

1 **Fatty alcohol/water reaction-separation platform to produce propylene**
2 **carbonate from captured CO₂ using a hydrophobic ionic liquid**

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10

11 **Abstract**

12 The combined use of a hydrophobic ionic liquid catalyst and a fatty alcohol is presented
13 to synergistically improve cycloaddition reaction of CO₂ to epoxides and envision
14 catalyst recovery by cyclic carbonate removal using water as extracting solvent. This
15 approach is described for the production of propylene carbonate using
16 trihexyl(tetradecyl)phosphonium 2-cyanopyrrolide catalyst -which chemically captures
17 CO₂ reactant- and 1-decanol/water mixture as extracting solvent. The novel use of fatty
18 alcohols on CO₂ cycloaddition reaction not only permits the effective separation of the
19 catalyst and the product purification, but also improves the CO₂ conversion in the reactor,
20 and opens the challenge of process intensification by integrated CO₂ capture and
21 conversion.

22 **Keywords**

23 CO₂ conversion; ionic liquids; cyclic carbonates; fatty alcohols; water

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26 **1. Introduction**

27 Among other processes related to Carbon Capture and Utilization (CCU) strategies, the
28 CO₂ fixation reactions to cyclic carbonates is a trending research in the literature,
29 preferably involving non-volatile homogeneous catalysts [1-3]. Ionic liquids stand out as
30 homogeneous catalysts because of their excellent properties such as negligible volatility,
31 adequate thermal stability, and the fine-tuning of their main catalyst features [4, 5],
32 showing a remarkable performance in CO₂ conversion [6-10]. In this sense, big efforts
33 are being carried out in the development of multifunctional catalysts [11-13], being ionic
34 liquids included in this big group. Recently, Chen and Mu (2019) [7] reviewed the ionic
35 liquid mediated catalytic strategies to produce cyclic carbonates together with other CO₂
36 valorization processes, giving good reasons to consider ionic liquids as a proper way to
37 enhance cycloaddition reactions. Nevertheless, among other challenges, authors advised
38 to use more stable ionic liquids, work at milder conditions, and pay especial attention to
39 product separation in an inexpensive way.

40 Recent literature reported effective specific advanced materials promoting CO₂ fixation
41 to cyclic carbonates. However, the process scale-up at industrial operating conditions of
42 interest and the reusability of the catalyst are still a challenge [14]. Scientific community
43 proposes the separation of the homogeneous catalyst from cyclic carbonates by a
44 traditional distillation operation [15]. Nevertheless, it is well known that high reboiler
45 temperatures are needed to evaporate cyclic carbonates at atmospheric pressure, which
46 are not compatible with the thermal stability of most ionic liquids. Even displaying
47 extreme vacuum conditions, the continuous production of cyclic carbonates demands
48 high energy but also incorporates electricity expenses [7]. Mainly, these regeneration
49 conditions are not compatible with most of the ionic liquids thermal stabilities reported
50 in the literature nor competitive in energy consumption terms [16-18].

51 Here, we propose a selective liquid-liquid phase separation between the catalyst and the
52 product to reduce energy consumption from cyclic carbonate production by selecting an
53 adequate extracting agent. Solvent requirements are favorable extractive properties to
54 recover the product and catalyst and sustainable compatibility. COSMO-RS method was
55 used to massively scan solvents (>5000) to separate trihexyl(tetradecyl)phosphonium 2-
56 cyanopyrrolide ([P₆₆₆₁₄][2-CN₂Pyr]) catalyst from propylene carbonate as benchmark
57 cyclic carbonate. Aprotic heterocyclic anion (AHA) based ionic liquids, such as
58 [P₆₆₆₁₄][2-CN₂Pyr], stand out as effective catalysts for CO₂ valorization, exhibiting high
59 epoxide conversion and selectivity to cyclic carbonates in short periods of time (2-24 h)
60 and mild conditions (100°C and 1.0 MPa) [19]. Regarding the kinetics of the CO₂
61 cycloaddition to propylene oxide to form propylene carbonate, it is well-described in a
62 previous work based on phosphonium cations and AHA anions, revealing that this kind
63 of ILs showed competitive reaction kinetics in comparison with those related to halide-
64 based ILs [20].

