



Reaction-extraction platforms towards CO₂-derived cyclic carbonates catalyzed by ionic liquids

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ABSTRACT

This work systematically monitors the keys to understand the applicability of two close-cycle processes recently proposed that enable the regeneration of homogeneous catalysts based on ionic liquids by liquid-liquid extraction. It aims at looking for more efficient CO₂ conversion platforms to prevent global warming. The universal character of these two platforms is here demonstrated for a substrate scope that accounts the 7 most representative cyclic carbonates of the literature and 17 ionic liquids that play the role of efficient homogeneous catalysts. Water-based platform proves to be more appropriate for separating hydrophilic IL catalysts from less polar and hydrophobic carbonates, improving the energy consumption when compared with distillation as benchmark separation approach in the literature. On the contrary, hydrophobic ionic liquids enhance the process combined with fatty alcohols to produce hydrophilic cyclic carbonates and drastically reduce energy consumption at reasonable lower product specifications when compared with benchmark process. Overall, liquid-liquid extraction stands out as a more efficient process scheme to separate cyclic carbonates from homogeneous catalysts based on ionic liquids.

1. Introduction

Carbon dioxide (CO₂) stands out as the principal greenhouse gas, main cause of the well-known actual global warming. CO₂ is mostly produced by hydrocarbon combustion and gasification processes and its concentration in the atmosphere has increased from 399 ppm in 2013 to 419 ppm in 2022 (Mauna Loa Observatory, 2022). The still continuous release of CO₂ remains damaging the environment nowadays. In this context, it is mandatory to mitigate these emissions by adopting different actions such as Carbon Capture and Storage (CCS) or Carbon Capture and Utilization (CCU) (Gür, 2022). In the actual decade, CCU capacity reached around 110 million metric tons, so it seems that preventing CO₂ emissions by transforming it into value added compounds has gained attention among scientific community (Adomaitis, 2020). CO₂ is used in the production of compounds of very different nature such as methane, urea, methanol, formic acid, polymers, or cyclic carbonates (Alper and Orhan, 2017). These last products are of special interest when produced from CO₂ since they can be generated by cycloaddition reactions at mild conditions, while avoiding the traditional synthesis

routes using phosgene (Buysch). Cyclic carbonates are used in several applications such as aprotic polar solvents, monomer in polymer synthesis, secondary batteries, cosmetics, resins, biomedical or pharma industries, among others (Pescarmona, 2021). Moreover, they were also demonstrated to be tunable solvents for different applications in traditional separations of the chemical industry, such as separation of aromatic-aliphatic by liquid-liquid extraction or extractive distillation (Hernández et al., 2021a). The research focused on the production of these CO₂-generated cyclic carbonates involves catalysts of very different nature like metal halide (Sodpiban et al., 2021), metal complex (Shen et al., 2003), organic bases (Stewart et al., 2016), metal organic frameworks (MOFs) (Pal et al., 2020), or ionic liquids (ILs) (Zhang et al., 2017). The use of ILs as catalysts for cycloaddition reactions has gained the attention of scientific community in last two decades due to the attractive properties that this kind of solvents present (Sang and Huang, 2020). ILs are liquid salts only formed by a cation and an anion with melting points below 100 °C (Holbrey and Seddon, 1999). Their practically null volatility (vapor pressure close to zero) remains as the main advantage of using these compounds in the chemical industry.

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Moreover, their easy chemical tunability, high thermal and chemical stability, high polarity and low melting points are other important properties of ILs that are crucial when using them as catalysts (Chiappe and Pieraccini, 2005). Finally, the possibility of tuning the cation and the anion for specific tasks, make ILs being considered as “designer solvents” (Plechikova and Seddon, 2007). ILs can be classified in hydrophobic and hydrophilic species, modulating their behavior with water (Rodrigues et al., 2021). It is well known that those ILs presenting voluminous and low polar cations, such as phosphonium based, exhibit high hydrophobicity (Rodrigues et al., 2021). On the other hand, those containing imidazolium cations completed with short alkyl chain length substituents or polar functional groups usually present high water affinity (Rodrigues et al., 2021). Regarding the anion, halide anions based ILs generally show a hydrophilic behavior, whereas amino acid anion-based ILs (aa-ILs) depend on the cation form, and numerous reported aprotic heterocyclic anion-based ILs (AHA-ILs) are found hydrophobic (Avelar Bonilla et al., 2019). During the last two decades, several authors studied ILs of very different nature as catalysts in CO₂ cycloaddition reactions to epoxides to form cyclic carbonates. In 2001, the use of ILs based on the 1-butyl-3-methylimidazolium cation and different anions, including fluorinated and chloride-based ILs, was reported for the first time (Peng and Deng, 2001). High conversion values were reached at 20 bar and 110 °C. It was the first time that this reaction was demonstrated using ILs as catalysts without any additional solvent. From that point, scientific community tried to improve the obtained yields and selectivities by using supercritical CO₂ and designing new ILs with functionalization that can improve conversion values (Wang et al., 2007). However, authors still pay special attention to those ILs with high availability, low price, and commercially synthesized. Therefore, anions based on chloride and bromide are of special interest because of their good catalytic properties and low price. The use of 1-ethyl-3-methylimidazolium bromide as catalyst was reported, obtaining conversion values higher than 90% with total selectivity to the cyclic carbonate of interest (Su et al., 2018), and also studied the influence of halide anions (chloride, bromide and iodide) on the catalytic activity, again reporting high conversion and selectivity (>90%) (Martínez-Ferraté et al., 2018). In the last decade, with the aim of integrating CO₂ capture and conversion operations, some ILs presenting CO₂ chemical absorption were proved as catalysts in CO₂ cycloaddition reactions. First, AHAs with phosphonium based cations were proved to chemically absorb CO₂ and they also reached conversions to cyclic carbonates higher than 90% at 10 bar and 100 °C (Moya et al., 2018). Amino acid based ILs are other family of ILs presenting CO₂ chemical absorption that were tested as catalysts in this kind of reactions, obtaining 80% of conversion at 120 °C and 4 bar (Hernández et al., 2021b). In this case, anions based on glycine, proline, and methionine were tested. In all these works, the cyclic carbonate of reference is propylene carbonate, but the catalytic activity of the ILs is extended to cyclic carbonates of very different nature, such as styrene, butylene or hexylene, among others (Chen and Mu, 2019). Slight differences are found in terms of conversion and selectivities when changing the starting epoxide (Chen and Mu, 2019). Therefore, it was demonstrated that the IL catalytic activity remains in almost the same values independently on the cyclic carbonate produced. However, the separation of these ILs used as catalysts from the obtained products is still a challenge because cyclic carbonates usually present high boiling points and ILs have volatilities close to zero (Chen and Mu, 2019). In last decade's works, distillation was proposed as catalyst-product separation operation, obtaining the cyclic carbonate from head and the IL from the bottom of the column (Xiao et al., 2014). It was demonstrated that this operation implies very high energy requirements in the reboiler and demands extreme vacuum conditions to avoid thermal degradation of the catalysts (Yue et al., 2014). As a response for this ineffective separation strategy standing out as benchmark in the literature, two recent works developed by our group proposed as alternative a liquid-liquid extraction operation to efficiently separate the catalyst and the product with significantly lower energy requirements, using water

(Hernández et al., 2021c) or fatty alcohol (Santiago et al., 2021) as solvents. In this sense, it is important to divide two different platforms depending on the IL nature to be separated. In the case that the IL presents hydrophilic behavior (as studied aa-ILs), the solvent required for liquid-liquid extraction separation is water (Hernández et al., 2021c). Thus, the catalyst can be recovered in the aqueous phase whereas the cyclic carbonate concentrates in the organic one. In our previous work, total recovery of the catalyst was achieved (high distribution ratios and selectivity), specially at low aa-IL concentrations when water is used as extracting agent (Hernández et al., 2021c). Moreover, a complete process was proposed using Aspen Plus process simulator obtaining propylene carbonate of high purity without any IL losses. On the other hand, in the case of using hydrophobic ILs (as studied AHA-ILs), a fatty alcohol is required to separate the compounds, finding alcohol/water biphasic system as an enhancer in terms of product/IL selectivity (Santiago et al., 2021). In this case, a phosphonium based cation with 2-cyanopyrrolide anion was used as catalyst and the strategy was validated by performing 5 consecutive reaction/separation cycles remaining almost the same conversion values (Santiago et al., 2021). Therefore, it was proved, at experimental and theoretical levels, that liquid-liquid strategy can efficiently separate cyclic carbonates from hydrophobic and hydrophilic ILs. Since ILs catalysts can be generally classify in both groups, liquid-liquid extraction is here presented as a universal product/catalyst separation strategy by properly selecting the solvents.

