Integrated carbon capture and utilization based on bifunctional ionic liquids to save energy and emissions

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ABSTRACT

The combination of CO_2 capture and conversion (CCU) to produce value-added chemicals is proposed as strategy to mitigate environmental impacts and resolve the cost for CO_2 conditioning, transport and storage. Although there are several CCU pathways in the literature, there are not large-scale designs of CCU processes based on ionic liquids (ILs). This work attempts to take advantage of the reported bifunctionality of ILs, as CO_2 chemical absorbents and CO_2 conversion catalysts, for designing new valuable CCU systems using well-stated absorption and reaction techniques. Separated and integrated CCU processes for propylene carbonate production based on trihexyl(tetradecyl)phosphonium 2-cyanopyrrolide ($[P_{66614}][CNPyr]$) were successfully modelled utilizing the COSMO-based/Aspen methodology. The performance of both CCU approaches was evaluated attending to energy consumption, utility costs and net CO_2 emissions. A novel integrated CCU process achieved promising energy (10.1 MW) and net CO_2 emissions (0.23 kg-eq. CO_2/kg CO_2 absorbed) results, demonstrating not only that dual-functional ILs can be suitable materials for CCU but also the successful integration of IL-based carbon capture and utilization with enhanced process performance.

1. Introduction

Carbon Capture and Utilization (CCU) has received meaningful attention in recent years in order to mitigate environmental and economic impacts [1]. Since CO_2 is already used as feedstock in many industrial sectors like food industry or value-added chemicals production (urea, methanol, propylene carbonate or syngas, among others), CCU processes offer an alternative pathway of useful and valuable products manufacture that promotes circular economy while saving greenhouse emissions and removing the burden of CO_2 compression, transport and storage regarding Carbon Capture and Storage (CCS) technologies [2].

CCU can be coupled either connecting independent capture and utilization techniques (Separated CCU process, SCCU) or designing a fully integrated system (Integrated CCU process, ICCU) [3]. SCCU benefits are attenuated by the high energy demand and cost of the CO_2 capture to supply purified CO_2 to the utilization step due to CO_2 desorption, which represents a major contribution to greenhouse emissions and total costs. The ICCU scheme removes the CO_2 desorption stage, thus absorbed CO_2 is now fed directly after capture to downstream conversion units that synthetize the value-added compound, instead of

pure CO_2. There are growing ICCU approaches proposed in the literature for different products [4–6], but the majority of currently operational ICCU large-scale projects convert CO_2 to methanol by thermocatalysis and CO_2 is captured from flue gases, commonly using amine-based chemical absorption, with high solvent regeneration energy requirement [4]. Hence, there is still a wide range of possibilities on developing novel industrial ICCU alternatives for manufacturing alternative CO_2-based fine chemicals with considerable market, like cyclic carbonates [7] or urea [8], using more efficient carbon capture and utilization technologies [4,9].

In this sense, Ionic Liquids (ILs) have been demonstrated to be promising materials for both CO_2 chemical absorption and conversion due to their unique characteristics [10,11]. Bifunctional ILs enable the integration of capture and utilization, even in a one-pot reactor for some synthesis like quinazoline-2,4(1H,3H)-diones [12]. ILs based on amino acid anions have been applied experimentally as catalysts for CO_2 capture and chemical conversion with epoxides (propylene oxide, PO) to propylene carbonate (PC) [13,14]. However, previous works determined their poor performance as CO_2 chemical absorbents in comparison with other ILs from different nature as Aprotic Heterocyclic Anion-

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based ILs (AHA-ILs) through process simulation [15]. AHA-ILs exhibited outstanding energy and solvent demand values on CO_2 capture processes, even compared to conventional amine-based processes in the techno-economic analysis carried out [16–18], particularly for pre-combustion CO_2 capture [17]. Among AHA-ILs, trihexyl(tetradecyl) phosphonium 2-cyanopyrrolide ([P_{66614}][CNPyr]) is a benchmark alternative for CO_2 chemical capture using ILs [19–21]. Regarding carbon utilization, [P_{66614}][CNPyr] has been also tested in the CO_2 cyclo-addition to epoxides to produce cyclic carbonates, showing adequate epoxide conversion and selectivity to cyclic carbonates with competitive reaction kinetics at mild conditions and short times [22,23]. Therefore, [P_{66614}][CNPyr] consolidates as a suitable bifunctional IL for CCU. Nevertheless, absorption and conversion of CO_2 using AHA-ILs have only been studied separately up to date.