65 A key interest of these kind of catalysts is in line with their bifunctional character, since
66 these ionic liquids are promising CO₂ chemical absorbents, showing high absorption
67 capacities, reasonable mass transfer features and competitive process performance in CO₂
68 capture [19-21]. The ability of hydrophobic ILs to capture CO₂ is well-known and
69 currently growing in the literature, which envisions the integration of capture and
70 conversion processes and demands effective separation platforms [22, 23]. The selected
71 ionic liquid in this work, ([P₆₆₆₁₄][2-CN₂Pyr]) presents a remarkably hydrophobic
72 character and, consequently, it is expected an easier separation from polar carbonate
73 media [24]. In fact, other hydrophobic ILs are demonstrated a low IL solubility in water
74 [25]. This makes affordable the challenging catalyst separation and product purification

75 by liquid-liquid extraction, opening opportunities for an integrated carbon capture and
76 utilization (iCCU) platform based on ionic liquids.

77

78 **2. Materials and methods**

79 *Chemicals*

80 Propylene oxide (99%), propylene carbonate (99.7%) and 1-decanol (99%) were
81 purchased from Sigma-Aldrich. CO₂ was supplied by Praxair, Inc., with a minimum
82 purity of 99.999%. For the AHA-IL synthesis, Amberlite® IRN78 of nuclear grade and
83 trihexyl(tetradecyl)phosphonium bromide (95%) were also purchased from Sigma
84 Aldrich. Pyrrole-2-carbonitrile (99%) was purchased from Alfa Aesar. Purified water
85 (Type I) was obtained from an Automatic purification system (Wasserlab). Acetone-d₆
86 (99.9%) was purchased from Sigma Aldrich. The IL was outgassed prior to its use as
87 catalyst at 60 °C and 10⁻³ mbar during 24 h to ensure a water content lower than 200 ppm.

88 *Trihexyl(tetradecyl)phosphonium 2-cyanopyrrolide synthesis*

89 Two solutions of trihexyl(tetradecyl)phosphonium bromide ([P₆₆₆₁₄][Br]) (1.1 g, 2 mmol)
90 in ethanol (200 mL) were mixed with Amberlite® IRN78 (10 g) for 2 days in two separate
91 500 mL bottles. Then, the AgNO₃ test was carried out, since no residual halide
92 precipitation verifies the complete formation of trihexyl(tetradecyl)phosphonium
93 hydroxide ([P₆₆₆₁₄][OH]). The mixtures were filtered and mixed in the same 1 L bottle
94 with pyrrole-2-carbonitrile (0.34 mL, 4 mmol) and stirred for 2 days. Ethanol and other
95 volatiles were removed at 70°C under reduced pressure (90 mbar). The structure of the IL
96 was verified by ¹H Nuclear Magnetic Resonance (NMR) spectroscopy in a Bruker Varian
97 Unity 500 and the complete removal of volatiles was confirmed.

98 *COSMO-RS computational analysis*

99 COSMOtherm program package (version 18.0.0) with its implicit parametrization
100 (BP_TZVP 1801) was used to perform a screening of the extractive properties of the
101 different solvents. To do this, the extended database of compounds present in
102 COSMOtherm package, including more than 5,000 components, was used. Then, a liquid
103 extraction calculation at 25 °C of temperature was carried out. The selected initial
104 conditions were pure solvent in phase I and 0.95 PC and 0.05 IL in phase II in molar basis.
105 Then, the data was filtered including only those solvents that allow the liquid-liquid
106 equilibria. Last, extractive properties such as partition coefficient and selectivity were
107 calculated in the phase that PC is present as major compound. COSMO-RS method was
108 used to massively scan solvents to separate trihexyl(tetradecyl)phosphonium 2-
109 cyanopyrrolide ([P₆₆₆₁₄][2-CN_{Pyr}]) catalyst from propylene carbonate as benchmark
110 cyclic carbonate.

