phase (S2), also containing CO<sub>2</sub>, is then fed back into T-100. Simultaneously, the liquid phase (S3) is introduced into the reactor (R-100, RCSTR model) operating at 15 bar and 120 °C.

In this reactor, CO<sub>2</sub> is desorbed from the exhausted IL through the reversible CO<sub>2</sub>-IL chemical absorption reaction and undergoes conversion to the corresponding carbonate in a cycloaddition reaction set at 80 % conversion of epoxide. Additionally, both the molar flow rate of epoxide fed to the reactor and P-101 as well as V-100, maintain the same



**Fig. 2.** Integrated capture and conversion process flow diagram.



specifications from SCCU. The vapor phase exiting V-100 (S4) undergoes a 3-stage compression to 32.7 bar (C-101). C-101 includes two intermediate cooling steps in which the resulting liquid fractions are mixed (S5, containing mainly PO) and recirculated to the reactor. The vapor phase obtained in C-101 (S6) is fed to V-103 to facilitate the recovery of CO<sub>2</sub> and H<sub>2</sub>. On the other hand, the liquid phase exiting V-100 (S7), primarily composed of carbonate, ionic liquid, epoxide, and CO<sub>2</sub>, is directed to T-102. This column (T-102) -operating as a RADFRAC model in vacuum conditions- is once again designed to preserve the thermal stability (<120 °C) of the IL while facilitating the evaporation of the carbonate [18]. The necessity for a higher vacuum in this case, compared to SCCU, is attributed to the lower vapor pressure of IL and the increased IL:carbonate molar proportion. The bottom stream (S8) from T-102 contains IL and carbonate, is conditioned to 32.7 bars and 40 °C through P-100 and E-101, and is then fed into the absorption column to serve as an absorbent. This configuration improves the physical absorption of CO<sub>2</sub> in the carbonates [13]. Notably, the carbonate recovery established in T-102 (S10) is intentionally lower than in SCCU. This adjustment aims to increase the carbonate concentration in the column, thereby demanding less extreme vacuum conditions. However, there is a compromise between the reduction of vacuum and the increase in energy consumption of the entire process due to the increase of the flow rate. As done previously in other research, the cyclic carbonate recovery in column T-102 was set at 80 % to reduce the vacuum conditions [13]. Nevertheless, a preliminary study was conducted by varying the amount of recirculated carbonate with respect to the feed in T-102 for all carbonates, ranging between 0.1 and 0.5. The aim was to examine the influence of this parameter on the final energy consumptions of the integrated process. The results of this sensitivity are represented in Figure S1 in the Supplementary Material. It is observed that for the ICCU strategy, the minimum energy demand is found when recirculating around 25–30 % of carbonate. However, the energy consumption hardly varies with an increase in recirculated carbonate. This is because, when recirculating a larger amount of carbonate, it is necessary to condition this additional flow in all the heating, cooling, or compression operations. Nevertheless, this additional consumption is offset by the reduction in vacuum related to T-102. It is noteworthy that cyclic carbonates can physically capture CO<sub>2</sub>. By increasing carbonate recirculation, a small portion of the IL utilized in chemical capture is minimized, enabling the recovery of 90 % of the CO<sub>2</sub> introduced to the column. For all of that, in the ICCU proposal, a recirculation rate of 20 % was selected for all cases, to compare them under the same conditions, and since from 20 % onwards of carbonate recirculation, the energy demand in the production of any of the carbonates barely changes.

The vapor phase in E-103 (S9) mainly consists of epoxide, cyclic carbonate, and CO<sub>2</sub>. Thus, it is compressed and cooled in C-102 and E-105 to reach 1 bar and 30 °C. Subsequently, the liquid and vapor streams are separated in a flash unit (V-101) operating at 1 bar. The liquid stream (S11), consisting in the epoxide and carbonate, is directed to the reactor after undergoing conditioning to 15 bar in P-101. Meanwhile, the vapor stream (S12), containing CO<sub>2</sub> and epoxide, is compressed to 15 bar (C-103) before being introduced into the reactor. Furthermore, the achieved cyclic carbonate mass purity in the liquid distillate (S10) is always above 99 %. As in SCCU, this stream undergoes pressurization and cooling to 1 bar and 30 °C using P-104 and E-106, respectively. The primary specifications of the process equipment are detailed in Table S2 in Supplementary Material. In addition, Table S3 in Supplementary Material depicts the differences in equipment and operations between SCCU and ICCU processes.

