

Toward Sustainable and Cost-Effective CO₂ Conversion Processes to Propylene Carbonate Based on Ionic Liquids

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The use of ionic liquids (ILs) for CO₂ capture and utilization into a valuable product is attracting interest even though literature evaluating their sustainability is scarce. A liquid–liquid extraction (LLE)-based separation is recently proposed as an alternative to the high energy-consuming distillation-based reference approach to produce propylene carbonate (PC). In this work, the environmental impacts associated to the distillation-based reference and two proposed LLE-based approaches to produce PC are evaluated by means of process modeling and life cycle impact assessment tools. Simulations prove that tuning operating variables in terms of environmental benefits also improves the cost-effectiveness of the process. In addition, sustainability of the processes is nearly not altered by the IL selection when an effective recovery is designed. The emissions associated to the proposed approaches vary between 0.12 and 0.22 kg CO₂ equiv. per kg_{PC}, while the operational costs range from 3 to 8 \$ per t_{PC}. The water-mediated LLE-based approach imposes the best environmental, capital expenditures, and operating expenses performance.

1. Introduction

Over the last decades, carbon capture and utilization (CCU) technologies have experienced a great development due to the imperative need to reduce CO₂ emissions,^[1] especially those associated with power generation, which peaked in the year 2021 at ≈36.3 GtCO₂.^[2] CCU often involves the capture of CO₂ either from a gaseous effluent or from the atmosphere; although, CO₂ can also be obtained as a product, for example,

in ammonia production. Then, CO₂ can be used directly in a variety of applications, as a solvent,^[3] refrigerant,^[4] or carbonating agent in the beverage industry as well as as a raw material for the synthesis of other products. There are different types of CO₂ conversion to other products, which can be divided into reactions that incorporate the complete CO₂ molecule (carboxylation) or merely a part of the molecule (reduction);^[1a] presenting the former reactions much lower energy demand than the latter, which increases the interest in carboxylation reactions. Some products that can be obtained by carboxylation are ureas,^[5] lactones,^[1a] carboxylic acids,^[1a] carbonates,^[6] polycarbonates,^[7] or polyurethanes.^[8]


To produce cyclic carbonates which find applications in common separations in the chemical industry^[9] as well as being electrolytes for batteries^[10] as final use, or

are well-known monomers in the polymer industry^[7,10] finding applications even in the biomedical field,^[11] the use of ionic liquids (ILs) as catalysts in both homogeneous and heterogeneous phases has been suggested.^[12] **Figure 1** shows the reaction scheme to produce propylene carbonate from propylene oxide using ILs with the corresponding pressure and temperature conditions considered in this work. Given their high CO₂ solubility, ILs are very competitive absorbents compared to amines^[13] plus they can also be used as catalysts,^[14] allowing for the integration of CO₂ capture and conversion.^[15] However, carbonate and IL separation by distillation has been revealed to be high energy-consuming.^[15a,16] Therefore, it was recently proposed to carry out this separation by liquid–liquid extraction, which reduces energy consumption.^[16,17] Depending on whether the IL is hydrophilic or hydrophobic, either water or a long-chain alcohol would be the preferred extracting solvent, respectively.^[18]

To advance in the development of more effective and sustainable IL-based CCU processes, techno-economic assessment and environmental impact evaluations need to be addressed comprehensively. It is necessary to analyze these systems globally, including the synthesis of the necessary compounds as well as the implications of their energy consumption and energy sources.^[19] In this line, several studies have already been conducted on the environmental sustainability of CO₂ capture and storage processes,^[20] including those based on ILs.^[21] However, in the case of carbon utilization processes, due to the variety of

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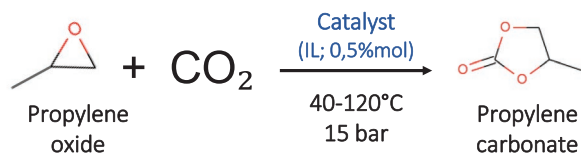


Figure 1. Reaction scheme for the synthesis of propylene carbonate from propylene oxide using ILs as catalysts.

possible products and the different synthesis routes, in-depth studies including guidelines for the development of sustainable conversion processes are difficult to find. More specifically, these studies tend to focus on electrochemical processes,^[22] while in the case of the few thermochemical synthesis studies, the most studied products are dimethyl carbonate and formic acid.^[21] In addition, many of these researches do not focus on sustainability at process level and as they cannot be extrapolated between products, the need for further studies remains.^[23] This is the case for cyclic carbonates derived from CO₂ for which the literature including process design is scarce; and thus, detailed environmental analyses are also limited and cannot be correlated or manipulated by process design.