111 *IL/Propylene carbonate phase separation study*

112 Different mixtures containing propylene carbonate, purified water, 1-decanol and
113 [P₆₆₆₁₄][2-CN_{pyr}] in different ranges of molar concentration were prepared. The liquid-
114 liquid extraction runs were stirred for 1 hour and phase separation is achieved by
115 centrifugation in a Serie Digicen 21 centrifuge (3000 rpms, 3 min). Samples were
116 thermostated in a Julabo bath at 25 ± 1 °C. Then, 20 µL of each phase were dissolved
117 in 0.5 mL of Acetone-d₆, and propylene carbonate, water, 1-decanol and IL concentration
118 were analyzed by ¹H NMR spectroscopy in a Bruker Varian Unity 500.

119 *Cycloaddition reaction of CO₂ to propylene oxide: procedure and analysis*

120 The reactions were carried out in a Berghof BR-100 high-pressure reactor of 100 mL at
121 1000 rpm of magnetic agitation. A solution of propylene oxide and [P₆₆₆₁₄][2-CN_{pyr}]

122 (1% mol) was introduced in the reactor. 1-Decanol in 1:1 molar proportion to propylene
123 oxide was added in the reactions involving this alcohol. Then, an initial pressure of 5 bar
124 of CO₂ was charged to the reactor. Once the set point temperature (120°C) was reached,
125 the pressure in the reactor was maintained at 20 bar (above propylene oxide vapor
126 pressure at the reaction temperature) keeping a continuous CO₂ feed, ensuring an excess
127 of CO₂. After 22h, the conversion to propylene carbonate was calculated by evaporating
128 all the remaining propylene oxide at 50°C and 200 mbar for 30 minutes and comparing
129 the resulting mass with the initial masses of AHA-IL and 1-decanol. Propylene carbonate
130 selectivities were estimated using ¹H NMR spectroscopy in a Bruker Varian Unity 500.