The aim of this work is to demonstrate the universality of the proposed product/catalyst separation strategy based on liquid-liquid extraction for CO₂ conversion to produce cyclic carbonates using ILs, by means of molecular and process simulations. For this purpose, a systematic evaluation of 17 IL catalysts (from hydrophilic to hydrophobic ones), 7 cyclic carbonates (with remarkable different structure) and 7 solvents (water, 1-octanol, 1-decanol, 1-dodecanol, palmitoleic alcohol, oleyl alcohol and erucyl alcohol) was carried out by an integrated molecular-process simulation approach, done up to process scale, where *ad hoc* solutions were accomplished for each particular combination. This allows concluding which solvent and catalyst are the best for each cyclic carbonate in terms of energy consumption and product standards. For this purpose, ILs and cyclic carbonates were analyzed in terms of their hydrophobic/hydrophilic behavior by means of octanol-water partition coefficients and polarized charge density calculated by COSMO-RS method. Then, liquid-liquid equilibria of binary (cyclic carbonate + solvent) and ternary system, and extractive properties of water/fatty alcohols to separate IL catalyst and cyclic carbonate product were evaluated by COSMO/Aspen methodology, analyzing the separation efficiency (catalyst recovery and product recovery and purity) by a single stage liquid-liquid extraction. Finally, the design of the complete CO₂ conversion process, including reaction and separation operations, was developed by process simulation to evaluate specific energy consumption and separation performance for all studied cyclic carbonate + IL + solvent systems. The strategy, combining both separation platforms, has been revealed universal and flexible to adapt itself to each product-catalyst scenario to produce CO₂-derived cyclic carbonates using ILs. In addition, the separation scheme remains as the key to reduce energy consumption of the process, leaving in a secondary role the catalytic reaction stage of the process.

2. Computational procedures

2.1. Compounds optimization and COSMO-RS calculations

The electronic structures of all the compounds (17 ILs, 7 cyclic carbonates, 7 epoxides, 7 solvents, Table S1 in Supplementary Material) involved in this work were optimized to their minimum energy state using the software Turbomole 7.4 (Ahlich, 2018). Turbomole focuses on electronic structure methods such as density functional theory (DFT), typical applications of Turbomole include structure optimization and the search for transition states in the ground and electronically excited

states (Balasubramani et al., 2020). In all cases, calculations were accomplished at two different computational levels: BP86/TZVP and BP86/TZVPD_FINE using the COSMO continuum solvation method (solvent effect) (Klamt and Schüürmann, 1993). In order to ensure that all the compounds' optimizations were done properly, a single point calculation was performed for each case to avoid negative vibrational frequencies. All the information of the compounds is collected in a *.cosmo file. Ionic liquids with different hydrophobicity that had been studied in previous CO₂ conversion works, such as AHA-ILs (Moya et al., 2018), aa-ILs (Hernández et al., 2021b), 1-butyl-3-methylimidazolium-based (Peng and Deng, 2001) or 1-ethyl-3-methyl imidazolium-based (Su et al., 2018), were chosen, and others with similar structures were used.

Then, the *.cosmo file obtained from the optimization of the molecules was used to predict different thermodynamic properties based on quantum chemical calculations of the compounds using COSMOtherm v. 19 software (COSMOlogic GmbH & Co. KG, 2019). This software employs COSMO-RS method (Conductor-like Screening Model for Real Solvents) for thermodynamic calculations. First, properties of pure compounds (molecular weight, density, boiling point), listed in Table S1 in Supplementary Material, were calculated. Then, σ -profiles of all the compounds were obtained in order to analyze the polarity of each compound. Finally, the octanol-water partition coefficients at infinite dilution of all the ILs and cyclic carbonates were calculated at 25 °C to elucidate the possible interactions with the solvents selected for this work.

2.2. COSMO/Aspen methodology

All the compounds treated in this paper were included in Aspen Plus v12 as pseudo-components according to the COSMO/Aspen-based methodology reported elsewhere (Hernández et al., 2021c). To do so, properties of pure compounds (density, normal boiling point, and molecular weight) previously calculated using COSMOtherm were included in this software. In order to define completely the compounds, σ -profile (collected in Table S2 in Supplementary Material) and COSMO volume were also calculated and implemented. Then, COSMO-SAC property model, developed by Lin and Sandler and with modified exchange energy by Mathias et al. (Lin et al., 2002), was used to predict the thermodynamic properties by estimating the activity coefficients of the different mixtures. This methodology was widely used in last years for different systems involving ILs such as liquid-liquid extractions (Larriba et al., 2018), CO₂ chemical and physical absorption (Hospital-Benito et al., 2022), H₂S chemical and physical absorption (Lemus et al., 2021), hydrocarbon (Ayuso et al., 2022) or siloxanes (Santiago et al., 2020), together with an incipient use in CO₂ conversion processes. In the previous works, it was properly validated in each case, and it provides results with enough accuracy for first stages of the conceptual design of new processes. It is important to remark that the selected *.cosmo files related to epoxides and cyclic carbonates were the ones using TZVPD_FINE parametrization, while those of ILs and solvents were those that use TZVP parametrization. This is because when validating the methodology, these combinations provided similar results to the experimental ones, as can be checked in the Supplementary Material Figs. S1 and S2.

2.2.1. Single stage liquid-liquid extraction modelling

First, liquid-liquid equilibria data of (cyclic carbonate + solvent) binary mixtures were calculated by COSMO-based/Aspen methodology at ambient conditions (1 bar and 25 °C), in a single equilibrium step (DECANTER model in Aspen Plus as default) and a molar ratio of 1:1.

Secondly, the same DECANTER model at identical operating conditions was used to predict liquid-liquid equilibria of (cyclic carbonate + IL + solvent) ternary systems with two streams fed to the unit. The first one with 100 kmol/h composed of a mixture of cyclic carbonate and 0.5%mol ILs (according to previous works on the literature (Hernández

et al., 2021c)) and a second of pure solvent (water or fatty alcohol for each platform). The solvent flow rate was modified as a function of cyclic carbonate's one to maintain a mass S/F ratio of 0.5 in the equilibrium stage. Then, extractive properties of the solvent to extract the IL catalyst from cyclic carbonate product, namely IL partition coefficient (K_{IL}) and ionic liquid/carbonate selectivity ($S_{IL/C}$), used in previous work (Navarro et al., 2022), were calculated using the equations:

$$K_{IL} = \frac{x_{IL}^E}{x_{IL}^R} \quad (1)$$

$$S_{IL/C} = \frac{x_{IL}^E \cdot x_C^R}{x_{IL}^R \cdot x_C^E} \quad (2)$$

where x_{IL}^i denotes the IL mass fraction in the extract (E, solvent-reach) or raffinate (R, carbonate-reach) phases, and x_C^i denotes the carbonate mass fraction in the extract (E) or raffinate (R) phase.

Last, IL and cyclic carbonate recovery and purity from single stage liquid-liquid extraction were calculated for all the (cyclic carbonate + solvent + ILs) ternary systems studied in the work, by using five different solvents (water, 1-octanol, 1-decanol, oleyl alcohol and erucyl alcohol) using the DECANTER model simulations in Aspen Plus.