The aim of this study is to evaluate the performance of SCCU and ICCU processes using [P_{66614}][CNPyr] both as CO_2 absorbent and catalyst, for propylene carbonate manufacture and point out the trade-off between both schemes in terms of energy consumption, utility costs and net CO_2 emissions. For this purpose, SCCU and ICCU configurations were simulated using the COSMO-based/Aspen methodology [15,24]. As novelty in CCU projects, pre-combustion CO_2 capture was considered due to the favorable results obtained previously for its application in hydrogen (H_2) production or combined cycle power plants [16,17]. It could enable the simultaneous production of two or even three value-added products: H_2, power and PC. Hence, a simplified syngas stream from coal gasification was used [15]. SCCU scheme is based on previous CO_2 capture [15,16] and conversion designs [25], whereas ICCU process is a completely new engineered. Both SCCU and ICCU configurations are also compared to current CCU projects to identify future optimization guidelines.

2. Process and simulation details

2.1. Component definition and property method specification

Both [P_{66614}][CNPyr]-based SCCU and ICCU processes were simulated in Aspen Plus v12 following a multiscale COSMO-based/Aspen Plus methodology. This methodology was successfully used to simulate previous systems containing ILs [15,16,18,25]. As performed in literature works involving other ionic liquids [26,27], quantum chemical structure optimizations to the minimum level of energy were carried out, presented in other works involving [P_{66614}][CNPyr] [15,16,23]. Then, COSMO-RS calculations were performed to obtain the molecular weight, boiling point, σ-profiles, and COSMO volume of the IL and its CO_2-IL reaction product, are required by the selected COSMO-SAC property method in order to introduce the compounds as pseudo-components in Aspen Plus.

Defining CO_2 as Henry component and using Aspen Plus built-in

temperature dependence expressions for Henry's Law and chemical equilibrium reaction constants (Aspen Plus's Reactive-Distillation equilibrium reaction) allowed the description of the experimental CO_2 physical and chemical absorption (1:1 stoichiometry) in [P_{66614}][CNPyr] as explained elsewhere [15]. Experimental [P_{66614}][CNPyr] temperature dependent viscosity data [19] were also included using Andrade equation to consider mass transfer kinetics during absorption. Thermodynamic properties, chemical reaction and kinetic parameters used to define the CO_2-IL system in Aspen Plus simulations are summarized in Table S1 of Supplementary Material. Propylene oxide and propylene carbonate are present in the conventional Aspen Plus databases, thus their COSMOSAC properties and Henry parameters for CO_2 are already included in Aspen Plus by default.