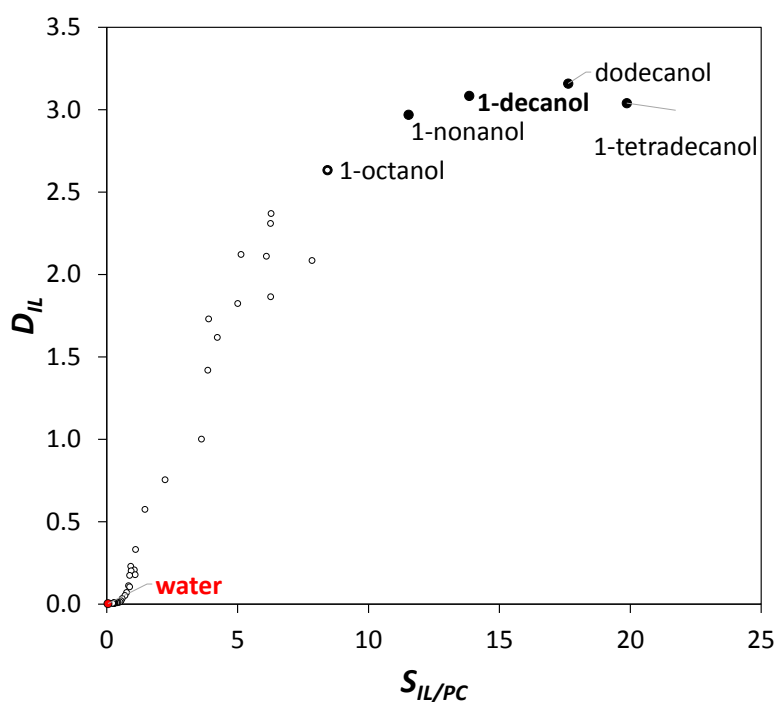
131 *IL reutilization*

132 Firstly, the remaining propylene oxide was evaporated from the system. Then, water was
133 added until complete dissolution of propylene carbonate. Therefore, a water/1-decanol
134 molar ratio of 3/2 was added to the mixture (being 240 g/L @ 20 °C the propylene
135 carbonate solubility in water [26]). Next, a Serie Digicen 21 centrifuge was used to
136 separate organic and aqueous phases by centrifugal forces. Then, the organic phase was
137 recovered (approximately 30 g) and kept at 80°C and 90 mbar for 2 hours, to remove any
138 possible water. Finally, 20 µL of the mixture were dissolved in 0.5 mL of Acetone-d₆,
139 and its composition was analyzed by ¹H NMR spectroscopy in a Bruker Varian Unity
140 500. The propylene carbonate, 1-decanol, and IL concentration, which determine the next
141 reaction quantities of propylene oxide and 1-decanol adjustments, were obtained.

142 **3. Results**

143 Figure 1 displays an extract of the computational results including ionic liquid partition
144 coefficient (D_{IL}) and ionic liquid/propylene carbonate selectivity (S_{ILPC}) for several
145 solvents forming two immiscible phases with propylene carbonate. All the data can be

146 found in Table S1 of Supplementary Material. This screening aims to select a solvent that
147 can act as effective extracting agent for catalyst in the mixture. The hypothesis was to
148 find a solvent that presents high affinity for the ionic liquid, instead of propylene
149 carbonate. As can be seen, long-chain alcohols appeared as ideal solvents to liquid-liquid
150 phase splitting separation the ionic liquid and propylene carbonate because of their high
151 selectivity and partition coefficients compared to the rest of solvents. It is clearly seen
152 how an increase in the alcohol alkyl chain impacts in enhanced extractive properties
153 (distribution coefficients and selectivities). Considering the liquid state of the solvent at
154 atmospheric conditions, 1-decanol was selected as promising extracting agent for next
155 stages.



156 **Figure 1.** Extractive properties from liquid-liquid equilibrium data provided by COSMO-RS predictions
157 for solvent screening at 25 °C to separate [P₆₆₆₁₄][2-CNPy] and propylene carbonate.

158 At this point, we considered improving the separation by the addition of a second solvent.
159 The addition of water to separate H₂S conversion products from an hydrophobic IL
160 [bmim][NTf₂] was successfully accomplished [25]. Thus, considering [P₆₆₆₁₄][2-CNPy]

161 (Figure S1 in Supplementary Material) as an hydrophobic compound [24], including
162 water in the system would increase the immiscibility of the phases, and enhance the
163 separation, since the catalyst is present in 1-decanol phase. Using a second solvent to
164 form a biphasic system with the first solvent (1-decanol) would help promoting polar and
165 non-polar affinities between polar solvent and product and between non-polar solvent and
166 catalyst, respectively. Figure 2 illustrates the hypothesis of the successful combination of
167 1-decanol and water in the biphasic system creation along with the individual behavior of
168 each neat solvent. To evidence this behavior, experimental liquid-liquid experiments were
169 carried out for synthetic quaternary systems composed by propylene carbonate, [P₆₆₆₁₄][2-
170 CNPyr], 1-decanol and water. Experimental results demonstrate that by selecting water,
171 the biphasic region is achieved, and allows an enhanced catalyst extraction in the 1-
172 decanol-rich phase. Water and a fatty alcohol, i.e. 1-decanol (Figure 2B), display a
173 biphasic system enhancing the extractive properties. In addition, the ionic liquid
174 hydrophobicity keeps the catalyst in the alcohol-rich phase. In contrast, the use of neat 1-
175 decanol (Figure 2A) allows the extraction of almost all the catalyst (high yield) but with
176 partial miscibility with propylene carbonate (low selectivity). On the other hand, using
177 neat water (Figure 2C), without fatty alcohols, promotes the formation of two immiscible
178 phases; however, the catalyst solubility in water is low [24], which concentrates the
179 catalyst in the propylene carbonate phase, avoiding its efficient recovery.