2.2.2. Close-cycle CO₂ conversion process modelling for propylene carbonate production

First, a process scale analysis was carried out to produce propylene carbonate (Pro-C). Pro-C is used as benchmark cyclic carbonate in this work since it is the most studied in the literature (Peng and Deng, 2001), obtained from propylene oxide (PO) reactant. Throughout the study, three processes configurations were compared, which are shown in Fig. 1, that mainly differ in the separation stage to recover the IL catalyst and to purify the Pro-C product. First, for the three configurations, the streams fed to the reactor (100 kmol/h of PO and the corresponding IL to ensure a 200:1 PO:IL molar proportion in the reactor) are heated up to 120 °C and compressed to 15 bar in E-100 and P-100. The operating conditions in the reactor and the PO:IL ratio have been determined from previous work (Hernández et al., 2022). Fresh CO₂ is already fed at 15 bar adjusting its molar flow rate so that it is at equimolar conditions with respect to the epoxide in the reactor. The PO conversion in R-100 is fixed to 90%, a reasonable value using ionic liquids (Su et al., 2018), which is followed by a flash operation (V-100) at 1 bar of total pressure and a stripping column (D-100) to eliminate the unreacted epoxide and CO₂.

The reference process (Fig. 1A) uses a traditional distillation column (D-101) to separate the IL catalyst and the cyclic carbonate product due to volatility differences. Based on previous studies (Hernández et al., 2021c), it was proposed to switch to an extraction column to recover the IL and separate it from the Pro-C in order to reduce the energy consumptions in this operation. In this proposal, two platforms can be differentiated according to the affinity of the cyclic carbonate/IL pair with water or alcohols. The water platform (Fig. 1B) presents a liquid-liquid extraction column (S-100) using water as solvent to recover the IL, which is then recycled to the reactor. Next, a traditional distillation column (D-101) is needed to purify the Pro-C product by eliminating the water dragged in raffinate phase. On the other hand, the alcohol platform (Fig. 1C) uses alcohol as solvent in a liquid-liquid extraction column (S-100) to separate the IL catalyst and the Pro-C product. For both extraction-based platforms, the S/F ratio in S-100 was adjusted to achieve a 99.9% IL recovery. It is important to point out that the maximum operating temperature was 120 °C for all the process configurations in order to ensure the thermal stability of the ILs. According to this, D-100 and D-101 columns need to work at vacuum conditions in the reference process and alcohol platform. In the case of the water platform, the S/F ratio is selected to meet IL recovery requirements, but also to avoid vacuum conditions both in D-100 and D-101. In all cases, D-100 distillate rate is modified in order to achieve at least a 99.9% of PO recovery, while D-101 was designed in order to

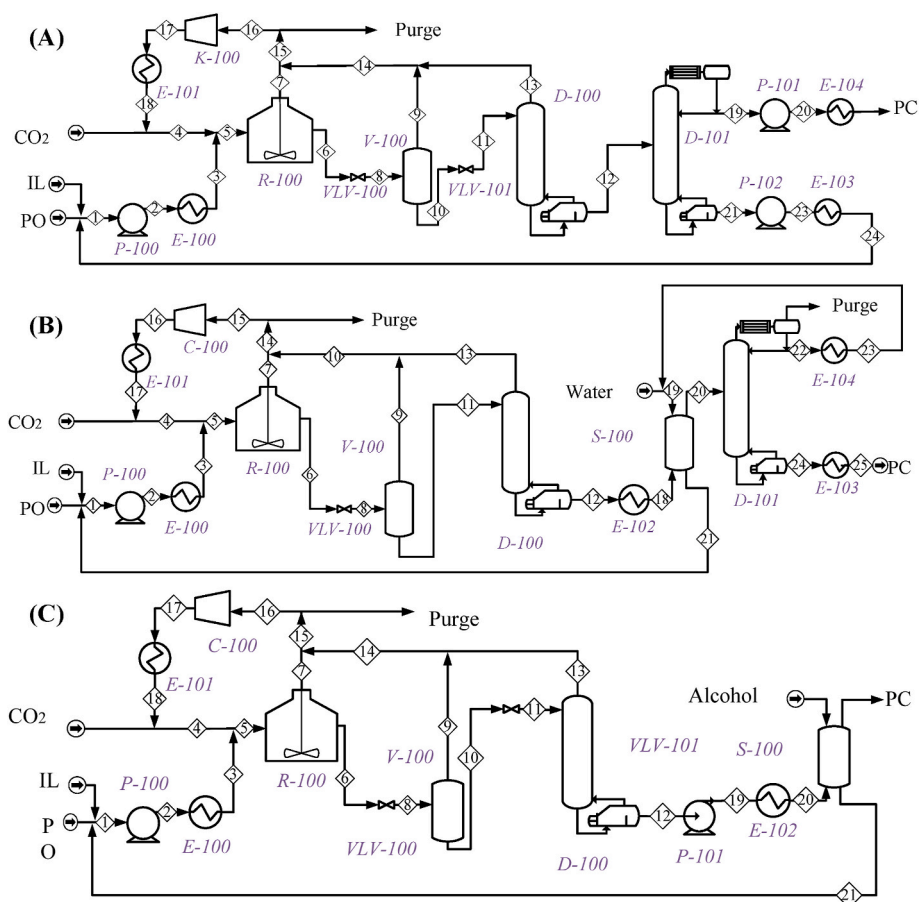


Fig. 1. Flowsheets of the three processes evaluated in this work. (A) distillation-based process reference, (B) water platform, and (C) alcohol platform.

achieve a 99.9% of Pro-recovery and purity (whether as distillate stream or bottom stream, depending on the configuration). In the case of the alcohol platform, Pro-C purity cannot be specified, being determined by the selected S/F ratio. A brief summary of the process equipment specifications can be found in Table 1, based on previous works (Hernández et al., 2022) were the distillation and water-based platforms were developed, and have been extended to the alcohol platform for better comparison.

Finally, the total energy consumed (kWh per kg of Pro-C produced) was calculated, adding all the energy consumption of the process equipment, both thermal and electrical, and dividing it by the final carbonate production, for the three process configurations using different ILs and different solvents in the case of the alcohol platform. Additionally, the influence of the reaction conversion on the specific energy consumption of the close-cycle process was studied for

distillation-, water- and alcohol-based platforms. Table S3 of the supplementary material shows the temperature, pressure and composition of the 5 streams intermediate in Fig. 1, for the production of propylene carbonate with each of the three platforms using the ionic liquid and solvent with the lowest energy consumption for each platform.

2.2.3. Close-cycle CO₂ conversion process modelling to produce other cyclic carbonates

Once the reference Pro-C production was studied, the methodology was extended to CO₂ conversion to produce other cyclic carbonates. Different separation configurations are proposed depending on the reactant volatility. To produce But-C, the close-cycle CO₂ conversion processes are identical to those used for Pro-C (Fig. 1), due to the relatively high volatility of butylene epoxide, i.e., using a stripping section (D-100) to recover the unconverted reactant. The production of Chl-C,

Table 1

Process specifications of CO₂ conversion to produce Pro-C using ILs in the reference process and water-based and alcohol-based platforms.

Case	Distillation-based Reference		Water platform			Alcohol platform	
Column	D-100	D-101	D-100	D-101	S-100	D-100	S-100
N stages	10	30	10	30	4	10	4
Feed	1	15	1	15	S1/F4	1	S1/F4
Stage							
Reflux	–	–	–	–	–	–	–
Pressure (bar)	0.022	0.005	1.000	1.000	1.000	0.021	1.000
Maximum temperature (°C)	120	120	120	120	25	120	25
Variable	Distillate rate	Distillate rate	Distillate rate	Bottoms rate	S/F ^a	Distillate rate	S/F
Specification	99.9% PO recovery	99.9% Pro-C mass purity and recovery	99.9% PO recovery	99.9% PO recovery	99.9% IL recovery	99.9% PO recovery	99.9% IL recovery

^a S/F in water platform is the minimum value that allows both IL designed recovery and avoiding vacuum conditions in the process.