The goal of this work is to improve the sustainability of the CO₂ conversion process to produce cyclic carbonates using IL as catalyst. The system boundaries in such assessments go from the CO₂ released in a previous ammonia production process to the PC production (as benchmark cyclic carbonate), excluding further use of this material. Three different approaches for the product–catalyst separation, already proposed in other works,^[18] are assessed: the reference one involving distillation and two alternatives involving LLE using water or alcohols as extracting solvents individually. The selected ILs to catalyze these processes are 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) and trihexyltetradecylphosphonium chloride ([P₆₆₆₁₄][Cl]), as benchmark IL catalysts. These ILs are selected because of their commonness, which makes their synthesis route well-known as well as their representativeness from the whole IL family of compounds because ILs derived from imidazolium and phosphonium cations have been extensively used in this type of reactions yielding good results.^[16,24] Different cations are selected to ensure hydrophilicity and hydrophobicity, with the aim of using different solvents to extract the ILs, while chloride-based anions are selected due to their high catalytic activity in this reaction. The COSMO-based/Aspen Plus methodology is employed to perform the simulations of the selected processes to be assessed. Based on the mass and energy balances calculated through simulation, the different conversion processes are evaluated and compared using different environmental indicators, estimated by ReCiPe methodology using SimaPro v9 software and Ecoinvent 3.7 database. Focusing on global warming potential (GWP) as main environmental indicator for CCU processes, different process variables are studied with the aim of reducing CO₂ equivalent emissions. Then, operational and capital costs are evaluated to examine the possible correlations between processes' environmental sustainability and economics. Last, the environmental and economic performances of the environmentally improved CO₂ conversion processes are recalculated and fairly compared. This method will provide an

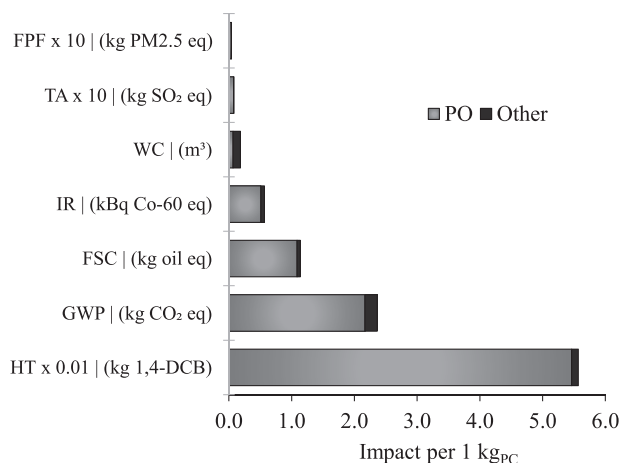


Figure 2. PO and total contribution to different environmental categories to produce 1 kg of PC using the benchmark process. Fine particulate matter formation (FPF), terrestrial acidification (TA), water consumption (WC), ionizing radiation (IR), fuel resource scarcity (FSC), global warming potential (GWP), human carcinogenic, and non-carcinogenic toxicity (HT).

eco-design guide to obtain more environmentally sustainable CCU processes.

2. Results and Discussion

2.1. Distillation-Based CO₂ Conversion Process Environmental Analysis

First, the main environmental impacts of the benchmark CO₂ conversion process in which the IL and PC are separated by a vacuum distillation are assessed. **Figure 2** collects seven different environmental impacts to produce PC using this separation strategy and selecting [bmim][Cl] as reference IL due to its commonness. As seen in **Figure 2**, the main contributor to almost every category of impact—except water consumption—is the reactant used in the CO₂ cycloaddition reaction: propylene oxide (PO). PO's contribution to water consumption is 36%, while for the rest of the impacts, it represents between 92% and 98% of the total. This is because the synthesis of PO involves very high impacts in all categories, for example, it emits 3.75 kg CO₂ equivalent per PO kilogram.^[25] Therefore, a process in which PO (synthesized by the conventional chlorohydrin process^[26]) is used as a reactant in the CO₂ cycloaddition reaction would emit more CO₂ than it consumes because 1 mole of CO₂ (44 g) reacts with 1 mole of PO (58 g); thus, 44 g of CO₂ are consumed but 218 g of CO₂ equivalent are emitted because of PO's synthesis. Consequently, in a 100% conversion yield reaction, for each mole of CO₂ reacted, ≈174 g of CO₂ would be emitted. This fact has already been demonstrated in the literature when using PO for the production of other compounds, such as polyols.^[8] Also, once again, it is demonstrated that using CO₂ as raw material does not ensure a sustainable process design.^[23] Looking at **Figure S1**, Supporting Information, which collects more environmental impact categories, this process does not imply a significant impact on categories

