

Solvent-catalyst optimization of ionic liquid-based CO₂ conversion to propylene carbonate: Laboratory validation and techno-economic analysis

Elisa Hernández^{a,1}, Alejandro Belinchón^{a,1}, Rubén Santiago^{a,b}, Cristian Moya^c, Pablo Navarro^{a,*}, José Palomar^a

^a Chemical Engineering Department, Autonomous University of Madrid, Calle Tomás y Valiente 7, 28049 Madrid, Spain

^b Chemical Engineering and Environmental Department, ETSI Industriales, Universidad Politécnica de Madrid, C/ José Gutiérrez Abascal 2, Madrid 28006, Spain

^c Chemical & Environmental Engineering Group, Universidad Rey Juan Carlos, 28933 Madrid, Spain

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ABSTRACT

Ionic liquids (ILs) have been widely suggested as efficient catalysts to produce propylene carbonate (PC) from CO₂ and propylene oxide (PO). Recently, the use of liquid-liquid extraction (LLE) has been proposed to efficiently separate ILs from PC since it reduces energy consumption, with fatty alcohols when selecting hydrophobic ILs. However, the study of this reaction-separation system at experimental level is scarce. In addition, the solvent-catalyst system design to improve the global process performance is a current challenge. This work develops an integrated experimental-computational multiscale approach to improve the PC production process by CO₂ cycloaddition to PO using the IL [P₆₆₆₁₄][Br] as catalyst. Reaction yield and liquid-liquid equilibrium measurements were carried out for the experimental validation of the proposed catalytic/separation systems using different solvents (fatty alcohol and water). Process modelling and techno-economic analysis were performed using Aspen Plus for solvent-catalyst optimization, proceeding with an integrated iterative experimental-computational approach to decrease energy requirements and operating costs. It was found that the presence of solvents in the reaction affects conversion and selectivity of the reaction, with fatty alcohols increasing PC yield and enabling IL/PC separation, while water reduces PC selectivity. On the other hand, the presence of water in the process allows reducing electricity demands as well as vacuum requirements. It was possible to modulate fatty alcohol and water dosages to minimize energy consumption, vacuum requirements and utility costs. Optimal configurations have an energy consumption of approximately 0.6 kWh/kg_{PC} and utility costs of 6.6 \$/t_{PC}.

1. Introduction

To keep the global warming-related temperature increase below 2°C as stipulated in the Paris Agreement [1] - it is undoubtedly necessary to reduce CO₂ emissions. To this end, it is essential to ensure that the largest possible share of electricity used on a global scale comes from renewable sources, to increase energy efficiency and to further develop CO₂ capture and utilization or storage (CCUS) technologies [2]. Within these technologies, CO₂ utilization stands out since CO₂ is an inexpensive and highly available raw material [3] that can be employed directly in various applications [4], or can be converted to other products [5], promoting circular economy.

Some of the products that can be obtained from CO₂ conversion are

synthesis gas, carboxylic acids, methanol, methane, ureas, or organic carbonates [6]. Among the latter, cyclic carbonates, and especially propylene carbonate (PC), have recently received increased attention due to the possibility of using them as green substitutes for other polar aprotic solvents [7,8]. PC presents low toxicity, low vapor pressure, easy biodegradability and obtainability [9], being used as a substitute for toxic solvents such as N,N-dimethylformamide, 1,4-dioxane, or tetrahydrofuran [10]. In addition, cyclic carbonates are used as electrolytes in batteries [11], in the preparation of polymers [12], and their possible different functional groups allow a greater affinity with compounds of varied nature, which enables their use as extracting solvents for hydrocarbons [13], aromatic compounds [14], and nitrogen- or sulfur-containing compounds [15].

* Corresponding author.

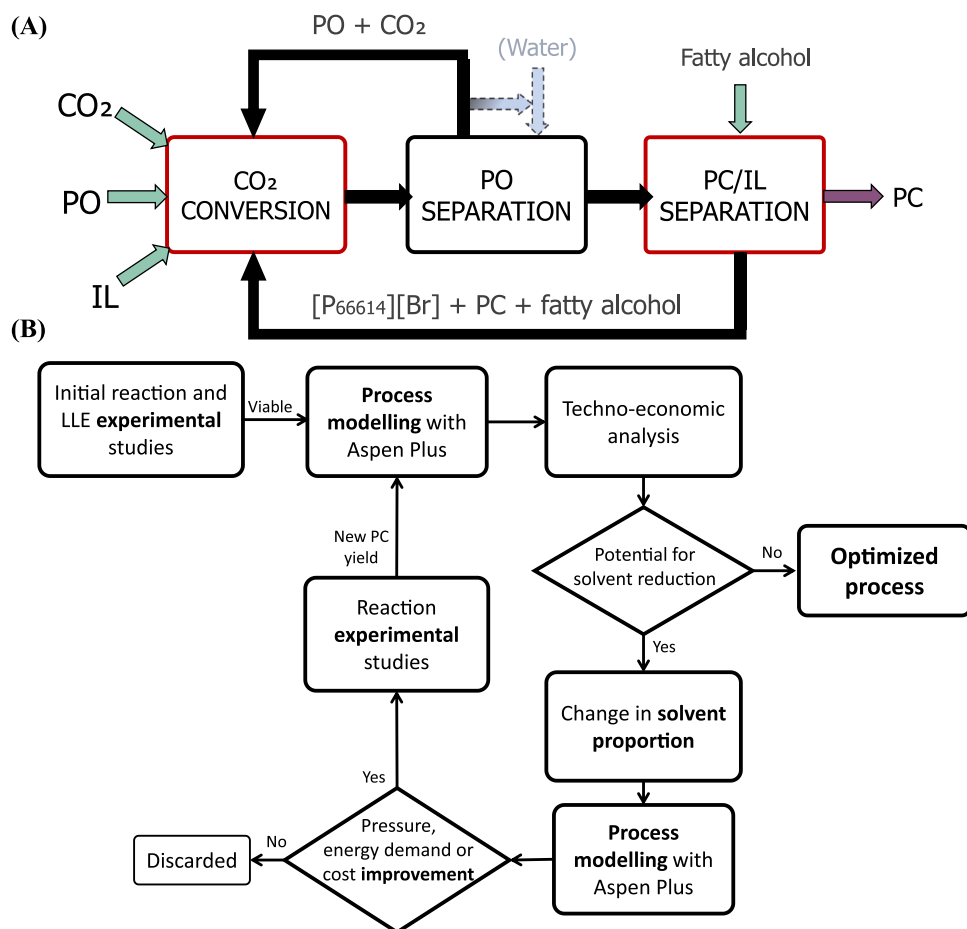
E-mail address: pablo.navarro@uam.es (P. Navarro).