Hex-C, Cyc-C, Gly-C and Sty-C, requires that the D-100 column presents a partial condenser, as shown in the process diagrams of Fig. 2, for the 3 platforms. This is due to the higher boiling temperature of their corresponding epoxides (Table S1 in Supplementary Material), which makes possible to condensate these compounds using cooling water. In this condenser, distillate stream temperature is ensured to be 55 °C, improving the epoxide recovery by reducing utility requirements. The rest of the equipment specifications are maintained as in the Pro-C production case.

As in the Pro-C case, 100 kmol/h of pure epoxide are fed as fresh stream, and reactor conversion is fixed to 90%. Then, for all these 6 other carbonates, specific energy consumption per kg of produced carbonate and product purity are calculated in order to assess the most energy-efficient production platform depending on the product and its purity requirement.

3. Results and discussion

3.1. COSMO-RS analysis

First, COSMO-RS model was used to classify the catalysts and the products, i.e. ILs and cyclic carbonates. Two main criteria were used to understand the structure-property relationship, namely octanol-water partition coefficient (K_{ow}) and sigma profile of the involved compounds. Fig. 3 portrays the octanol-water partition of the selected ILs (A) and the selected cyclic carbonates (B). As can be seen, the selected ILs

exhibit a diverse range of values of K_{ow} , with ILs presenting a clearly hydrophobic behavior ($K_{ow} \gg 1$, represented in red), a clearly hydrophilic behavior ($K_{ow} < 1$, represented in blue), and ILs of intermediate behavior (values of K_{ow} close to 1, represented in light red or blue). More than this valuable rough classification, the result is a scale of strongly different IL behaviors ranging from 10^{14} to 10^{-7} values as a function of the IL nature. Moving from catalysts to products, a smooth similar picture is found, accounting for four hydrophobic cyclic carbonates (Sty-C, Hex-C, Cyc-C and But-C; $K_{ow} > 1$), and three hydrophilic ones (Chl-C, Pro-C and Gly-C, $K_{ow} < 1$).

Three catalysts and products are selected to understand the hydrophobicity/hydrophilicity behavior in terms of compound polarity by analyzing their sigma profiles, collected in Fig. 4. As can be seen in Fig. 4A, the hydrophobic IL [P₆₆₆₁₄][Inda] presents a high peak in the non-polar region and the intermediate [bmim][MET] presents a smaller peak in said region, while the hydrophilic [Choline][Cl] presents noticeable peaks in both hydrogen bond acceptor and donor regions and low amount of electronic density in the non-polar region. This clearly states an increasing polarity trend in the order [P₆₆₆₁₄][Inda] < [bmim][MET] < [Choline][Cl] that matches the affinity with water that was anticipated in Fig. 3. Looking at the product (Fig. 4B), the three portrayed carbonates present a characteristic peak in the hydrogen bond acceptor region, which relates to the carbonate group, being clear that Gly-C presents the higher hydrogen bond acceptor character due to the greater height of said peak. Regarding the non-polar region, it is clear that Hex-C presents the highest peak, followed by Pro-C and then Gly-C.

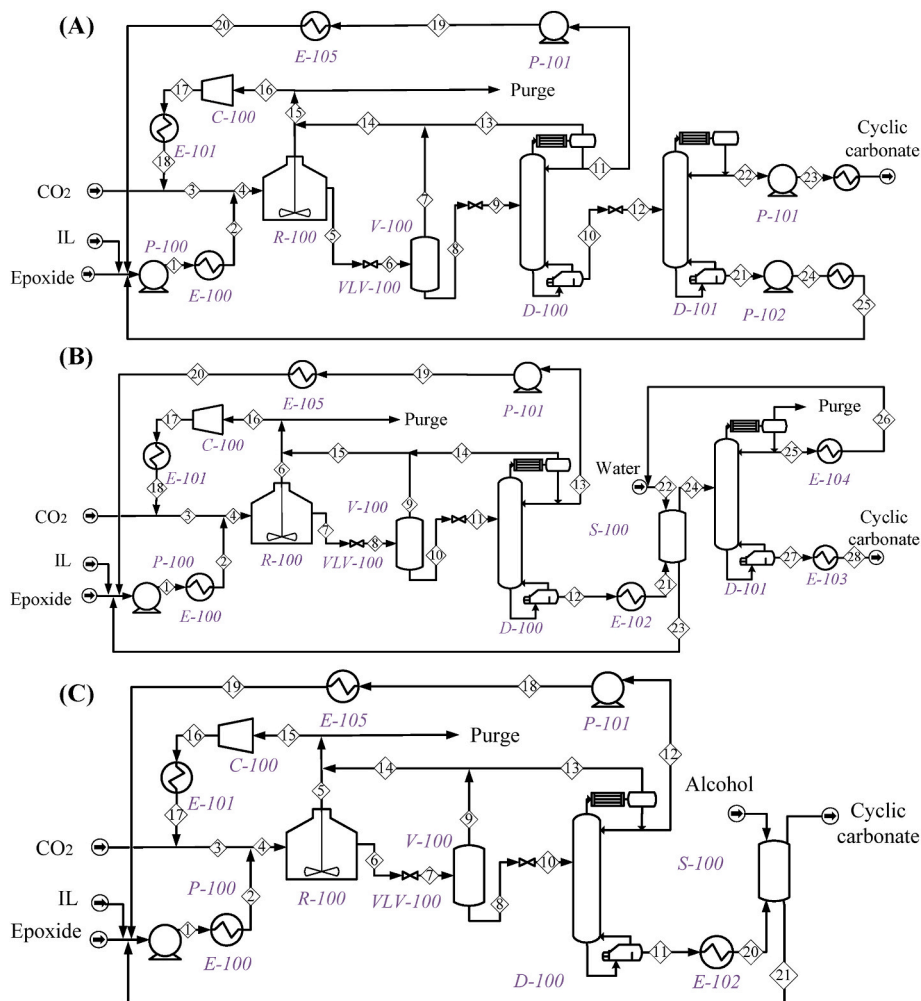


Fig. 2. Process diagram to produce Chl-C, Hex-C, Cyc-C, Gly-C and Sty-C using the distillation-based reference process (A), water platform (B) or alcohol platform (C).

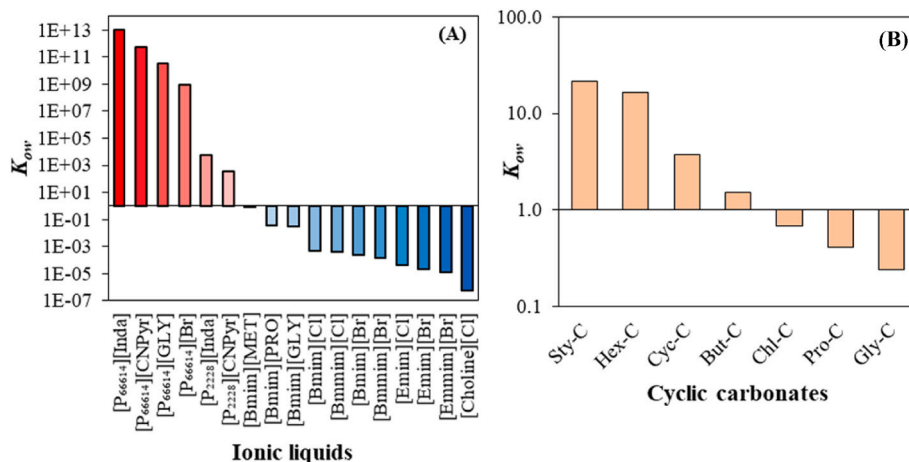


Fig. 3. Octanol-water partition coefficient of selected ILs (A) and cyclic carbonates (B) calculated by COSMO-RS method at 1 bar and 25 °C.