## 2.4. Key performance indicators (KPI) of CCU process

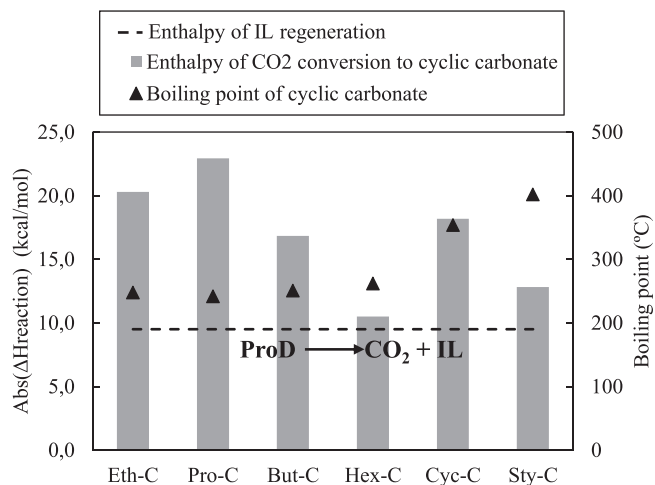
To compare the SCCU and ICCU processes, specific energy requirements were collected for all cyclic carbonate productions to assess the most energy-efficient strategy. Cooling water was utilized in equipment requiring cooling, low-pressure steam was used for heating,

and electricity was employed to power pumps and compressors. This comprehensive energy analysis is essential for determining the optimal process in terms of energy efficiency and overall sustainability.

The environmental impact potentials associated with the utilities consumed by the processes were calculated using the OpenLCA software, version 1.11.0 using the datasets available on Ecoinvent (version 3.8) life cycle inventory database. Previous work stated that epoxide imposed the main contribution for GWP, avoiding properly evaluating the process impact by itself, whereas the IL role is almost null due to the negligible losses in the process [39]. According to these reasons, here LCA is partially executed to compare GWP associated with energy consumption for all ICCU and SCCU processes (see Figure S2). For this purpose, within the Ecoinvent database, the heat consumption was specified as "steam production, as an energy carrier, in chemical industry | heat, from steam, in chemical industry | Cutoff, S," and the electricity consumption was specified as "heat and power co-generation, biogas, gas engine, renewable energy products | electricity, high voltage, renewable energy products | Cutoff, S." On the other hand, since cooling water is not available in the database, it was modeled as tap water to provide a more conservative estimate of the impacts. In that case, the heat capacity of the cooling water included in the Aspen Plus v12 database (-0.021 MJ/kg) was used for calculating the required mass flow of water. The ReCiPe Midpoint (E) methodology was applied to assess the selected impacts, including the global warming potential (GWP).

## 3. Results

First, molecular simulation was used to predict the enthalpy of the CO<sub>2</sub> cycloaddition reaction to epoxide to produce all cyclic carbonates investigated in this research. These reaction enthalpies predicted by DFT method were correlated against the available experimental reaction enthalpy for the cases of ethylene, propylene, and glycol carbonates, which are, to the best of our knowledge, the values available in the literature. The fitting is shown in Figure S3 in the Supplementary Material, with a R<sup>2</sup> over 0.99. This regression was used to correct the DFT estimations for the other cyclic carbonates, namely butylene, hexylene, cyclohexene, and styrene. The reaction enthalpy of the CO<sub>2</sub> cycloaddition to epoxide for cyclic carbonate production is a key thermodynamic parameter that determines the energy consumption in the reactor in the global CO<sub>2</sub> conversion process. The estimated reaction enthalpies in the