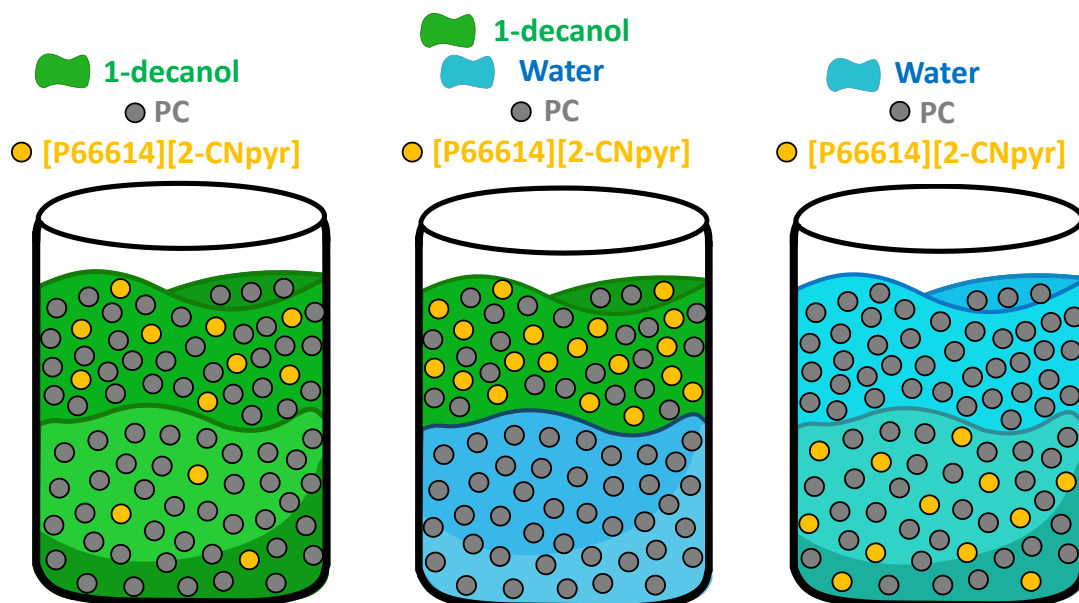
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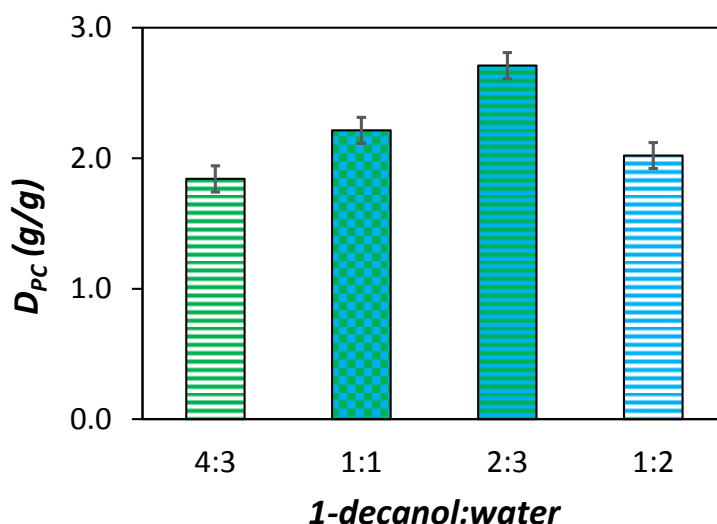
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185 **Figure 2.** Schematic representation of the 1-decanol/water (B) separation platform of [P₆₆₆₁₄][2-CNpyr]
186 and propylene carbonate (PC) and the behavior of the neat solvents (A and C).