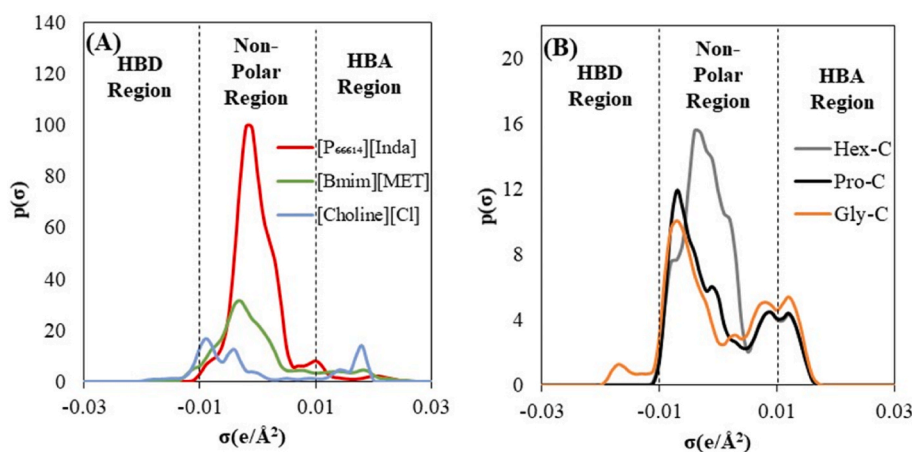


Fig. 4. Sigma profile of (A) representative IL catalysts and (B) cyclic carbonates products from COSMO-RS method.

Finally, Gly-C presents a polar group with hydrogen bond donor capacity. Thus, it can be concluded that the polarity of these carbonates increases in the order Hex-C < Pro-C < Gly-C, demonstrating how the polarity of carbonates can be increased by decreasing the alkyl chain length (from Hex-C to Pro-C) or by the addition of acid groups (Gly-C).

3.2. Liquid-liquid extraction

Once COSMO/Aspen was validated as predictive tool for mixtures

composed of ILs, cyclic carbonates, water and fatty alcohols (see details in Fig. S1 in the Supplementary Material), a systematic evaluation of the mutual solubilities in (cyclic carbonate + solvent) binary mixtures is presented in Fig. 5. It is found that all the cyclic carbonates mixtures with water (excepting Gly-C) result in a biphasic system. The six carbonates with highest K_{ow} and low polarity exhibit immiscibility with water, i.e. low water solubility in the organic phase (Fig. 5A) and reasonable low cyclic carbonate concentration in the aqueous phase (Fig. 5B). In the case of 1-decanol (used as benchmark fatty alcohol),

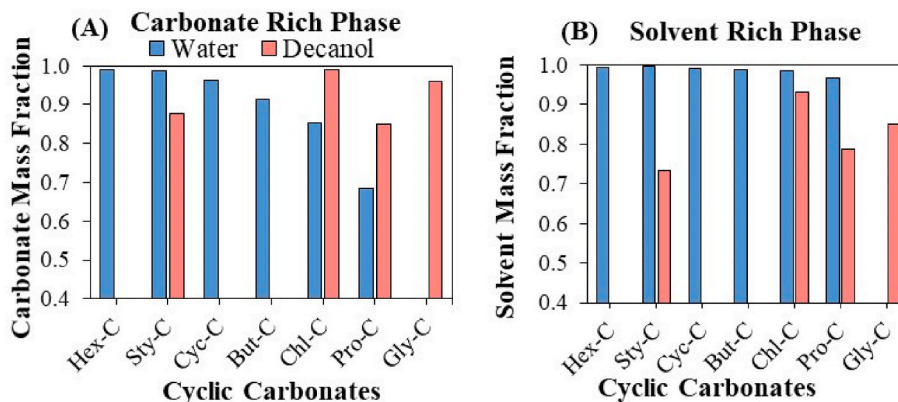


Fig. 5. Liquid-liquid equilibrium data of (cyclic carbonate + solvent) binary mixture calculated by COSMO/Aspen at 1 bar and 25 °C.

those cyclic carbonates with the lowest K_{ow} and more polar character (as Chl-C, Pro-C and Gly-C) present partial immiscibility with the alcohol solvent (Fig. 5B). The biphasic system formed by alcohol-cyclic carbonate pair imposes larger cyclic carbonates solubilities in the solvent and comparable high solvent losses in the cyclic carbonate phase. Nevertheless, the designer role of the alcohol can be used to promote more selective binary systems. Fig. 6 displays the mutual solubilities of propylene carbonate and different well-known fatty alcohols. As can be seen, it is possible to select a more favorable alcohol-based system, in which the solvent losses in the carbonate phase (Fig. 6A) and the carbonate solubility in the alcohol (Fig. 6B) can be decreased, standing erucyl and oleyl alcohols as the best candidates. This point is crucial since fatty alcohols present high boiling points, comparable with cyclic carbonates, which would limit further purifications for the cyclic carbonate isolated from the liquid-liquid separation.

To complete the computational evaluation, the extractive properties of water/fatty alcohol solvent were estimated from (cyclic carbonate + IL + solvent) ternary systems. Fig. 7 compares the IL distribution ratio (K_{IL}) and IL/cyclic carbonate selectivity ($S_{IL/C}$) obtained by COSMO/Aspen simulations. As shown, Fig. 7A contains the extractive properties of the 102 systems evaluated using water as solvent, covering a wide range of values for K_{IL} (from 10^{-14} to 10^6) and $S_{IL/C}$ (from 10^{-12} to 10^{10}). It is clear that the partition coefficient and selectivity are closely related in (cyclic carbonate + IL + water) systems. Water presents very favorable extractive properties for separating hydrophilic ILs (blue colors), with large values of K_{IL} and $S_{IL/C}$, specifically 10^6 and 10^{10} , while hydrophobic ILs (red colors) impose very low values of K_{IL} and $S_{IL/C}$, specifically 10^{-14} and 10^{-12} . On the other hand, carbonate structure does not seem to have a significant effect on the extractive properties of water for IL catalyst, since when the extractive properties are favorable for the hydrophilic IL extraction from cyclic carbonate, they fall in a favorable range for all carbonates, while they lie in an unfavorable range for all carbonates if the IL is hydrophobic. Nonetheless, all carbonates compatible with water-based platform (as shown in Fig. 5) can be satisfactorily separated when selecting the adequate IL.

Moving from water-based systems to fatty alcohol driven ones (Fig. 7B), it is observed a similar linear relationship between K_{IL} and $S_{IL/C}$, but obtaining less extreme extractive properties ranges (K_{IL} extending from 10^{-6} to 10^7) and $S_{IL/C}$ (from 10^{-5} to 10^9). As opposed to water systems, the highest extractive properties are those involving hydrophobic ILs (red colors), and the lowest extractive properties of fatty alcohols are found for hydrophilic ILs (blue colors). Once again, the effect of the cyclic carbonate on extractive properties of alcohol solvent is marginal, but the nature of the alcohol shows a clear influence on the extractive properties. Among the alcohols, the most hydrophobic ones (erucyl and oleyl alcohols) show the greatest potential, concluding that

the most favorable system for alcohol-based platform would be the one containing a hydrophobic IL, a hydrophilic cyclic carbonate and one of the most hydrophobic fatty alcohols.