2.2. SCCU process description and simulation procedure

The SCCU process depicted in Fig. 1 treats a 250 kmol/h inlet gas stream (S1) composed of a 40%mol of CO_2 and a 60%mol of H_2. It enters the absorption column (T-100), modelled in Aspen Plus as a packed column using RADFRAC rigorous model with a rate-based calculation to consider mass transfer kinetics, at 40 °C and 32.7 bar. T-100 is supplied with enough IL to achieve 90% of CO_2 absorption in the IL and operates at adiabatic operating conditions. A H_2-rich stream with a purity of 94 % mol (clean gas) is obtained on top of T-100, while the bottom stream contains the exhausted IL, which is regenerated in a stripping column working at 0.1 bar (T-101, RADFRAC model in Aspen Plus). The regenerated IL (S2) exits the bottom of the stripper and is pressurized (P-100) and cooled (E-102) to the absorption column inlet conditions (32.7 bar and 40 °C) [15,16]. On the other hand, the captured CO_2 (S3) is conditioned to 15 bar and 60 °C in C-100 and E-100 and enters the isothermal reactor (R-100, modeled as RStoic conversion reactor) that operates at 120 °C and 15 bar. Additionally, a PO stream, which has been previously pressurized to 15 bar in P-101, is fed to the reactor. The specified conversion for the CO_2 cycloaddition is 80%mol of PO, based on literature values [23]. The molar flow of the PO stream is adjusted accordingly to be at equimolar conditions to the CO_2 in the reactor, while the PO:IL molar proportion in the reactor is ensured to be 200:1, based on other CO_2 conversion experimental assays and process designs using ILs [25,28,29]. Then, the stream exiting the reactor is fed to a flash (V-100) operating at 5 bar, in which the gas phase (S4) is separated and conditioned in a 3-stage compression to 32.7 bar (C-102). C-102 includes 2 intermediate cooling steps in which the subsequent liquid fractions (S5, containing mainly PO) are recirculated to the reactor, and the final gas phase (S6, containing mainly CO_2 and H_2) is recirculated to the absorption column. The liquid stream leaving V-100 (S7) is fed to the downstream rectification column (T-102), which operates at 0.018 bar in order to evaporate propylene carbonate while avoiding a reboiler temperature higher than 120 °C [30], ensuring that the thermal stability
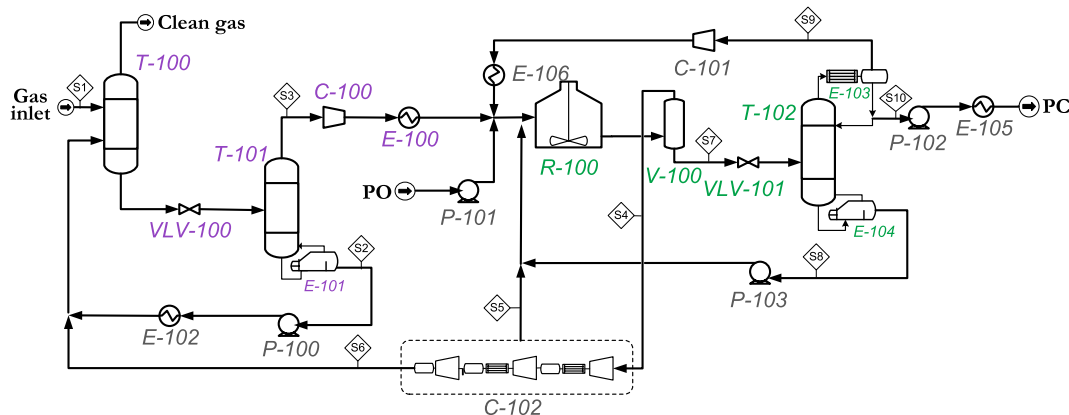

Fig. 1. Process flow diagram of the separated capture and conversion process.

of the IL is not compromised. T-102 is a RADFRAC model rectification column that operates in equilibrium conditions, since the high temperature prevents mass transfer problems related to viscosity, with a partial condenser (E-103). The IL is recovered in the bottom stream of T-102 (S8), which is then pressurized to 15 bar in P-103 and recirculated to the reactor. The vapor phase in E-103 (S9) contains mainly PO and CO_2 and it is conditioned to the reaction conditions in C-101 and E-106 before entering back to the reactor. On the other hand, a 95% recovery of PC in the liquid distillate of T-102 (S10) is specified, as well as a mass purity of 99.8%. Finally, the PC product stream (S10) is pressurized and cooled to 1 bar and 30 °C in P-102 and E-105. The main process equipment specifications are collected in Table 1.

2.3. ICCU process description and simulation procedure

The ICCU process, depicted in Fig. 2, follows a similar approach to the SCCU but it includes certain and crucial modifications that allow for better integration between capture and conversion. This redesign affects to recirculation streams, in addition to the avoided IL regeneration. The same gas stream as in SCCU (S1, 250 kmol/h, 40%mol of CO_2 and 60% mol of H_2) is treated in the absorption column (T-100, RADFRAX model with rate-based calculations), obtaining a 94 %mol H_2 purity stream on top (clean gas). The absorbent is a mixture of IL and PC resulting from the process recirculation, in which the IL proportion is adjusted to obtain the designed CO_2 capture percentage. After T-100, the exhausted absorbent is fed to a flash (V-101, operating at 32.7 bar) where most of the H_2 is recovered in the gas phase to avoid its downstream accumulation, and the resulting gas phase (S2, also containing CO_2) is fed to T-100. Then, the liquid phase (S3) is fed to the reactor (R-100, RCSTR model) operating at 15 bar and 120 °C in which the CO_2 is desorbed from the IL, by means of the equilibrium reaction, and converted to PC in a cycloaddition reaction set at 80% conversion of PO. In addition, PO molar flow fed to the reactor, P-101, V-100 and C-102 maintain specifications from SCCU. Nevertheless, in this case, pressurized stream leaving C-102 (S6) is fed to V-101. On the other hand, liquid phase exiting V-100 (S7, containing mainly PC, IL, PO and CO_2) enters T-102 (RADFRAC model, operating at 0.0096 bar to preserve the IL thermal stability while enabling PC evaporation [30]) to undergo PC purification. In this case, the required vacuum is higher than in SCCU due to the low IL vapor pressure and the higher IL:PC molar proportion. The bottom stream (S8) contains IL and PC and is conditioned to 32.7 bar and 40 °C in P-100 and E-102 and fed to the absorption column to act as absorbent, exploiting the physical absorption of CO_2 in PC [31]. In this case, the vapor phase in E-103 (S9) contains mainly PO, PC and CO_2, thus it is compressed and cooled in C-101 and E-106 to 1 bar and 30 °C, and then the liquid and vapor streams are separated in a flash (V-102, 1 bar). The liquid stream (S11) contains PO and PC and is sent to the reactor after being conditioned to 15 bar in P-101, while the vapor stream (S12) contains CO_2 and PO and it is compressed to 15 bar (C-103)