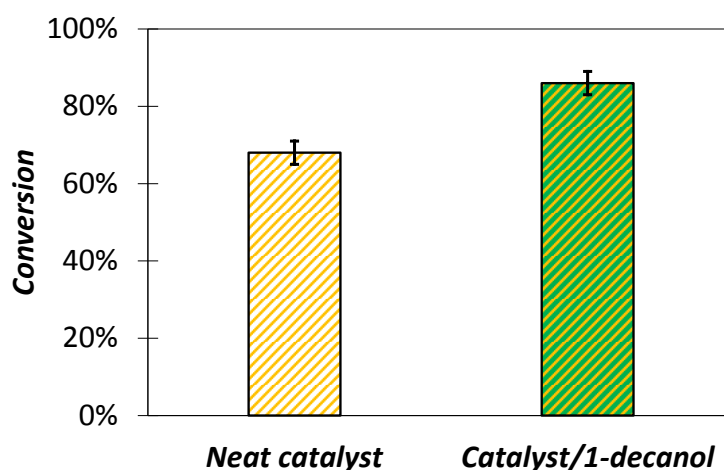
187 Figure 3 depicts propylene carbonate distribution coefficient in the aqueous phase from
188 measured liquid-liquid equilibrium data, whereas propylene carbonate/[P₆₆₆₁₄][2-CNpyr]
189 selectivity tends to infinite. The presence of more water in the system improves the
190 PC/catalyst separation, revealing a 2:3 (alcohol:water) ratio as the optimal. This confirms
191 that water can enhance the propylene carbonate recovery when is simultaneously used
192 with 1-decanol. Moreover, the catalyst is not detected by NMR in the aqueous phase, as
193 evidenced in the NMR spectra in Figure S2 in the Supplementary Material. Therefore,
194 experimental results corroborate that propylene carbonate can be effectively separated by
195 liquid-liquid extraction from the catalyst by using the 1-decanol/water biphasic system.
196 Summarizing, the proposed separation based in 1-decanol/water biphasic system enables
197 the catalyst full regeneration from product and carbonate purification, envisioning a close
198 cycle process for ionic liquid-based cyclic carbonate production. This strategy has been
199 recently patented by our research group [27].



200 **Figure 3.** Propylene carbonate mass-based distribution coefficient as function of water loadings at 25 ± 1
 201 $^{\circ}\text{C}$ for quaternary mixtures at 1 % molar fraction of $[\text{P}_{66614}][2\text{-CNPy}]$ in propylene carbonate. 1-decanol is
 202 in equimolar proportions to propylene carbonate and water loadings referred to 1-decanol benchmark
 203 compound in molar relationship.

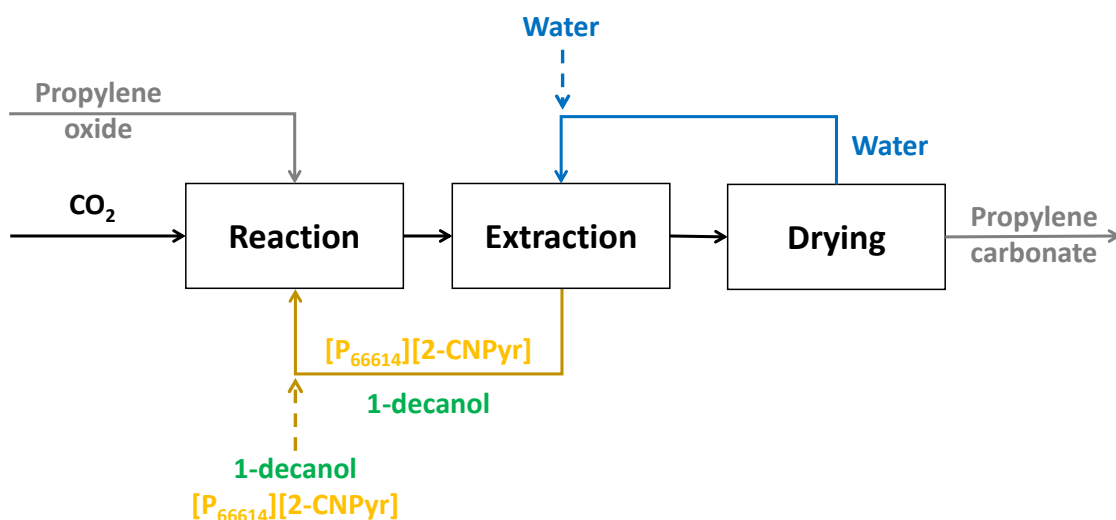
204 Long-chain alcohols were recently suggested as good CO_2 physical absorbents [28], that
 205 theoretically increases the CO_2 concentration in the liquid phase and, thus, could shift the
 206 reaction to more favorable kinetics. Supercritical CO_2 conversion to cyclic carbonates is
 207 another key to support the proposal of fatty alcohols as effective reaction media since the
 208 CO_2 concentration in the reaction media is essential from a kinetic point of view [29].
 209 Based on these evidences, we evaluated the use of 1-decanol as reaction media to convert
 210 CO_2 and propylene oxide to propylene carbonate using $[\text{P}_{66614}][2\text{-CNPy}]$ catalyst. As
 211 shown in Figure 4, the propylene oxide conversion moves from 68 to 86 % by adding 1-
 212 decanol from benchmark conditions detailed in figure caption. PC selectivity found is
 213 higher than 99% in both cases in agreement with ^1H NMR spectra. This improvement is
 214 explained in the literature [10, 30] due to the presence of -OH groups, such as water, short
 215 alkyl chain alcohols, aliphatics, and glycols, among others. The hydroxyl group stabilizes
 216 the cycle opening of the epoxide and makes easier the CO_2 cycloaddition to form the
 217 carbonate. In fact, recent efforts are focused on incorporating -OH groups in the