Moving from extractive properties to liquid-liquid extraction analysis, these extractive properties are deployed to model the separation unit responsible to regenerate the catalyst. In order to evidence the role played by the IL and the cyclic carbonate, one-stage extraction is simulated by means of COSMO/Aspen approach. Fig. 8A and B displays the IL recovery for the water-based and alcohol-based platforms, respectively. It is worth mentioning that only compatible cyclic carbonates (immiscible with solvent) are tested for each platform (driven by water or alcohol). Clearly, the IL recovery is determined by its nature, since hydrophilic ILs are properly extracted by water, while hydrophobic ILs are effectively collected in the alcohol, but not the other way around, as expected from the previous extractive properties analysis. For water-based platform, the cyclic carbonate nature does not play any relevant role in the IL recovery, whereas interesting trends are found for the alcohol-mediated platform. Thus, ILs with intermediate hydrophobicity, i.e. cations with butyl substituents and/or anions composed by amino acids, show relatively good separations from more hydrophobic cyclic carbonates (as Pro-C and Sty-C), whereas these ILs cannot be recovered from cyclic carbonates containing polar hydroxyl groups (as Gly-C) due to competitive IL-solvent and IL-product molecular interactions. In any case, the alcohol-driven platform preferably recovers hydrophobic ILs, with basic nature, from the four compatible cyclic carbonates.

Regarding the product, the cyclic carbonate recovery (collected in Fig. 8C for the water-based platform and Fig. 8D for the alcohol-based platform) is determined by its solubility in the solvent, water or alcohol, and the IL has no effect on this product recovery in any platform, independently from the IL nature. Following the same trend, product purity (evidenced in Fig. 8E and F) responds to the immiscibility with the solvent, being determined by solvent solubility in carbonate-rich phase. For the water-based platform, product purity is closely high (>96%) for all cyclic carbonates, while for the alcohol-based platform the purities are more diverse, being hydrophilic carbonates the purest of all. On the other hand, the effect of the IL nature on the product purity is negligible for both platforms (Fig. 8E and F).

3.2.1. Processes outlook for Pro-C production: general remarks

Once evaluated the catalyst-product separation by liquid-liquid extraction single stage, the complete process for the production of Pro-C by water-based, fatty alcohol-based and distillation-based processes was simulated following the flowsheets detailed in Fig. 1. Obtained specific energy consumption and Pro-C purity are shown in Fig. 9. In Fig. S3 in the supplementary material it is detailed to which category

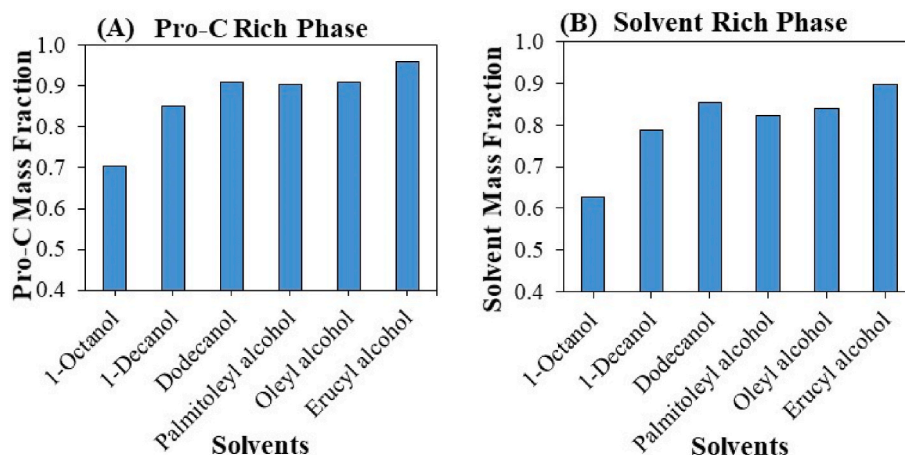


Fig. 6. Liquid-liquid equilibrium data of (cyclic carbonate + fatty alcohol) binary mixture calculated by COSMO/Aspen at 1 bar and 25 °C.

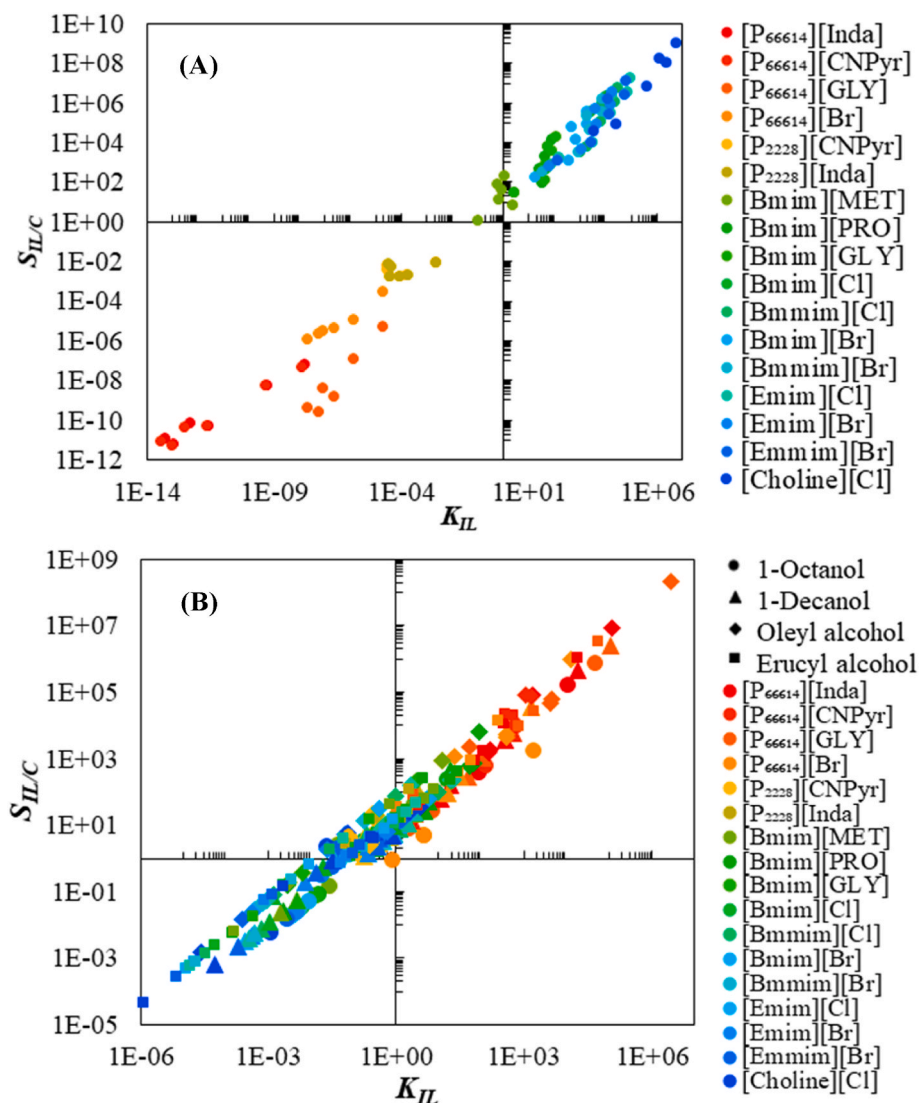


Fig. 7. Ionic liquid distribution ratios (K_{IL}) and ionic liquid/carbonate selectivity ($S_{IL/C}$) for the water-based platform (A) and the alcohol-based platform (B).

(conditioning, reaction or separation) each equipment is assigned depending on its purpose. As can be seen in Fig. 9A, the reference process energy demands, and product purities are nearly independent from the IL selected. Water-based platform significantly improves energy consumption when compared with the reference process (mainly due to the decrease of the required heating; see Fig. S4 in Supplementary Material), preserving the same process specifications in terms of product recovery (99.9%) and purity (99.9%wt.), so it is demonstrated as a more efficient approach to accomplish IL catalysts regeneration and Pro-C product purification for compatible systems, although for some ILs (such as [Choline][Cl]) the energy demands reduction is greater due to the more efficient separation. Moving to alcohol-based platform, the benefit in terms of energy consumption is even deeper (due to the lower required heating, see Fig. S4 in Supplementary Material), but it is independent from the IL type, because it is determined by reaction stage. Nevertheless, alcohol platform provides propylene carbonate purities below commercial standards.