and fed to the reactor. Finally, PC recovery established in T-102 (S10) is lower than in SCCU, in order to increase PC concentration in the column, so that the vacuum conditions required are less extreme. The selected recovery value allows to reduce the required vacuum to acceptable values without significantly affecting the overall consumption of the process, while PC mass purity in liquid distillate (S10) is also set to 99.8%. As in SCCU, this stream is pressurized and cooled to 1 bar and 30 °C in P-102 and E-105. The main process equipment specifications are collected in Table 1.

3. Calculation of performance indicators of the processes

To compare SCCU and ICCU processes, energy requirements, utilities cost and net CO_2 emissions from energy demand were calculated.

3.1. Energy demand and utilities cost estimation

The energy needed for thermal and power operations was estimated by corresponding Aspen Plus simulation blocks. A pumping/compression efficiency of 70% and a driver efficiency of 95% were used for pumps and compressors power demand calculation according to literature [32,33]. The total energy requirement is the sum of all of them. Therefore, the utilities cost was also calculated as the sum of the costs of the electricity consumed by pumps and compressors (for pressurization and vacuum operation), the low-pressure steam (with 5 °C minimum approach) required in the reboilers of the IL regeneration column (T-101, E-101) in the SCCU case and the PC purification column (T-102, E-104) in both cases, and the cooling water used as refrigerant in cooling steps, assuming their default prices implemented in Aspen Plus v12 ($7.75 \cdot 10^{-2}$ \$/kWh for electricity, $1.90 \cdot 10^{-6}$ \$/kJ for LP steam and $2.12 \cdot 10^{-7}$ \$/kJ for cooling water) [16].

3.2. Net CO_2 emissions from energy demand

Aspen Plus utility calculation can also estimate the CO_2 emissions associated to each utility type attending to different data sources. For electricity and LP steam, carbon tracking tool applied the CO_2 emissions factor from US-EPA-Rule-E9-5711, using natural gas as fuel source and CO_2 energy source efficiency factors of 0.58 and 0.85 for electricity and LP steam, respectively. Cooling water has no CO_2 emissions as many other cooling waters from natural resources considered in several LCA studies and databases as Ecoinvent [34,35]. The sum of these values for all energy-demanding units of SCCU and ICCU processes result in the environmental impact of CO_2 emissions associated to the utility generation required to absorb 3960 kg of CO_2.

4. Evaluation of SCCU and ICCU processes

SCCU and ICCU processes are evaluated and compared attending to

Table 1
Main SCCU and ICCU process equipment specifications.