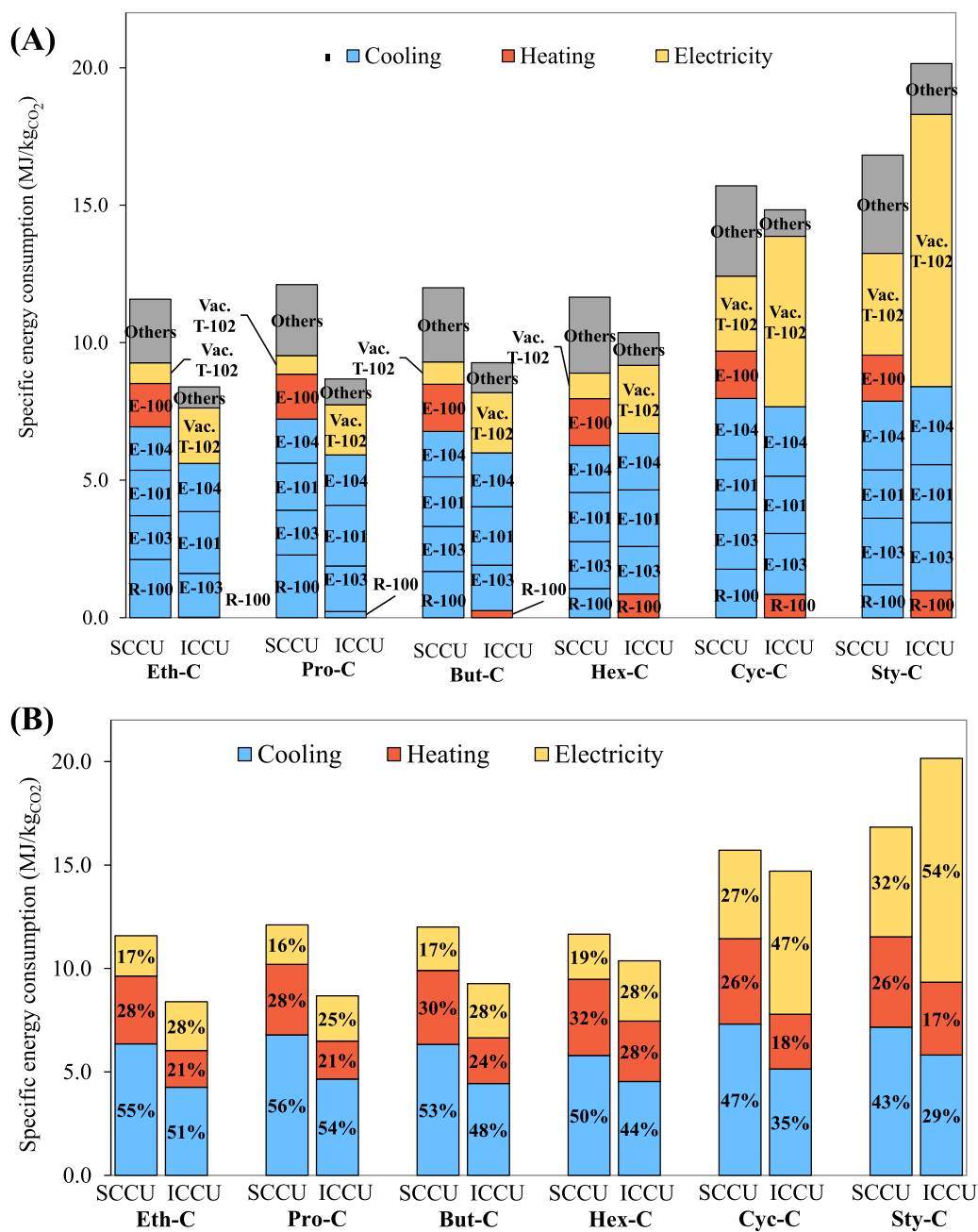


**Fig. 3.** The absolute value of exothermic reaction enthalpy of the CO<sub>2</sub> cycloaddition to epoxide for cyclic carbonate production (bar chart), estimated from DFT calculations at 298 K, the endothermic reaction enthalpy of the regeneration of [P<sub>66614</sub>][CNPy] and CO<sub>2</sub> from carbamate product of chemical capture (dash line) at 298 K [57], and the experimental [42] and COSMO-RS boiling points of the studied cyclic carbonates.