¹ Both authors contribute equally

Heterogeneous catalysts such as metal organic frameworks, zeolites or metal oxides [16], and homogeneous catalysts such as metal complexes, alkali salts, ionic liquids or amines [17], among others, can be used for the synthesis of cyclic carbonates. Ionic liquids (ILs) outstand among these catalysts due to their absence of metals, their negligible vapor pressure -which avoids catalyst losses- and their high tunability [18], in addition to being excellent CO₂ absorbents both physically and chemically [19,20]. These compounds have been extensively studied as catalysts in CO₂ cycloaddition reactions to epoxides [21–23] however, one of the major problems they present is their separation from the reaction product. Both cyclic carbonates and ILs present high boiling points, so a separation by distillation would be very energy-demanding [24] and, given the thermal stability of ILs, it would be necessary to perform it under vacuum conditions in order not to exceed high temperatures in the reboiler [25]. Recently, separation strategies based on liquid-liquid extraction have been proposed to recover the catalyst by separating it from the carbonate, enabling catalyst reutilization [26], requiring lower energy consumption at process level than distillation and even enhancing catalytic activity [24,27]. From the energetic viewpoint, the separation of hydrophobic ILs using fatty alcohols as extracting solvents is recommended, since it presents a minimum energy consumption, and the recovery of these ILs is favorable independently of the anion [28]. In addition, in the case of PC production from propylene oxide (PO) and CO₂ it has been shown that halide anions-based ILs show good yields in very competitive reaction times [29,30], besides an increase in PO conversion is observed in the presence of fatty alcohols [26].

The purpose of this work is to advance in the development of a more efficient carbon conversion process for CO₂ cycloaddition to PO to

produce PC based on the IL trihexyltetradecylphosphonium bromide ([P₆₆₆₁₄][Br]) catalyst and liquid-liquid extraction (Scheme 1A). The main studied variables in this work are reaction temperature and influence of different alcohol amounts both in reaction and in PC/IL separation (marked in red in Scheme 1A). Also, a new process scheme in which water is used to reduce vacuum requirements in reactants separation has been explored. For this purpose, an integrated experimental-computational multiscale methodology is followed to proceed with reliable re-designs, that allow different improvements (Scheme 1B) while always enabling an almost complete IL recovery. The IL [P₆₆₆₁₄][Br] was selected because of its low price and availability, and also because ILs containing bromide anion are excellent catalysts for the studied reaction [31]. In addition, its cation has been previously tested in the separation with 1-decanol giving optimal separation results [26]. Catalytic tests were carried out to experimentally study the influence of different chain length fatty alcohols on PC yield at 80, 100 and 120°C reaction temperatures and 20 bar reaction pressure. Furthermore, the influence of water and {alcohol + water} mixtures on the selectivity of the reaction was studied to narrow down what are the enchanter roles of water in the process. Additionally, the performance of different fatty alcohols as extracting solvents to separate IL from PC was also experimentally validated as first time. Afterwards, a process-level analysis of the influence of these solvents and the use of water to improve energy consumption is performed using COSMO-based/Aspen Plus methodology. Finally, a utility cost assessment is carried out to focus the process re-design that minimize the operational costs.



Scheme 1. (A) Process block diagram for the CO₂ conversion to PC using [P₆₆₆₁₄][Br] as catalyst. (B) Process design strategy combining experimental tests and simulation.

2. Experimental and computational details

2.1. Materials

The compounds that were used experimentally and their main properties are listed in Table 1. [P₆₆₆₁₄][Br] used as catalyst in the reactions, was previously outgassed at 60°C and 0.2 bar to eliminate any volatile impurities it might contain.

2.2. Experimental catalytic tests: Solvent influence on CO₂ conversion using [P₆₆₆₁₄][Br] catalyst

A Berghof BR-100 High Pressure Stirred Reactor was used for the catalytic reactions, which was always fed with an initial volume of 30 mL of PO and [P₆₆₆₁₄][Br] mixture with 100:1 PO:IL molar proportion. The influence of extracting solvent concentration and nature on PC yield was experimentally analyzed, since the IL recovery by liquid-liquid extraction and IL reuse (Scheme 1A) implies the presence of extracting solvent in the reactor [28]. To the initial volume of 30 mL of PO/IL mixture, different solvents, namely 1-octanol, 1-decanol, 1-dodecanol, oleyl alcohol and water, were added in a 2:1 PO:alcohol molar ratio or a 1:1 PO:water molar ratio.