| Process	SCCU			ICCU		SCCU and ICCU
Equipment	T-100	T-101	T-102	T-100	T-102	R-100
N° stages	10	6	5	10	5	–
Feed stage	Liquid: 1	1	2	Liquid: 1	2	–
	Gas: 10			Gas: 10		
Packing	FLEXIPAC 700Y	FLEXIPAC 700Y	FLEXIPAC 700Y	FLEXIPAC 700Y	FLEXIPAC 700Y	–
Packing height (m)	15	8.25	15	15	15	–
Diameter (m)	1.24	1.64	2.84	1.24	3.64	–
Reflux ratio	–	–	0.1	–	0.1	–
Pressure (bar)	32.7	0.1	0.018	32.7	0.0096	15
Maximum temperature (°C)	70	100	120	68	120	120
Specifications	90% CO_2 recovery on bottom	96% CO_2 recovery on top	95% PC recovery and 99.8% wt. PC purity	90% CO_2 recovery on bottom	50% PC recovery and 99.8% wt. PC purity	80% PO conversion
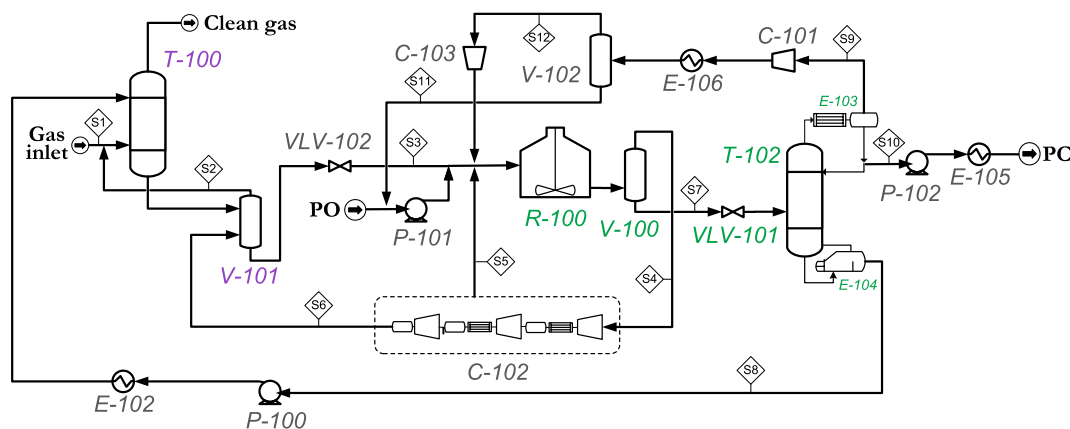
Fig. 2. Process flow diagram of the integrated capture and conversion process.

energy consumption, utilities cost, and net CO_2 emissions associated to energy demands. First, the energy required by each process is analyzed. Fig. 3 classifies energy consumption according to whether it concerns capture, conversion or intermediate conditioning units between capture and conversion for the two CCU processes. The classification of these equipment and their energy consumption can be found in Table S2 in Supplementary Material. As can be seen, SCCU process requires 39% higher energy demands (13.9 MW) than ICCU process (10.1 MW) for the same CO_2 capture, H_2 purification and PC production. Since the sum of energy consumption associated with conversion and conditioning is practically the same for both the SCCU and ICCU processes (≈ 10 MW), the main difference between energy consumptions is associated with the CO_2 capture system, which represents 26% of the total consumption in the SCCU process; in contrast to the ICCU scheme in which it is virtually zero because the CO_2 desorption step is removed. Besides that, the ICCU conversion step is also improved with 1.3 MW less than the SCCU one.

The reduction in the energy demand achieved with the ICCU scheme can be further explained in detail by looking at Fig. 4, which represents the energy required by the most energy-demanding equipment in both SCCU and ICCU processes (A) and illustrates the contribution of each type of energy used (electricity, heating and cooling) to the total energy demand (B). The greatest energy savings (3.7 MW, 26%) in ICCU compared to SCCU are related to the absence of the IL regeneration step as stated before, namely the stripping column reboiler (E-101, 1.6 MW) and vacuum operation (0.3 MW included in "Others" category in