liquid-phase are presented in Fig. 3. The bar chart represents the exothermic enthalpy reaction in terms of kcal/mol of the reaction between the CO<sub>2</sub> with the epoxide to produce the respective cyclic carbonate. On the other hand, Fig. 3 also shows the endothermic chemical reaction involved in the regeneration of exhausted IL absorbent, [P<sub>66614</sub>] [CNPy], corresponding to the reversible reaction from the CO<sub>2</sub>-IL chemical absorption product (carbamate in Scheme 1), with a constant endothermic enthalpy of 9.5 kcal/mol for all studied CO<sub>2</sub> conversion processes [57], since it only depends on the selection of the IL. The main first conclusion is that the dissipated energy in the exothermic cyclic carbonate production is, in all cases, higher than the required energy for IL regeneration from the CO<sub>2</sub> chemical absorption complex, which anticipates a favorable energy balance in the integrated CCU process. It is generally observed that increasing the substituent size decreases the

reaction enthalpy of cyclic carbonate production, implying lower energy consumption in the reactor step. Another key property determining the CO<sub>2</sub> conversion process performance is the boiling point of the cyclic carbonate, since a higher boiling point implies a higher vacuum requirement in the distillation stage to recover the IL catalyst and purify the carbonate product [13,32,58]. Fig. 3 shows that the boiling point of ethylene, propylene, and butylene carbonates remain nearly constant, drastically increasing from hexylene to cyclohexene to styrene carbonates.

Once the reaction enthalpy was estimated and included in Aspen Plus, the entire process to produce the six different cyclic carbonates was simulated following the flowsheets detailed in Fig. 1 for the sequential process (SCCU) and in Fig. 2 for the integrated process (ICCU). The SCCU processes were simulated for the minimum amount of recirculated



**Fig. 4.** Specific energy consumption (per kilogram of converted CO<sub>2</sub>) of the separated and integrated carbon capture and conversion processes. **Figure A** displays the data categorized by process equipment to produce all studied carbonates, and **B** categorized by utility type for every equipment, which is also listed in Table S3 in the Supplementary Material.

carbonate possible (around 4 %), since in the case of SCCU, the vacuum requirements are not too extreme, and there is no energy consumption saving by recirculating the carbonate, also deteriorating the reactor behavior. However, in the case of ICCU, a recirculation rate of 20 % was selected for all cases, to compare them under the same conditions, given the evidence found in the previous work on propylene carbonate production, which indicated that carbonate recirculation allowed a decrease in the vacuum requirement and energy consumption in the distillation column (T-102 in Fig. 2). Fig. 4 illustrates the specific energy consumption (per kg of CO<sub>2</sub> converted) for both SCCU and ICCU proposals in this research to produce the six studied cyclic carbonates.