218 formulation of ionic liquid-based catalyst for the cycloaddition of CO₂ with epoxides
219 [31]. On the other hand, 1-decanol has a long alkyl chain that could improve catalytic
220 activity of [P₆₆₆₁₄][2-CNPyrr] IL, since the use of linear hydrocarbons combined with
221 halide-based salts showed an enhancement in the propylene oxide conversion to produce
222 propylene carbonate [30]. Here we synergistically combined both with a strategy to
223 enhance CO₂ conversion close to values related to best ionic liquid catalysts that also
224 provides chemical CO₂ absorption [20, 32], drafting an effective capture-conversion
225 platforms, at the same time that assays the catalyst regeneration and the isolation of the
226 cyclic carbonate by simple and effective liquid-liquid extraction.



227 **Figure 4.** Propylene oxide conversion to propylene carbonate at 120 °C and 20 bar using [P₆₆₆₁₄][2-CNPyrr]
228 as catalyst in 1:99 molar ratio to propylene oxide. 1-Decanol is fed at 1:1 molar ratio to propylene oxide.
229 Reaction time was fixed in 22 h in a reactor with a volume of 100 ml.

230 Therefore, 1-decanol stands as synergetic solvent to improve the catalytic behavior in the
231 reaction step while selectively separating the reaction mixture, allowing the catalyst
232 recovery and the product purification. These combined results support the conceptual
233 process design displayed in Figure 5.

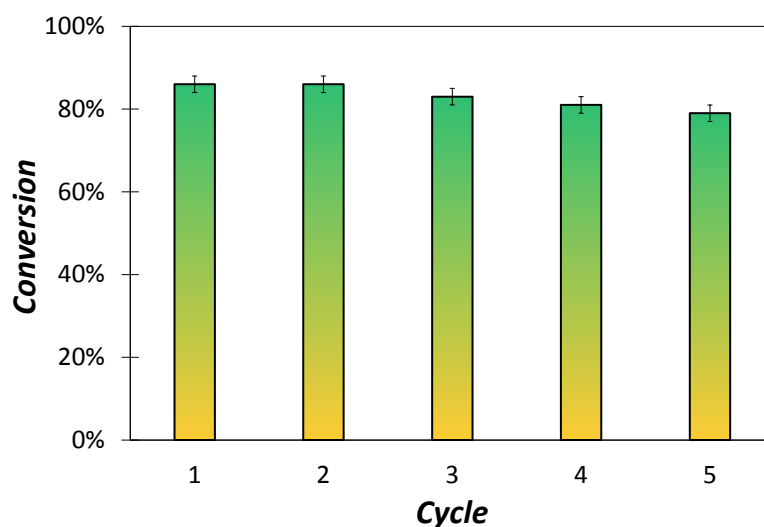


234 **Figure 5.** Conceptual design of the CO₂ conversion process proposal. Dashed lines denote fresh make up
235 streams.