Experiments were carried out at different temperatures (80 °C, 100 °C and 120 °C) with an initial CO₂ pressure of 6 bar. Once the selected temperature was reached, a continuous CO₂ supply of 20 bar was fed to maintain the pressure stable during a reaction time of 1.5 h, ensuring that PO remains liquid during reaction time. After the reaction was finished and cooled down, the mixture was taken to a rotary evaporator to remove unreacted PO, and water if applicable, for 2 h at 70 °C and 0.1 bar. The conversion and the product selectivity to PC was determined by the initial and final mass difference together with the characterization of the phases by proton Nuclear Magnetic Resonance (¹H NMR) in a Bruker Varian Unity 500.

2.3. Experimental-computational analysis of liquid-liquid equilibria: IL/PC separation by liquid-liquid extraction using fatty alcohol

Previous work evaluated liquid-liquid extraction as an efficient alternative for postreaction IL catalyst recovery [26–28]. Due to the hydrophobic character of [P₆₆₆₁₄][Br], fatty alcohols were proposed as extracting solvents. In this work, 1-octanol, 1-decanol, 1-dodecanol and oleyl alcohol were studied as solvents for this task. To experimentally analyze the extractive properties of binary {PC + fatty alcohol} and ternary {PC + [P₆₆₆₁₄][Br] + fatty alcohol} systems, mixtures ranging different molar concentrations of IL (0.5%, 1.0% and 3.0%mol) and mass S/F ratio (0.1, 0.21 and 0.3) were measured at 25°C. The mixtures were centrifuged in a Digicen Series 21 centrifuge and 40 μL of each phase were dissolved in 0.5 mL of deuterated acetone and analyzed by ¹H NMR on a Bruker Varian Unity 500 to determine the compounds concentrations. Then, extractive properties were estimated, namely, partition coefficient (K_{IL} ; Eq. 1) and selectivity ($S_{IL/PC}$; Eq. 2).

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

$$S_{IL/PC} = \frac{K_{IL}}{K_{PC}} = \frac{\frac{x_{IL}^E}{x_{IL}^R}}{\frac{x_{PC}^E}{x_{PC}^R}} \quad (2)$$

where x_{IL}^i and x_{PC}^i denote the IL and the PC molar fraction, respectively, in the extract (E, solvent-rich) or the raffinate (R, PC-rich) phase.

The equilibria data predicted by the COSMO-based/Aspen methodology [32,33] were validated with the binary and ternary equilibria with all fatty alcohol proposed in the experimental part in terms of extractive properties. All compounds in this work were included in Aspen Plus v12 as pseudocomponents according to the COSMO-based/Aspen methodology reported elsewhere [33], using COSMO-SAC property model developed by Lin and Sandler [34].

2.4. Process modelling and techno-economic analysis of IL-based CO₂ conversion process to produce PC

Once the reaction and the catalyst-product separation stages had been experimentally validated, a process to produce PC from CO₂, using PO as a reactant, catalyzed by [P₆₆₆₁₄][Br] was modelled. For the simulated processes, only the two best fatty alcohols in terms of IL extractive properties were selected. Two processes configurations were employed, which are shown in Fig. 1. In all cases, the reactor conversion (R-100) was set to the experimental PC yield value obtained previously. First, feed streams were conditioned to the pressure and temperature at which the experimental values were obtained (100 kmol/h of PO, and the corresponding CO₂ flow rate to achieve a 1:1 PO:CO₂ molar proportion in the reaction, as well as an IL make-up to guarantee a 100:1 PO:IL molar proportion in the reactor).

For the first configuration, Fig. 1A, the reactor outlet stream was fed to a flash vessel (V-100) at 1 bar of total pressure and into a stripping column (D-100) to remove unreacted PO and CO₂. D-100 distillate rate was modified to achieve at least 99.9% of PO and CO₂ recoveries. Then, in an extraction column (S-100), the IL was recovered using fatty alcohol solvents, which was then reconditioned and returned to the reactor. Given the solubility of the fatty alcohols in PC, the product stream contains alcohol impurities, which results in the need to replenish the alcohol as an extracting solvent, which is fed directly to S-100. Due to the thermal stability of catalyst (Fig. S1 in Supplementary Material), a maximum temperature of 120°C was set to avoid thermal decomposition of the IL. Consequently, in the stripping column (D-100) it was necessary to operate under vacuum conditions to satisfy at least a 99.9% recovery of PO and CO₂.

Once this process was modeled, alcohol flow rates were modified, and their influence on the process was observed, as depicted in Scheme 1B. The S/F ratio in S-100 was adjusted to the minimum to achieve a 99.9% recovery of the IL. Thus, in Scheme 1B, the potential for solvent

Table 1
Chemicals: properties and specifications.