The comparison of the energy consumption according to process equipment to produce the six cyclic carbonates examination is presented in Fig. 4A, whereas the specific energy consumption categorized by utility type is shown in Fig. 4B. As can be seen, for nearly all cyclic carbonates production (i.e. ethylene, propylene, butylene, hexylene, and cyclohexene, with the exception of styrene) the ICCU strategy provides lower energy consumption (8.4, 8.7, 9.3, 10.4 and 14.8 MJ/kgCO<sub>2</sub>, respectively) compared to the conventional SCCU strategy (11.6, 12.1, 12.0, 11.7 and 15.7 MJ/kgCO<sub>2</sub>, respectively). It is mainly due to the energy consumption removal in the IL absorbent regeneration (E-100 in Fig. 1) and in the reaction (R-100) stages, as can be seen in Fig. 4A. Thus, the energy requirement in the CO<sub>2</sub> conversion reactor (R-100) is noteworthy for SCCU processes (7–20 % of the total consumption depending on the cyclic carbonate), whereas means a minor contribution (3–8 %) in the ICCU process. In the integrated strategy, two reactions take place in the same equipment, reactor R-100: the transformation of the [CO<sub>2</sub>+IL] complex to yield separate CO<sub>2</sub> and IL, and the cycloaddition of this CO<sub>2</sub> to the epoxide. The first reaction is endothermic with a value of 9.5 kcal/mol, while the second one is exothermic. Hence, given that in all cyclic carbonates, the enthalpy of the cycloaddition reaction is higher than the regeneration of the ionic liquid, the exothermic nature of the reaction provides sufficient energy to reverse the CO<sub>2</sub> chemical absorption in the IL, regenerating the IL and providing the required CO<sub>2</sub> for conversion. Consequently, the final energy in the reactor with the integrated strategy decreases compared to the sequential one. Furthermore, since ICCU does not require an additional absorbent regeneration operation, it is possible to eliminate the demands related to E-100, which is the reboiler for regenerating the IL in SCCU. As a result, except for the production of Sty-C, the integration of CO<sub>2</sub> capture and conversion processes is demonstrated to be a preferable alternative for the production of cyclic carbonates based on AHA bifunctional IL catalyst.

By contrast, in the case of styrene carbonate production process, the sequential CCU strategy demonstrates lower energy consumption (16.8 MJ/kgCO<sub>2</sub>) compared to the integrated strategy (20.2 MJ/kgCO<sub>2</sub>). This is attributed to the significant increasing in vacuum condition in the column T-102 (Fig. 4A). Because of the thermal stability of the IL, the maximum temperature in the reboiler must remain at 120°C. Therefore, it is necessary to increase the vacuum conditions to 0.002 mbar due to the high boiling point of the styrene carbonate (402 °C). As described in previous works [13,32,58], it is worth mentioning the high energy consumption attributed to the vacuum requirements in the IL/carbonate separation column (T-102), resulting from the combination of the high boiling point of carbonates and the low thermal stability of ILs. This is particularly evident in the case of ICCU due to the high IL:carbonate ratio, where the electricity consumption is quite higher compared to SCCU, as shown in Fig. 4B. The breakdown of utilities by type also allows to highlight this effect. It reflects how the energy consumption associated with electricity, i.e., compressions and vacuum generation represents the lowest contribution for most of the SCCU processes, while in the case of ICCU this contribution increases, but keeps a similar consumption value. In other words, part of the thermal consumption has been reduced by slightly increasing the electrical consumption. This contributes to the electrification of the process. However, for the styrene carbonate and cyclohexene carbonate cases the vacuum generation accounts for a great part of the energy consumption. Again, this favors

electrification but, in the Sty-C case, the electricity consumption increases up to be the 54 % of the overall energy production in ICCU compared to the 37 % of SCCU strategy. The same happens with cyclohexene carbonate, the energy consumption increases from 27 % to 47 % due to the vacuum conditions because of the high boiling point of carbonate (354°C), but not being enough to reverse the tendency of the integrated as the best strategy in terms of energy consumptions. The mass balance of main streams and energy consumption of the relevant equipment in the process are listed in Tables S4 and S5 of the Supplementary Material.

Regarding the feasibility of integrating capture and conversion and considering the significance of the boiling point of the carbonates, Fig. 5 represents the energy consumptions in the separated and integrated strategies as a function of carbonate boiling point. For the ICCU proposal strategy, except of the slight deviation of propylene carbonate case, the higher the boiling point of the carbonate, the higher the energy demands. As we noted, this is mainly due to the increased vacuum requirements during the purification of the carbonate (T-102). The slightly lower specific energy consumption for propylene carbonate in comparison with ethylene carbonate case may be related to the higher formation enthalpy of Pro-C over Eth-C.