Fig. 4A), the subsequent compressor (C-100, 0.9 MW) and the successive cooler after it (E-100, 0.8 MW), since these equipment are not present in the ICCU process as depicted in Fig. 4A. In addition, the energy balance between cycloaddition exothermic reaction and CO_2 desorption endothermic reaction leads to 82% lower cooling requirement in the reactor (R-100) for ICCU (0.5 MW) than for SCCU (2.8 MW), in which the CO_2 cycloaddition to PO reaction exothermicity also entails high-intensive cooling, but the CO_2 desorption heat requirement is negligible due to the low IL concentration in the reactor. Therefore, the integration of capture and conversion processes based on bifunctional ILs by eliminating the IL regeneration step is a much more energy-efficient approach than carrying out both processes separately, accomplishing equal capture and production specifications. However, the electricity related to vacuum operation in PC purification column (Vac. T-102) is 75% higher in the ICCU process than in SCCU one (0.9 MW greater) due to a greater IL:PC ratio in the column, which increases the vacuum pressure requirement (ICCU: 0.0096 bar vs. SCCU: 0.018 bar) and forces the recirculation of a larger amount of carbonate to avoid extremely implausible pressures. Nevertheless, the recirculation of PC allows decreasing the IL load in T-100 due to its CO_2 absorption capacity, allowing to reduce the required IL flow rate from 41.2 t_{IL} /h in SCCU to 40.4 t/h in ICCU and resulting in an IL holdup in T-100 of 2.0 t_{IL} for SCCU and 1.8 t_{IL} for ICCU. In fact, the greater flow rate in the ICCU scheme as a result of higher PC recirculation and IL flow increases 14% (0.2 MW) the reboiler (E-104) duty and 54% (0.9 MW) the cooling demand in E-102 (absorbent conditioning) compared to SCCU. Other equipment as PC purification column condenser (E-103) and conditioning units (part of "Others" category in Fig. 4A) maintain similar energy consumptions in both processes. As a result, the electricity demand remains similar in both processes, but heating and cooling requirements are highly reduced in ICCU scheme (41% or 1.4 MW and 28% or 2.2 MW, respectively, hence demanding less LP steam and cooling water) as shown in Fig. 4B. There are few CCU processes in the literature to be compared with for context. As example, for CCU methanol production processes, heat consumption values of 1.2 GJ/t_{CO2} in the separated process and 2.6 GJ/t_{CO2} in the integrated one were reported [3], compared to 3.1 GJ/t_{CO2} (3.4 MW in Fig. 4B) and 1.8 GJ/t_{CO2} (2 MW in Fig. 4B) for the SCCU and ICCU processes presented in this paper, respectively. Regarding electricity consumption, the same CCU methanol production processes exhibited 2.2 GJ/t_{CO2} for the separate process and 1.2 GJ/t_{CO2} for the integrated scheme, compared to 2.5 GJ/t_{CO2} (2.7 MW, SCCU) and 2.3 GJ/t_{CO2} (2.5 MW, ICCU) of this work. Thus, our CCU processes are reasonably close in terms of energy demand even dealing with a heavier CO_2-based product.

Regarding operating costs derived from utility needs represented in Fig. 4B, Table 2 collects the cost associated with each utility per ton of CO_2 absorbed in both processes. The total utility-derived operative cost of the SCCU process (60.7 $/t_{CO2}$) is 14% higher than that of the ICCU
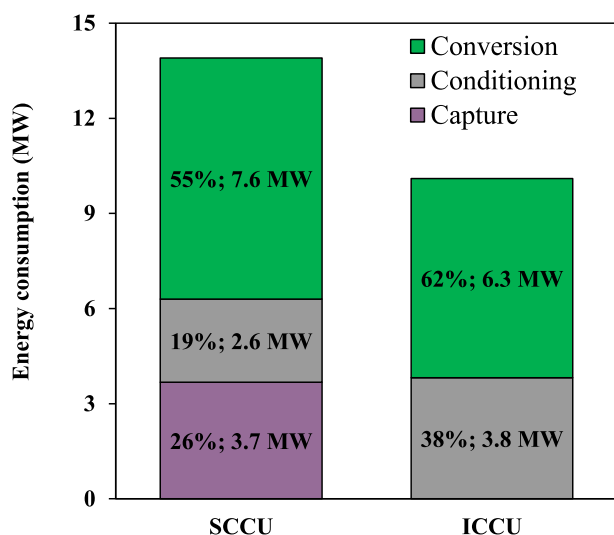