236 The reaction step works with CO₂ and propylene oxide loadings together with recycled
237 catalyst/fatty alcohol hybrid media. The liquid output stream (gas stream is omitted for
238 ease of understanding) undergoes a liquid-liquid extraction which involves water to
239 enhance the extractive properties. The ionic liquid-rich phase resulting from the
240 extraction is mainly a mixture of 1-decanol and [P₆₆₆₁₄][2-CNPyr] and it is recycled to the
241 reaction step, whereas the carbonate-rich phase is dried, obtaining high purity propylene
242 carbonate and recycling water to the liquid-liquid extraction. It is relevant to highlight
243 that recovered catalyst can be used as CO₂ absorbent since both compounds, IL and
244 alcohol, are excellent chemical and physical absorbents, respectively. This strategy of
245 combining physical and chemical absorbents has been recently explored with ionic
246 liquids and low viscosity solvents to mitigate mass transfer control [33-37]. Therefore,
247 future challenges will be conducted to evaluate current reaction/separation proposal at

248 high catalyst content, compatible with iCCU processes (Figure S3 in the Supplementary
249 Material).

250 Regarding the stability of the system, thermal ionic liquid stability at the reaction
251 temperature was confirmed by thermogravimetric analysis (TGA), as shown in Figure S4
252 of Supplementary Material. Then, five consecutive cycles (reaction + separation) were
253 accomplished to validate the feasibility of the proposal. Figure 6 demonstrates that the
254 propylene carbonate yield remains constant as well as the separation rate of propylene
255 carbonate. The amount of catalyst in the consecutive cycles remains almost invariable as
256 well as its catalyst activity, probably due to the mild conditions of regeneration stage. The
257 [P₆₆₆₁₄][2-CNPy^r], 1-decanol and propylene carbonate quantities fed in the different
258 consecutive cycles can be found in Table S2 in Supplementary Material. This confirms
259 liquid-liquid extraction using 1-decanol/water as an outstanding option to effectively
260 recover PC and selectively regenerate the IL. Moreover, the recovery of propylene
261 carbonate in the water phase is almost complete in each cycle with only one-step. The
262 approximately 4 wt% propylene carbonate remaining in the organic phase, which is then
263 used for the next cycle, nearly does not affect the consecutive reaction outcomes. It is
264 relevant to detail that propylene oxide added to each cycle is related to the catalyst in 99:1
265 ratio in favor to the epoxide.



266 **Figure 6.** Consecutive reaction and separation cycles to convert propylene oxide and CO₂ to propylene
 267 carbonate. Reaction was performed at 120 °C and 20 bar using [P₆₆₆₁₄][2-CNPy] as catalyst in 1 % molar
 268 fraction with respect to propylene oxide. 1-Decanol is fed at 1:1 molar ratio to propylene oxide. Reaction
 269 time was fixed in 22 h. Water added to perform the catalyst/product separation was in 3/2 molar ratio with
 270 respect to 1-decanol.

271

272 **4. Conclusions**

273 In summary, as first time, it is presented a biphasic system based on a fatty alcohol (1-
 274 decanol) and water in cycloaddition reaction of CO₂ to propylene oxide involving a
 275 hydrophobic ionic liquid as catalyst, able to chemically capture CO₂. This system allows
 276 the effective recovery of both the catalyst and product at mild conditions of temperature
 277 and pressure, which implies lower energy demands in the regeneration stage and longer
 278 catalyst usability.

279 In addition, the CO₂ conversion is enhanced by using 1-decanol as reaction media.
 280 Therefore, a first step is done to design a sustainable reaction-separation platform to
 281 produce CO₂-derived cyclic carbonates through a homogeneous catalytic process
 282 complemented by liquid-liquid phase separation with green chemicals, synergistically
 283 impacting in reaction extension.

284 The proposed approach may promote in the near future the developing of new integrated
285 carbon capture and conversion process since the ionic liquid [P₆₆₆₁₄][2-CN₂Pyr] and 1-
286 decanol are, respectively, favorable CO₂ chemical and physical absorbents.

287

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293

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