Fig. 9B shows the most suitable ILs selected for each platform with different solvents in the case of the alcohol-based platform. As seen, the nature of the alcohol plays an important role in the reached purity of the product but is less important for energy consumption. By increasing the alcohol chain length and adding unsaturation, product purity and energy consumption are improved, standing erucyl alcohol as the best

candidate. In any case, the required product grade is closely related to the application of the compound, and fatty alcohol impurities can be compatible with polymerization processes and its use as solvents, among others (Schwarz, 2018).

Considering that the catalytic activity of each IL can be different, an evaluation of several PO conversions in the reactor is of interest. As depicted in Fig. 10, the conversion does not alter the liquid-liquid impact on the energy reduction but completely sets the energy consumption within the process configuration since a more effective catalyst will demand less energy in the whole process. In any case, it is advisable to select ILs compatible with liquid-liquid extraction approach rather than optimizing the catalyst role within the reactor framework exclusively. In addition, both water and fatty alcohols have been demonstrated to improve ILs catalytic activity (Hernández et al., 2021c), which implies that the use of the LLE-based platforms also enhances the catalytic stage.

3.2.2. Guidelines for the process design of CO₂ conversion to produce other cyclic carbonates

The conclusions obtained for Pro-C benchmark product are here extended for the whole cyclic carbonate collection selected in this work (Table S1), performing COSMO/Aspen process simulation for the flowsheets detailed in Fig. 2. There are combinations of carbonates and platforms that are not compatible due to the total solubility of the

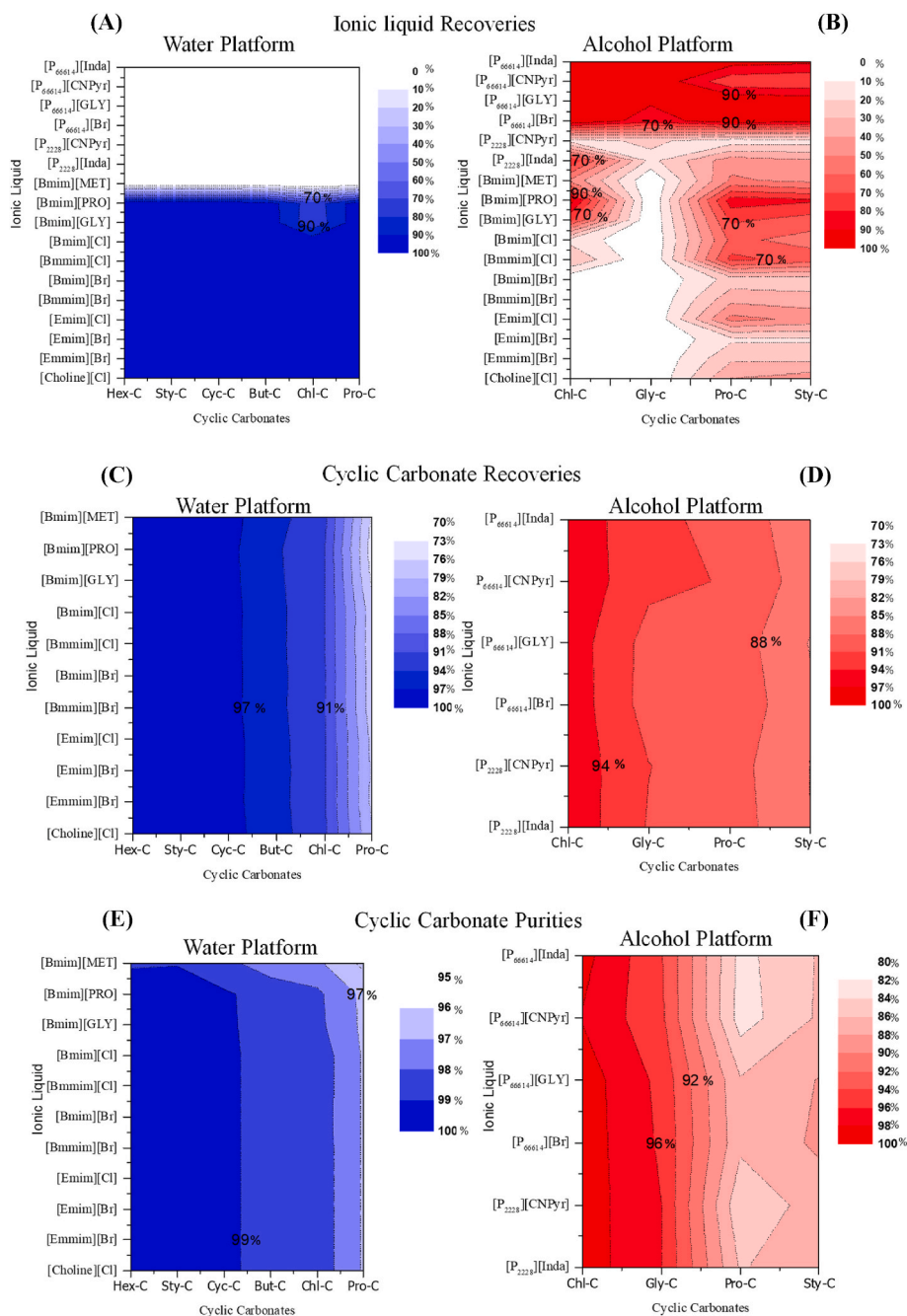


Fig. 8. Ionic liquid recoveries (A and B), carbonate recoveries (C and D), and carbonate purities (E and F) for water platform (A, C and E; blue) and alcohol platform with 1-decanol (B, D and F; red).

product in the solvent. Fig. 11 pictures the specific energy consumption of all feasible processes for each cyclic carbonate and using the best IL selected for each platform, namely i) distillation benchmark process, ii) water-based platform and, iii) fatty alcohol driven platform. The main trend observed for the compatible pairs is that the strategy based on liquid-liquid extraction provides, for all carbonates, a significant energy reduction.

In the case of Chl-C, the distillation-based reference process and the alcohol-based process require extreme vacuum conditions (<0.0005 bar) in D-100 with extremely low distillate temperatures, which is considered unfeasible. Regarding the water-based platform, 99.9%wt product purities can be obtained with lower energy consumption than the reference process, except for the production of Sty-C, in which this platform increases the energy demands. Nevertheless, the energy

demands of production of Sty-C and Pro-C can be reduced by selecting the alcohol platform, however, it is necessary to consider that the product purity in the alcohol-based platform for Pro-C and Sty-C are 96%wt. and 97%wt., respectively, while in the case of Gly-C commercial standard purity of 99.9%wt. is achieved. From the above, it can be deduced that the liquid-liquid extraction allows reducing energy consumption in the production of all these cyclic carbonates, however, depending on the required product purity the most suitable platform may differ. The impurities of fatty alcohols are above current standards for cyclic carbonates but are not conventional impurities. *Ad hoc* evaluation of these impurities are recommended for cases of direct use as solvents or in polymerization cases. To ease the comprehension of these results, the main features of the developments done for each cyclic carbonate are collected in Table 2.