Fig. 3. Energy consumption in capture, conversion and conditioning units of separated (SCCU) and integrated (ICCU) processes.
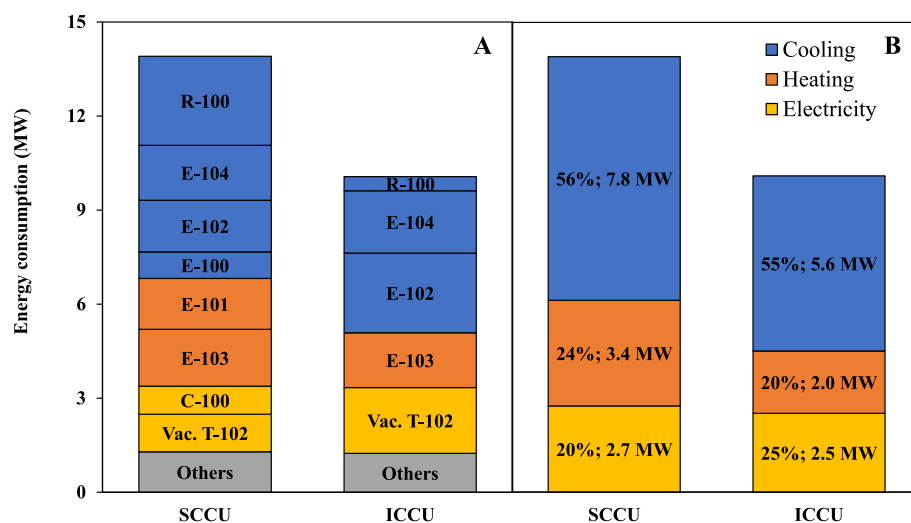
Fig. 4. Energy consumption according to process equipment (A) & thermal and power contributions (B) for both SCCU and ICCU processes.

Table 2
Operating costs associated with SCCU and ICCU process utilities.

		Cost ($/t$_{CO2}$)			
		Capture	Conditioning	Conversion	Global
SCCU	**Heating**	2.8	–	3.0	5.8
	Cooling	0.2	0.4	0.9	1.5
	Electricity	23.6	6.5	23.3	53.4
	Total	26.5	7.0	27.2	60.7
ICCU	**Heating**	–	–	3.4	3.4
	Cooling	–	0.6	0.4	1.1
	Electricity	–	9.0	39.8	48.8
	Total	–	9.7	43.6	53.3

(53.3 $/t$_{CO2}$). Considering 1.68 $/kg as PO purchase price [36] and a selling price of 2 $/kg for PC [37], the economic potential of these processes -taking into account only operating costs and not capital costs- would be up to approximately 2,400 $/t$_{CO2}$ in both cases. A positive economic potential value usually indicates a favorable profitability of the process, since operating costs' economic impact is generally higher than capital costs' economic impact. Moving into utility type, electricity expenses are 9% greater in SCCU process than in ICCU process due to the slightly higher electricity requirements in SCCU. As discussed in Fig. 4, high electricity demands in SCCU and ICCU are mainly caused by vacuum operation in T-102, unavoidable considering that PC boiling point and IL thermal stability limit the operation scenarios of the rectification unit. This vacuum requirement in T-102 has a related electricity cost of 23.3 $/t$_{CO2}$ in SCCU (38% of total cost), while it accounts for 39.8 $/t$_{CO2}$ in ICCU (75% of total cost). Thus, novel strategies as selective liquid–liquid phase separation between the IL and PC that substitutes the problematic rectification column [23] could further improve both energy demand and utilities cost of future ICCU alternatives bases on bifunctional ILs. In addition, as shown in Table 2, LP steam costs are 71% higher in SCCU (5.8 $/t$_{CO2}$) than in ICCU (3.4 $/t$_{CO2}$) due to CO$_2$ desorption, while cooling water costs are slightly decreased 0.4 $/t$_{CO2}$. Nevertheless, there are other CCU alternatives using amines-solutions for CO$_2$ capture and CO$_2$ methanation that present more cost-effective values (utilities cost of 20 $/t$_{CO2}$ [38] using the same utility prices from Aspen Plus). Therefore, other synthesis routes for CO$_2$ conversion may be tested to develop new IL-based CCU alternatives if the restrictive separation between PC and IL is not resolved, since CO$_2$ capture based on AHA-ILs was demonstrated to be a competitive cost-effective alternative to conventional processes [17,18]. On the other hand, the calculated IL losses are negligible, however, a mass loss of 2% has been estimated as an indication of cost penalty. Then, assuming an IL price of

50 $/kg [16,39], the costs associated to the IL make-up would be 220 $/t$_{CO2}$ in the case of SCCU and 204 $/t$_{CO2}$ in the case of ICCU.