Compound	Alias	CAS	Molecular Weight (g/mol)	Density (g/cm ³)	Provider
1-Octanol	Oct	111–87–5	130.23	0.824	Sigma-Aldrich
1-Decanol	Dec	112–30–1	158.28	0.83	Sigma-Aldrich
1-Dodecanol	Dodec	112–53–8	186.34	0.831	Sigma-Aldrich
Oleyl alcohol	Oleyl	143–28–2	268.48	0.845	Sigma-Aldrich
Trihexyltetradecylphosphonium bromide	[P ₆₆₆₁₄][Br]	654057–97–3	563.76	0.96	IoLiTec
CO ₂	CO ₂	124–38–9	44.01	1.9·10 ⁻³	Nippon
Propylene carbonate	PC	108–32–7	102.09	1.2	Sigma-Aldrich
Propylene oxide	PO	75–56–9	58.08	0.83	Sigma-Aldrich
Purified water ^a	W	7732–18–5	18.02	1	

^a Purified water (Type I) was obtained from an Automatic purification system (Wasserlab)

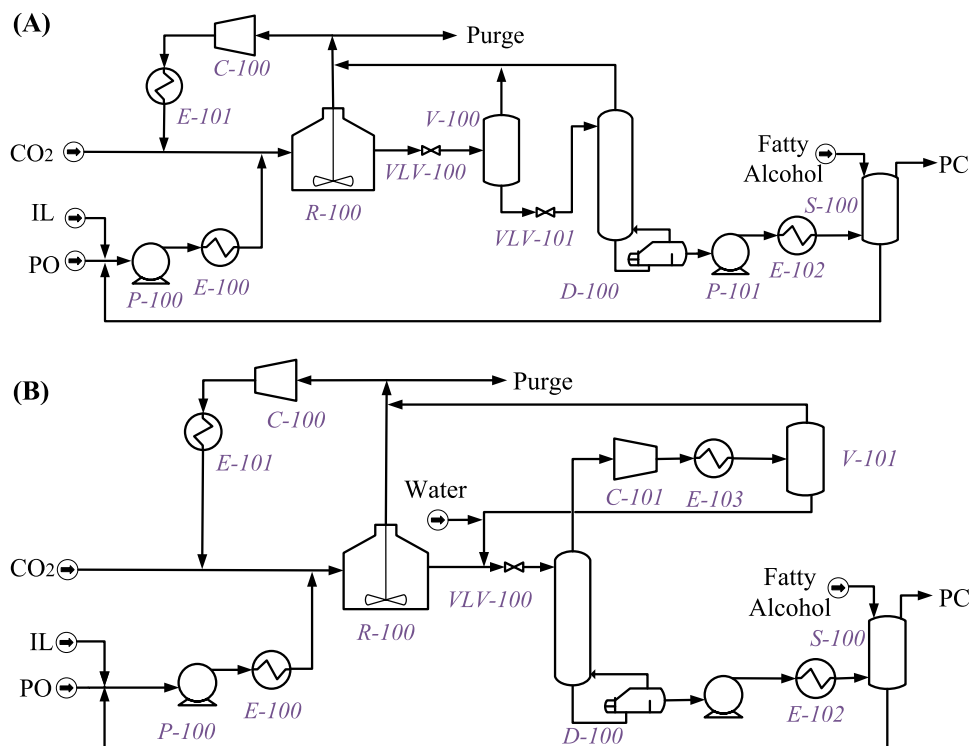


Fig. 1. Process diagram to produce PC using $[P_{66614}][Br]$ as catalyst using (A) fatty alcohol or (B) fatty alcohol/water mixture as solvent.

reduction is based on whether the IL can be recovered. Then, experimental reactions were performed with the existing composition in the simulated reactor to obtain the precise conversion value under these conditions, and the simulation was redone accordingly (Scheme 1B).

On the other hand, Fig. 1B depicts a different process configuration. It uses an extraction column (S-100) and fatty alcohol solvents to recover the IL as before, but adding water to the stripping column (D-100) to reduce its vacuum conditions [28]. The water flow rate selected was the minimum that enabled 99.9% PO and water recovery with vacuum pressures above 0.2 bar in said column. Due to the small water losses, a minor water make-up is necessary, which is fed after the reactor. In this configuration, D-100 distillate rate was modified to achieve at least 99.9% of PO and water recovery to prevent it from reaching the extraction column (S-100). The outlet vapor of D-100 was compressed to 2 bar and cooled down to 55°C (C-101, E-103) to condense and recover 95% of water in the flash column V-101 as liquid. Then, water is decompressed and send back to D-101. As before, experimental reactions were carried out with the existing composition in the simulated reactor to obtain PC yield, and the simulation was redone accordingly. The rest of the specifications remain the same as in the previous

Table 2

Process specifications of CO₂ conversion to produce PC using $[P_{66614}][Br]$ for the two processes' configurations.

Solvent	Alcohol		Alcohol/Water	
	D-100	S-100	D-100	S-100
N stages	10	4	10	4
Feed Stage	1	S 1 / F 4	1	S 1 / F 4
Maximum temperature (°C)	120	25	120	25
Design Variable	Distillate rate	S/F	Distillate rate	S/F
Specification	99.9% PO recovery	99.9% IL recovery	99.9% PO and water recovery	99.9% IL recovery

configuration. A summary of the process equipment specifications can be found in Table 2.

The total energy consumption (kWh per kg of PC produced) was calculated from the thermal and electrical energy requirements of the entire process and divided by the final production of PC, to compare the two configurations. The Aspen Process Economic Analyzer (APEA) was used to calculate the operating costs resulting from utilities consumption. Different utilities were selected in each operation with their respective Aspen Plus v12 default costs, namely cooling water ($2.12 \cdot 10^{-7}$ \$/kJ), low pressure steam ($1.90 \cdot 10^{-6}$ \$/kJ), and electricity ($7.75 \cdot 10^{-2}$ \$/kWh). The total operating cost (\$ per kg of PC produced) was calculated from the utilities cost divided by the final production of PC, regardless of its purity.