In the case of SCCU, the trend can be divided into two zones: first, cyclic carbonates with closer boiling points (propylene, ethylene, butylene and hexylene carbonates) in which they are ordered according to molecular weight differences and enthalpy of reaction. This is due to the fact that the two reactions work independently in SCCU. The second zone is integrated by cyclohexene and styrene carbonates with consumes totally influenced by the large consumption of vacuum. Then, it can be preliminarily deduced that for carbonates for which the boiling point is higher than ~257 °C, it is preferable to follow a strategy in which capture, and conversion are conducted separately. Nevertheless, in Figure S4 of the Supplementary Material, vacuum conditions associated with the production of cyclohexene carbonate (Cyc-C) and styrene carbonate (Sty-C) have been included. It can be observed the extreme vacuum pressures in T-102, even in the case of the SCCU strategy, which we consider impracticable (around 10<sup>-4</sup> to 10<sup>-6</sup> bar, and even higher in the case of ICCU). Therefore, in these cases, the technical and economic feasibility may present significant difficulties.

Regarding the global warming potential of these processes, Fig. 6 shows the potential CO<sub>2</sub> equivalent emissions per unit of converted CO<sub>2</sub> related solely to the required utilities. It is observed that for all processes, utility requirements do not result in emitting a greater amount of CO<sub>2</sub> than what is being converted, thus maintaining the goal of these processes: contributing to the reduction of CO<sub>2</sub> emissions. As expected, the CO<sub>2</sub> balance is more favorable in the case of ICCU than SCCU for all carbonates, as the same trend as energy consumption is maintained. This is more noticeable for cyclic carbonates with smaller substituent (ethylene and propylene). Therefore, if the goal is to achieve a CO<sub>2</sub>

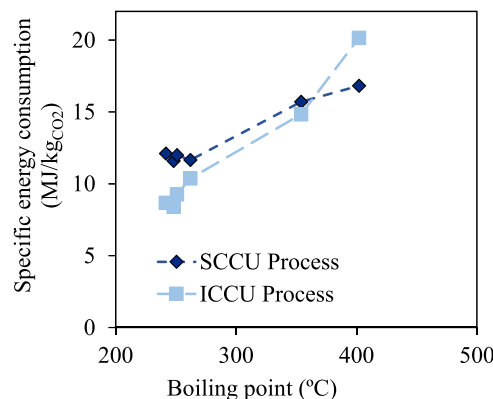


Fig. 5. Specific energy consumption as a function of cyclic carbonates' boiling point for both SCCU and ICCU processes.



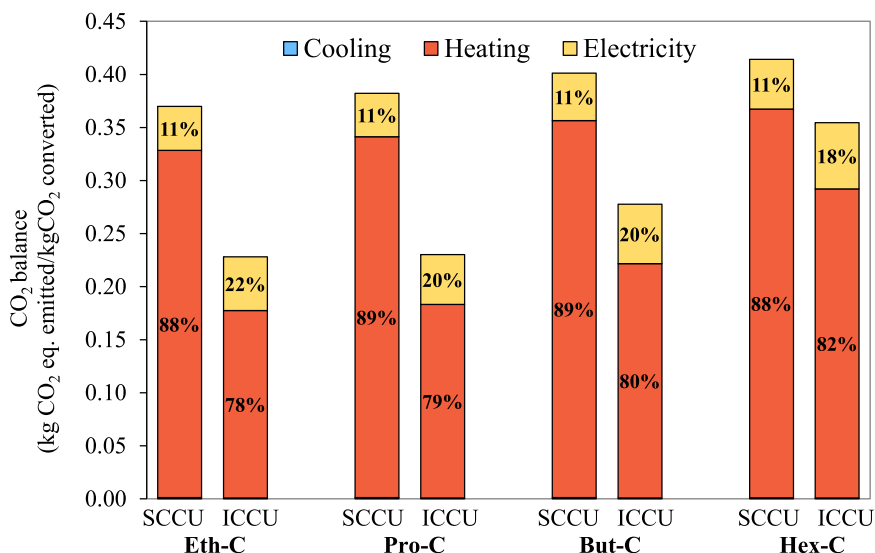


Fig. 6. Potential CO<sub>2</sub> balance associated with utility consumption for the production of the 4 carbonates using SCCU and ICCU strategies.