Moving to net CO$_2$ emissions due to energy utilization in the processes, Table 3 summarizes the equivalent emissions according to the different contributions of the SCCU and ICCU processes. As shown, both processes net CO$_2$ equivalent emissions per unit of absorbed CO$_2$ are less than 1. In other words, the processes capture and transform more CO$_2$ than the amount they emit due to their energy consumption. However, ICCU process emits 26% less CO$_2$ per unit of CO$_2$ absorbed (0.23 kg-eq./kg) than SCCU (0.31 kg-eq./kg). Regarding these emissions' allocation, since they are directly related to utility consumption, they present a very similar picture to energy consumption and utility-related operating costs: CO$_2$ equivalent emissions associated with capture in ICCU are non-existent given the absence of IL regeneration step, whereas they account for 32% of total emissions in SCCU. The conversion step entails the largest part of total emissions, accounting for 48% and 90% in SCCU and ICCU, respectively. On the opposite, conditioning units present the lowest contribution to the global emissions in both processes. Regarding the emissions distribution according to the type of utility, cooling has no influence in any process since cooling water is considered to come from a natural source (0 net CO$_2$ emissions in Table 3). On the contrary, heat and electricity each account for approximately half of the emissions of each process. In the case of SCCU, heat contribution to emissions is greater due to the CO$_2$ desorption reboiler duty. Finally, ICCU process has a higher influence of electricity than heat, due to the higher electricity consumption in T-102 and non-existent steam consumption in capture. Our estimations are in good agreement with methanol production using ICCU (0.3 kgCO$_2$ eq./kg CO$_2$ converted [3]), other CO$_2$ to PC conversion processes based on ILs (0.26 lb CO$_2$ eq. emitted/lb CO$_2$ utilized [40]) and they demonstrate that ICCU processes have even less

Table 3
Net CO$_2$ equivalent emissions related to energy consumption per unit of CO$_2$ absorbed, for both SCCU and ICCU processes.

		Net CO$_2$ equivalent emissions (kg CO$_2$ eq. emitted/kg CO$_2$ absorbed)			
		Capture	Conditioning	Conversion	Global
SCCU	**Heating**	0.08	–	0.09	0.17
	Cooling	0.00	0.00	0.00	0.00
	Electricity	0.06	0.02	0.06	0.14
	Total	0.14	0.02	0.15	0.31
ICCU	**Heating**	–	–	0.10	0.10
	Cooling	–	0.00	0.00	0.00
	Electricity	–	0.02	0.11	0.13
	Total	–	0.02	0.21	0.23

environmental impact of net CO_2 emissions than conventional sources of CO_2 feedstock manufacture as ammonia plants (0.525 kg CO_2 eq. per 1 kg of feedstock CO_2 [41]). Current results could be further improved if electricity came from renewable sources.

5. Conclusions

Separated (SCCU) and integrated (ICCU) carbon capture and utilization processes using [P$_{66614}$][CNPyr] both as CO_2 absorbent and catalyst for propylene carbonate production were successfully simulated using the COSMO-based/Aspen methodology. The new-engineered ICCU scheme exhibited the best performance results regarding energy consumption, utility costs and CO_2 emissions. The energy demand was reduced in 27% -from 13.9 MW in SCCU to 10.1 MW in ICCU- by eliminating the stripping column to desorb CO_2 as well as its posterior conditioning for CO_2 utilization and integrating it in the conversion reactor, which indicates that one pot solution could be feasible. Moreover, this reduction in the energy requirement leaded to 14% lower costs (53.3 $/t$_{CO_2}$ in ICCU against 60.7 $/t$_{CO_2}$ in SCCU) and 26% less CO_2 emissions (0.23 against 0.31 kg-eq. CO_2/kg CO_2 absorbed for ICCU and SCCU, respectively) in the ICCU process. Results that are in line with other CCU projects. Hence, bifunctional [P$_{66614}$][CNPyr] was demonstrated to be a promising material for ICCU. However, a major drawback related to PC purification was identified. The vacuum operation required to produce PC while ensuring the thermal stability of the IL limits the operating configurations and increased the power demand, its utility cost, and the associated CO_2 emissions. Therefore, optimizing the thermal stability of ILs, developing new ILs-PC separation alternatives, or applying ICCU strategy to produce other value-added products are improvement guidelines for future IL-based ICCU research.

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.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cej.2022.137166.

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