3. Results and discussion

3.1. Solvent influence on CO₂ conversion to PC using $[P_{66614}][Br]$ catalyst

Experimental conversion to propylene carbonate obtained at different temperatures in the presence of the $[P_{66614}][Br]$ catalyst alone (100:1 PO:IL molar proportion) and the catalyst combined with extracting solvents in a 2:1 PO:solvent molar ratio is shown in Fig. 2. As seen, neat $[P_{66614}][Br]$ is an efficient catalyst for this reaction, with competitive PC yield in short reaction times (1.5 h) compared to other studies with similar systems [27,35]. As expected, a higher reaction temperature implies higher PC yield in all the studied systems. In addition, the presence of most of the alcohols in the reaction media causes a noticeable increase in the conversion at high temperatures, rising from 79% to around 87% at 120°C and rising from 45% to 56–69% at 100°C. On the other hand, it seems that increasing alcohol chain length from C8 to C12 produces no relevant effect: the conversions obtained with those different alcohols are similar at the same temperatures and are within error. Nevertheless, the results obtained with oleyl alcohol are very similar to those of neat IL, thus it does not appear to be a very beneficial alcohol in terms of conversion. In any case, higher

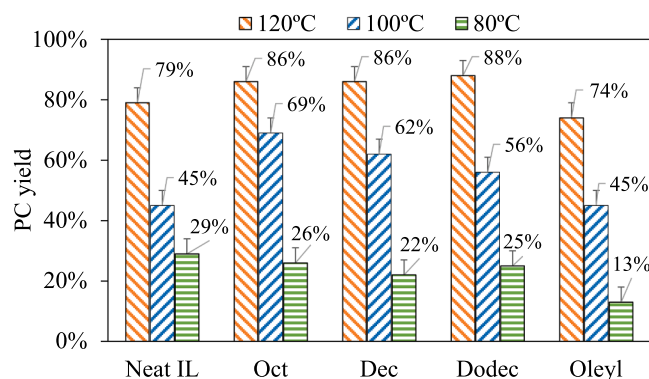


Fig. 2. Alcohol presence and chain length influence on experimental PC yield at different temperatures within 1.5 h. The IL is used in a 100:1 PO:IL molar proportion, while the solvents are used in a 2:1 PO:alcohol molar proportion. Operating pressure: 20 bar.

temperature and the use of C8-C12 alcohols seem generally beneficial for conversion stage.

On the other hand, previous works [24,27] stated that water can also improve PC yield. Hence, this effect is examined for $[P_{66614}][Br]$, as well as the influence of using {alcohol + water} solvent mixtures in the conditions that provide the highest PC yield (120°C) resulting in the values shown in Fig. 3. As can be observed, the presence of water in the reaction media decreases the PC yield obtained, e.g., from 86% with 1-octanol to 64% with an {1-octanol + water} mixture. In addition, both PC yield and selectivity decrease with larger alcohol chains. This fact can be corroborated by looking at the ¹H NMR spectra in Fig. S2 in Supplementary Material. As can be seen, when neat IL is employed or the reaction is carried out also in the presence of only a fatty alcohol, the formation of by-products is not observed. On the other hand, when the reaction is carried out in the presence of water (either alone or mixed with a fatty alcohol), the appearance of propylene glycol is observed. Summarizing, the use of alcohols decreases the formation of propylene glycol caused by the presence of water in the reaction media. Nevertheless, the presence of water in the reactor is discouraged, since even when mixed with alcohols, PC selectivity is reduced.

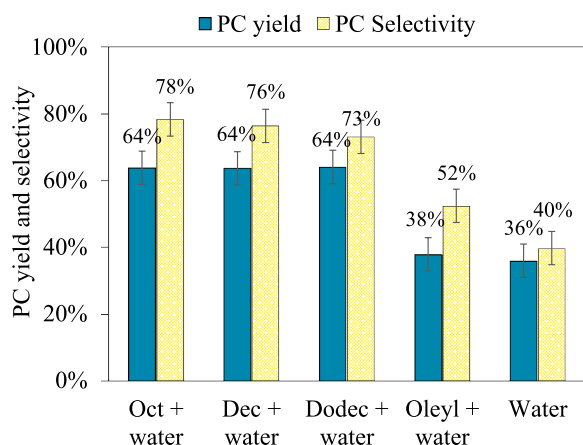


Fig. 3. Influence of using water or {alcohol + water} mixtures in PC yield and selectivity observed in the experimental reactions at 120°C within 1.5 h of reaction. IL is used in a 100:1 PO:IL molar proportion, while the solvents are used in a 2:1 PO:alcohol molar proportion and 1:1 PO:water molar proportion. Operating pressure: 20 bar.

3.2. IL/PC separation by liquid-liquid extraction using fatty alcohol: experimental and computational validation

Once the influence of the different alcohols on the reaction has been established, their influence on the PC/IL separation by liquid-liquid extraction is analyzed. First, the binary {alcohol + PC} system is experimentally studied. Table 3 collects the experimental compositions of the extracting solvents and PC in the binary mixtures with the different fatty alcohols. As seen, the alcohol-rich phase presents a similar composition regardless of the selected alcohol. On the other hand, PC purity in the PC-rich phase rises as the alcohol chain-length increases. Thus, the phase separation obtained is successful for any alcohol since PC purity is always above 90%mol, but 1-decanol, 1-dodecanol and oleyl alcohol are the most suitable alcohols for this task due to rendering a > 95%mol PC purity.