balance that allows for the conversion of the greatest amount of CO<sub>2</sub> possible, selecting a more volatile carbonate and using the ICCU strategy is the most advisable approach, since in the integrated case the differences between carbonates are greater than in the separate case. Compared to energy consumption (Fig. 4B), the main difference lies in the low contribution of cooling water to CO<sub>2</sub> emissions (around 0.2–0.4 %). On the other hand, electricity consumption had much more weight than heating consumption in both SCCU and ICCU, and in spite of this, due to the low emission factor of electricity compared to steam, it represents a much lower contribution in terms of global warming potential. Therefore, the electrification strategy leads to reduce CO<sub>2</sub> footprint of the processes. This electrification of the processes associated to ICCU configuration is the reason why the difference between one carbonate and another in SCCU was minimal for energy consumption, but there is a slight increase with boiling point in the case of CO<sub>2</sub> emissions equivalents. However, it should be considered that net CO<sub>2</sub> fixation is possible never achieved due to the impact of epoxide production on the overall process [39].

In addition, other significant environmental impact categories are collected in Table S6 in Supplementary Material. Overall, the trend remains consistent across all impact categories, though there are some exceptions such as metal depletion or agricultural land occupation. The ICCU alternative consistently proves more favorable compared to the SCCU option, with the production of the most volatile carbonates standing out as particularly advantageous once again.

#### 4. Conclusions

In this work, a systematic and representative screening of sequential and integrated processes to capture CO<sub>2</sub> and produce CO<sub>2</sub>-derived cyclic carbonates has been performed using bifunctional [P<sub>66614</sub>][2-CNPy] IL. A precombustion carbon source has been selected (32.7 bar and 40 % molar content of CO<sub>2</sub>). Regarding methodology, COSMO/Aspen and DFT tools have been deployed. First, the sequential (capture + conversion) processes have been simulated and energy consumption and GWP have been evaluated. Second, the integrated (capture-conversion) configuration has been simulated together with the estimation of energy consumption and GWP. ICCU was found to be a less energy demanding configuration because of the coupling between the exothermicity of the CO<sub>2</sub>-derived cyclic carbonate reaction and the endothermicity of the regeneration of the IL-CO<sub>2</sub>. ICCU for bifunctional AHA ILs (chemical absorbents and catalysts) is less energy-demanding, turning from heating requirements to cooling needs and electrification of the process, the

latter helping the drastically reduction of the GWP of the integrated processes. To fine tune the energy consumption, the product must be as lighter as possible, whereas some product should be recycled to the absorber to smooth energy requirements. The efforts must be oriented to find materials that show CO<sub>2</sub> desorption processes (regeneration) equivalent to current or new CO<sub>2</sub> conversion reaction enthalpies to describe autothermic integrated reactors. Additionally, discovering new epoxides with low boiling points and minimal CO<sub>2</sub> emissions during synthesis is crucial for improving the net CO<sub>2</sub> balance of the overall process. In these more adequate conditions, a more rigorous and deep inspection can be deployed to enable technology comparison against other CCU approaches.

#### CRedit authorship contribution statement

**José Palomar:** Writing – review & editing, Software, Methodology, Investigation, Formal analysis. **Pablo Navarro:** Writing – review & editing, Supervision, Investigation, Funding acquisition, Conceptualization. **Elisa Hernández:** Writing – review & editing, Formal analysis, Data curation. **Alvaro Pereira:** Writing – review & editing, Formal analysis, Data curation. **Alejandro Belinchón:** Writing – original draft, Investigation, Formal analysis, Data curation.

#### Declaration of Competing Interest

Authors declare no conflict of interests of any kind.

#### Data availability

Data will be made available on request.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jcou.2024.102886.

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