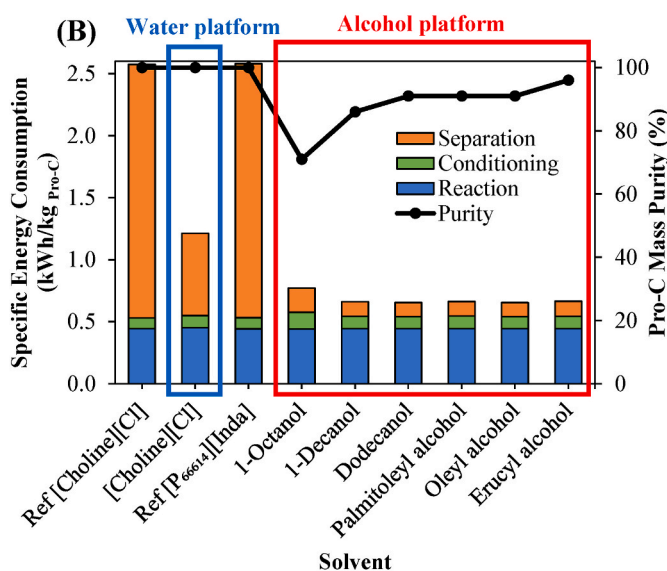
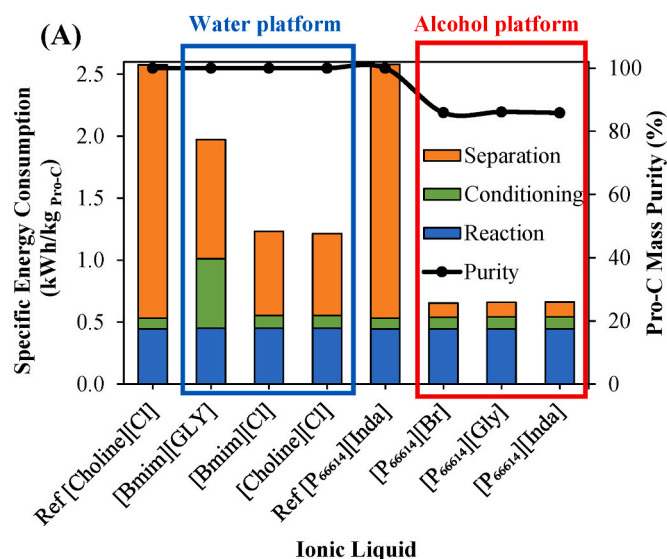


Fig. 9. Specific energy consumption and Pro-C mass purity (%) as a function of platform, catalyst and solvent, for a 90% specified conversion in the reactor. (A): different ILs in the reference process (ref), water-based platform, and alcohol-based platform (with 1-decanol as solvent). (B): best separation performance ILs ([Choline][Cl] and [P₆₆₆₁₄][Inda] for the water-based and alcohol-based platform, respectively) with different solvents. When using erucyl alcohol as solvent, the temperature of the liquid-liquid extraction in S-100 was fixed to 35 °C due to the solvent melting point.

4. Conclusions

A systematic evaluation of 17 ionic liquids, as catalysts, and 7 cyclic carbonates, as CO₂ conversion products, has been driven by computational analysis from thermodynamic fundamentals (DFT and COSMO-RS methods) to process scale (COSMO/Aspen methodology), moving from conventional distillation process to liquid-liquid extraction strategy to regenerate the catalyst and purify the product with two platforms based on the use of water or fatty alcohols as solvent.

The liquid-liquid strategy, combining both (alcohol and water-based) separation platforms, has demonstrated universal use in the separation of a wide number of representative cyclic carbonates, since it can reduce energy consumption in the process design to meet commercial standards. Water-based platform was found very efficient to

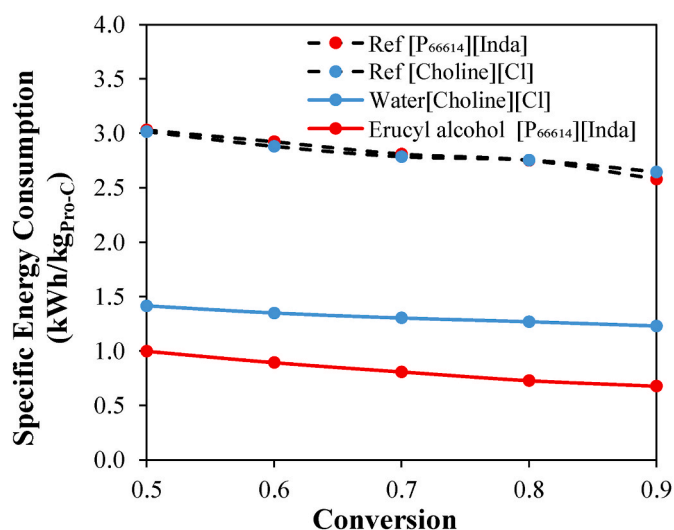


Fig. 10. Influence of PO conversion in the specific energy consumption of the studied Pro-C production processes.

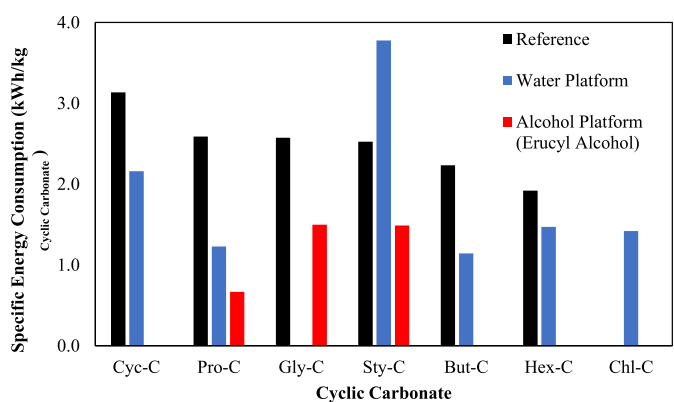


Fig. 11. Specific energy consumption for all feasible processes for the seven common cyclic carbonates selected and the best separation performance ILs ([Choline][Cl] for the water platform and [P₆₆₆₁₄][Inda] for the alcohol platform).

Table 2

Recommendations for the production of each cyclic carbonate depending on its specified purity, using ILs as homogeneous catalysts in CO₂ cycloaddition to alkylene epoxides.

Products	Description	Guidelines
Hex-C, Cyc-C, But-C, Sty-C	The products are almost insoluble in water. High boiling point of the epoxide imposes drawbacks with water platform. Alcohol-driven approach does not reach 99.9 wt% purity.	Water-based platform with hydrophilic ionic liquids. Low grade (97 wt%) with alcohol impurities of 3%: alcohol-based platform and hydrophobic ionic liquids. Commercial grade: conventional distillation and any ionic liquid.
Pro-C	The product is partially soluble in water and alcohol.	Low grade (96 wt%) with alcohol impurities of 4%: alcohol-based platform and hydrophobic ionic liquids. Commercial grade: water-based platform with hydrophilic ionic liquids.
Chl-C	High epoxide boiling point imposes extreme conditions in its recovery by distillation.	Water-based platform with hydrophilic ionic liquids.
Gly-C	The product is completely soluble in water.	Alcohol-based platform and hydrophobic ionic liquids.

recover hydrophilic IL from hydrophobic cyclic carbonate, obtaining higher product purity and lower energy consumption than distillation-based reference separation process. Fatty alcohol-based platform was demonstrated to allow the efficient recovery of hydrophobic ILs from compatible alcohol immiscible cyclic carbonate, with even lower energy requirements; however, lower product purity is achieved, being improved for more hydrophilic cyclic carbonates up to commercial grade.

More than a new approach in emerging research, this work highlights the role of integrated molecular and process design, in particular the IL selection, to improve the catalyst-product separation, as the main point to build low energy-consumption processes, extending the more widely applied criteria of developing homogeneous IL catalysts to decrease the energy barriers in the reaction step, enhancing the reaction conversion. In this sense, to propose new cleaner technologies for cyclic carbonates production, more efforts must be turned on the energy-demanding steps identification and replacement, i.e. regeneration step. To ease this focus, the use of a priori tools combined to process simulators, such as COSMO/Aspen approach used in this work, must be the leading methodologies to quickly mitigate the potential impact of developing technologies.

CRedit authorship contribution statement

Alejandro Belinchón: Formal analysis, Investigation, Data curation, Writing - original draft. **Rubén Santiago:** Data curation, Formal analysis, Investigation, Writing – review & editing. **Elisa Hernández:** Data curation, Formal analysis, Investigation, Writing – review & editing. **Cristian Moya:** Data curation, Formal analysis, Investigation, Writing – review & editing. **Pablo Navarro:** Conceptualization, Formal analysis, Investigation, Writing – review & editing. **José Palomar:** Conceptualization, Funding acquisition, Project administration, Resources, Software, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2022.133189>.

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