Moving to ternary systems containing $[P_{66614}][Br]$, Table 4 collects the molar fractions of the three components in raffinate (PC-rich) and extract (alcohol-rich) phases and the extractive properties (K_{IL} and $S_{IL/PC}$) of the systems containing the different alcohols. As can be observed, both IL/PC selectivity and IL distribution ratio are remarkably favorable to catalyst/product separation. K_{IL} and $S_{IL/PC}$ values increase with lengthier alcohol carbon-chain, since when selecting 1-octanol the K_{IL} moves from 3 to 7 and the $S_{IL/PC}$ ranges from 3 to 23, while when selecting oleyl alcohol K_{IL} ranges 16–24 and $S_{IL/PC}$ ranges 51–159. Such behavior with 1-octanol was expected based on the results in Table 3. However, some dispersion can be noted in the values of 1-dodecanol, probably due to the closeness of the experimental tests' temperature (25°C) to its melting point (24–27°C). This closeness between the melting point and the process operating point could lead to phase change problems in the process. Therefore, 1-decanol and oleyl alcohol are selected as the 2 most suitable alcohols for IL recovery, due to their favorable extractive properties, especially IL/PC selectivity, being used for the computational modeling of the process.

As required step before process modelling, COSMO-SAC thermodynamic model used in Aspen Plus process simulation was validated by comparison to experimental liquid-liquid equilibria data. Thus, Fig. 4 compares the ternary equilibrium diagrams of 1-decanol and oleyl alcohol mixtures both experimentally and computationally obtained. As seen, the concentrations of both phases are adequately described using this thermodynamic model. In both cases an almost pure carbonate phase is obtained both experimentally and computationally. In the case of the alcohol-rich phase, the model accurately describes the system with 1-decanol, while the binary {PC + oleyl alcohol} mixture is not as well predicted, but it is still reasonable, as the computational model assumes higher PC losses. This misdescription of the binary system would imply higher energy consumption than the real one, due to the higher flow of PC passing through the equipment, hence the simulations would be fairly conservative in any case.

Table 3
PC (1) and alcohol (2) molar fractions for the two phases resulting from the different {alcohol + PC} binary mixtures at 25°C.

Extract phase		Raffinate phase	
x_1	x_2	x_1	x_2
<i>{PC+ 1-octanol}</i>			
0.096	0.904	0.909	0.091
<i>{PC+ 1-decanol}</i>			
0.074	0.926	0.954	0.046
<i>{PC+ 1-dodecanol}</i>			
0.076	0.924	0.980	0.020
<i>{PC+ oleyl alcohol}</i>			
0.081	0.919	0.990	0.010

Table 4

Experimental liquid-liquid equilibrium data (molar fractions, molar distribution ratio and IL/PC selectivity) of the different {PC (1) + alcohol (2) + IL (3)} ternary systems at 25°C.

Extract phase			Raffinate phase			Extractive properties	
x_1	x_2	x_3	x_1	x_2	x_3	K_{IL}	$S_{IL/PC}$
<i>{PC + 1-octanol + [P₆₆₆₁₄][Br]}</i>							
0.638	0.294	0.068	0.846	0.127	0.027	2.5	3.3
0.369	0.577	0.054	0.869	0.122	0.010	5.6	13.1
0.288	0.675	0.037	0.871	0.122	0.007	5.7	17.3
0.270	0.692	0.038	0.872	0.122	0.005	7.0	22.6
<i>{PC + 1-decanol + [P₆₆₆₁₄][Br]}</i>							
0.150	0.796	0.054	0.955	0.038	0.007	7.5	47.8
0.115	0.858	0.027	0.959	0.038	0.002	11.3	94.0
0.182	0.775	0.043	0.945	0.052	0.004	12.3	63.7
0.243	0.696	0.061	0.943	0.052	0.005	13.0	50.5
0.332	0.575	0.093	0.946	0.047	0.007	13.1	37.2
<i>{PC + 1-dodecanol + [P₆₆₆₁₄][Br]}</i>							
0.153	0.840	0.047	0.850	0.142	0.010	4.9	27.2
0.184	0.804	0.068	0.856	0.134	0.012	5.7	26.5
0.144	0.806	0.050	0.874	0.119	0.008	6.4	39.0
0.356	0.588	0.157	0.913	0.074	0.014	11.3	29.0
0.246	0.651	0.102	0.976	0.020	0.005	17.4	69.1
<i>{PC + oleyl alcohol + [P₆₆₆₁₄][Br]}</i>							
0.307	0.538	0.155	0.982	0.008	0.010	15.8	50.6
0.312	0.601	0.087	0.987	0.008	0.005	18.9	59.9
0.123	0.837	0.040	0.989	0.009	0.002	19.7	158.8
0.162	0.770	0.068	0.985	0.012	0.003	21.3	129.3
0.170	0.776	0.055	0.988	0.010	0.002	23.7	138.2

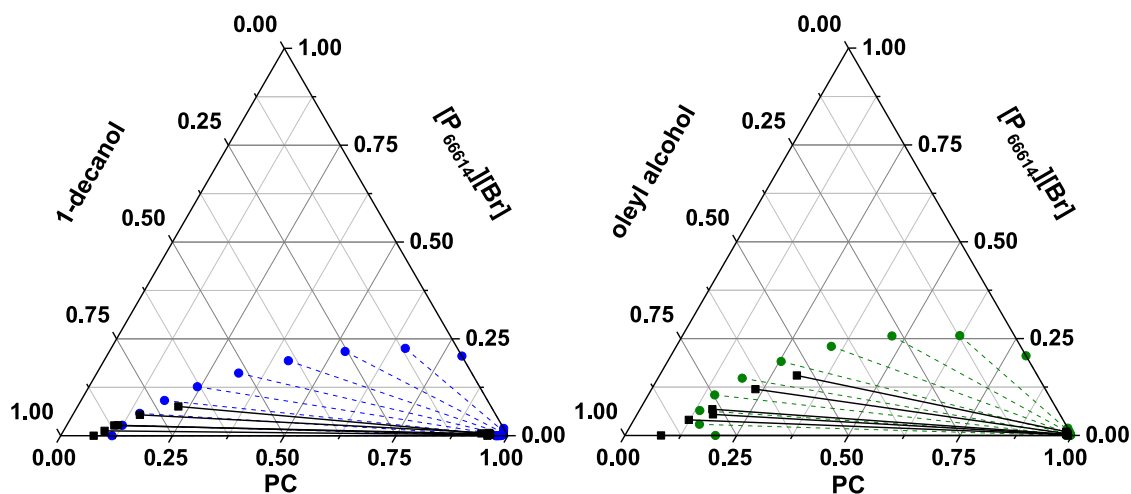


Fig. 4. Experimental (black; solid line) and computational (blue and green; dashed line) {IL + PC + alcohol} ternary diagrams for 1-decanol (left) and oleyl alcohol (right) in molar composition.

3.3. Techno-economic analysis of the IL-based close-cycle CO₂ conversion process to produce PC, using liquid-liquid extraction with fatty alcohols

Once the reaction and PC/IL separation had been experimentally studied, the close-cycle CO₂ conversion process to produce PC is modelled by COSMO-based/Aspen methodology using [P₆₆₆₁₄][Br] as catalyst and 1-decanol and oleyl alcohol as extracting solvents. In a recent work [36], it was reported that low temperatures do not significantly improve key performance indicators, so the process scale evaluation is done at 120°C to maximize the conversion of the process which has been shown to have a substantial impact on energy consumption [28,36]. Fig. 5 collects the specific energy consumption related to the CO₂ conversion processes including 1-decanol or oleyl alcohol in the reactor, in the same proportions previously studied experimentally (2:1 PO:alcohol molar proportion). As can be seen, the energy and vacuum requirements when selecting oleyl alcohol are greater than when selecting 1-decanol, due to the higher molecular weight of oleyl alcohol (268.5 g/mol) with regards to 1-decanol molecular weight

(158.3 g/mol), which implies a higher mass flow in the process. Furthermore, the energy demand of this process alternative is significantly lower than that of processes that use distillation as a separation strategy (2.6 kWh/kg_{PC}) [28].

Nevertheless, in both cases the S/F ratio in S-100 is a consequence of the proportions used in the reactor. Thus, new simulations were run in which the S/F ratios were adjusted to the minimum to recover 99.9% of the IL, with the aim of reducing the unnecessary alcohol amounts flowing through the process. The results of these new simulations showed that the necessary PO:alcohol molar proportions in the reaction account for only 31:1 in the case of 1-decanol and 14:1 in the case of oleyl alcohol. New experimental reactions were carried out using these molar proportions and lead to an 88% and an 84% PC yield with 1-decanol and oleyl alcohol, respectively, thus PC yield is not significantly affected by this change. Then, the simulations were redone, and the energy consumption obtained is shown in striped bars in Fig. 5. As can be seen, this adjustment allows the improvement of energy consumptions, especially when using oleyl alcohol, decreasing from 0.69 to 0.54

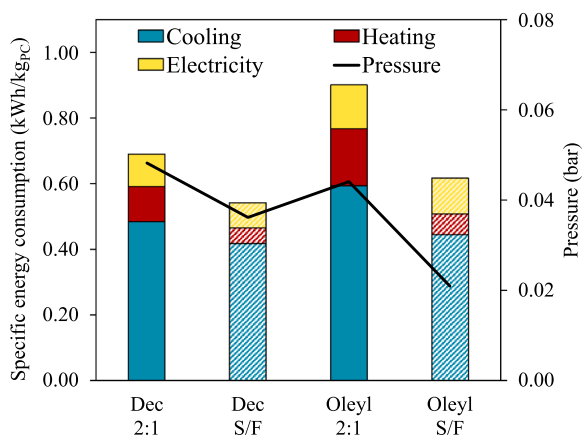


Fig. 5. Energy consumption per kilogram of product stream and pressure in D-100 for the process designs in the presence of 1-decanol or oleyl alcohol in a PO: alcohol 2:1 molar proportion (solid bars) and adjusting the fatty alcohol molar proportion (striped bars).

kWh/kg_{PC} for 1-decanol and from 0.90 kWh/kg_{PC} to 0.62 kWh/kg_{PC} in the case of oleyl alcohol. However, vacuum requirements are extreme for all cases -ranging from 0.02 to 0.05 bar- resulting slightly higher in these new cases.

Based on a previous work, which showed that water can be useful in reducing vacuum requirements [28], an attempt was made to introduce water into PO separation without reaching the reactor to avoid sub-products formation, as shown in Fig. 1B. It was found that a small amount of water (50:1 PO: water molar proportion) does not reach the reactor, so these solvent proportions were mimicked in experimental reactions as to obtain the real PC yield in said conditions. An 87% PC yield was obtained using 1-decanol and an 84% PC yield with oleyl alcohol, with traces of propylene glycol (>97% PC selectivity), as reflected in the ¹H NMR spectra in Fig. S3 in Supplementary Material. Then, the simulations were redone, and the vacuum and energy requirements obtained are portrayed in Fig. 6. The results show that the presence of water slightly increases the energy consumption with both alcohols (from 0.54 to 0.68 kWh/kg_{PC} for 1-decanol and from 0.62 to 0.68 kWh/kg_{PC} for oleyl alcohol). Nevertheless, the aim of reducing vacuum conditions was achieved given that the pressure increases by an order of magnitude in cases where water is used (from approximately 0.02 to 0.20 bar). Hence, thanks to the presence of water, reasonable working pressures can be achieved.

To complete the techno-economic analysis, the cost of the utilities of

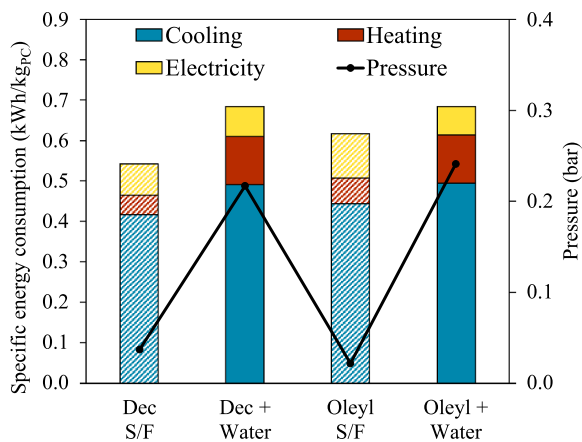


Fig. 6. Energy consumption per kilogram of product stream and pressure in D-100 for the process designs adjusting fatty alcohol S/F ratio (striped bars) and adding water to the separation stage (solid bars).

the studied CO₂ conversion processes is assessed and depicted in Fig. 7. As seen, in the case of 1-decanol the use of water does not represent an advantage in economic terms, given that the process using only 1-decanol and the one in which water is added present similar utilities costs (6.6 and 7.0 \$/t_{PC}). However, the case of oleyl alcohol has a contrasting behavior, since the use of water implies a great improvement in economic terms, dropping from 9.2 to 5.5 \$/t_{PC}, due to the large reduction in electricity consumption. Therefore, it can be concluded that tuning the solvents proportions can be advantageous for the processes design, since the purity of the product is not altered -all the studied alternatives PC purities are over 95wt.- and the operating costs and vacuum requirements can be reduced.

4. Conclusions

In this work, a multiscale integrated experimental-computational study is performed to evaluate the influence of different solvents on the CO₂ conversion to PC processes, using the IL [P₆₆₆₁₄][Br] as catalyst, involving laboratory experimental validations and techno-economic analysis from process simulations. First, the influence of fatty alcohols and water on the experimental reactions was analyzed, as well as the experimental separation of IL and PC using these alcohols as extracting solvents. It was found that the presence of fatty alcohols combined with high temperatures improve the conversions obtained. On the other hand, water notably decreases PC yield and although when combined with fatty alcohols the reduction is mitigated, its presence in the reactor should be avoided. From these conclusions it can be deduced that using fatty alcohols for IL/PC separation is feasible, since the presence of this solvent in the reactor does not impair the catalyst performance, but rather improves it. Then, IL/PC separation was experimentally studied using fatty alcohols as extracting solvents, concluding that this separation is possible with all alcohols because the IL extractive properties reported were favorable ($K_{IL}=3-25$; $S_{IL/PC}=3-159$). It was further determined that the best alcohols to carry out such separation are 1-decanol and oleyl alcohol due to their optimal extractive and physical properties. After that, COSMO-SAC predictions of the ternary liquid-liquid equilibria were successfully validated.

Finally, COSMO-based/Aspen process simulations were carried out by first simulating the experimental reaction conditions and then tuning the alcohol concentrations with an integrated multiscale iterative strategy (experimental + process simulation) to improve the efficiency of this carbon conversion process. It was determined that the amount of alcohol can be reduced to a minimum that allows the recovery of the IL, thus reducing energy consumption. On the other hand, water can be used in the separation stage to reduce energy consumption and vacuum requirements. Lastly, techno-economic analysis reveals that the utility

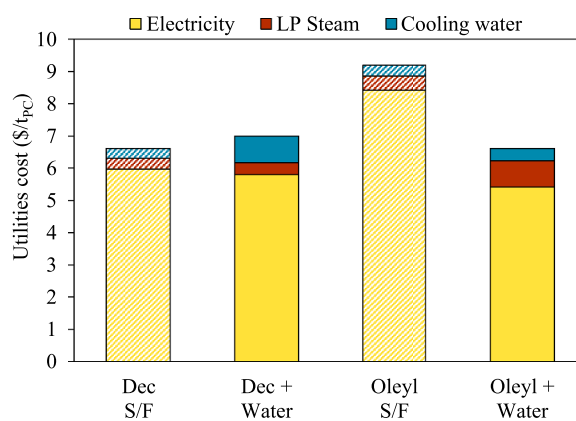


Fig. 7. Utilities cost per produced tonne of PC for the processes adjusting fatty alcohol S/F ratio (striped bars) and adding water to the separation stage (solid bars).

costs of the process can be reduced by 28% in the case of oleyl alcohol when adding water in the adequate proportion. Optimal configurations have an energy consumption of approximately 0.6 kWh/kg_{PC} and utility costs of 6.6 \$/t_{PC}, to the best of our knowledge the best process key performance indicators reported to date.

CRedit authorship contribution statement

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

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.2023.102417](https://doi.org/10.1016/j.jcou.2023.102417).

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