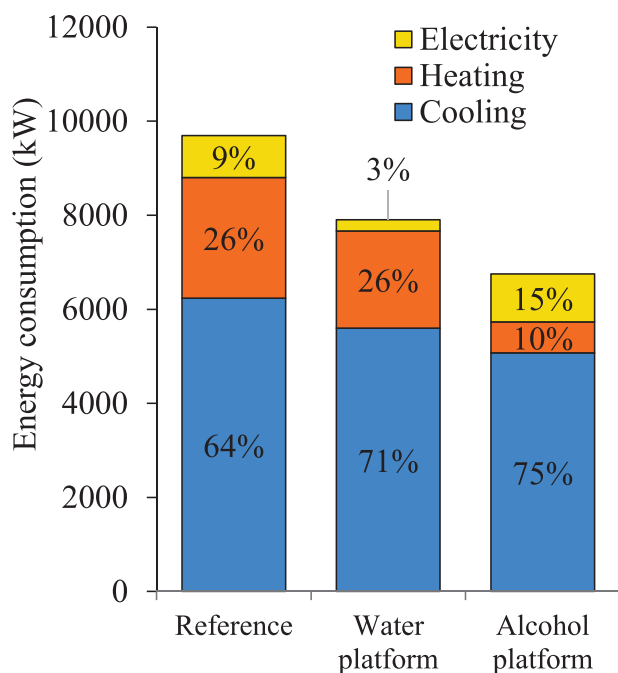


Figure 3. Energy consumption allocated among energy nature for the three CO₂ conversion process strategies.

such as ozone formation or depletion, eutrophication. On the other hand, for the categories in which it presents a relevant impact (marine and terrestrial ecotoxicity, human toxicity, global warming, etc.), it is, as mentioned above, due to propylene oxide synthesis, implying that the CO₂ conversion process entails very low impacts. Despite the above results, to pursue the goal of applying techno-environmental assessment for developing new and more sustainable CCU process, in this work, we consider analyzing the environmental impact parameters excluding the reagent from the analysis. To this respect, it should be highlighted that, although propylene oxide is one of the most studied reactants for this reaction,^[27] the proposed reaction-separation is feasible with other reactants and products;^[18] therefore, presenting the current approach with a wider interest for other similar CCU processes.

2.2. Separation Strategy and Solvent Environmental Implications

Recently, two product/catalyst separation strategies based on liquid-liquid extraction have been developed, using water or fatty alcohols as extraction solvents, depending on the IL hydrophobic or hydrophilic character. As presented in **Figure 3**, which collects the energy consumption for the three separation strategies, they differ widely in their consumptions. The reference process presents the greatest energy consumption, while the alcohol-based platform presents the lowest energy consumption. For all three processes, cooling implies the main contribution to energy consumption (64–75%), heating is the second greatest contribution for reference and water-based LLE process, while electricity expenses are similar in reference and alcohol-based LLE process. However, due to the low heating consumption in alcohol strategy, electricity is the second greatest contribution. The detailed breakdown of energy consumption by operation and energy nature can be found in Table S2, Supporting Information. It is worth mentioning that water-based LLE strategy allows to reduce electricity consumption to a minimum.

Figure 4A collects various environmental impacts of the different separation strategy processes. As seen, in all categories, the water-based LLE platform presents the lowest impact while the alcohol-based LLE platform always presents the highest impact. This trend does not match that of the energy consumption (**Figure 3**) for which the alcohol-based platform presented the lowest values. Thus, in **Figure 4B**, the contribution of the different process elements to global warming potential—being one of the most important impact categories in CCU processes due to the aim of reducing CO₂ emissions—is assessed for the three strategies. As observed, the water platform allows a reduction of 78% and 16% in GWP with respect to the alcohol platform and the reference process, respectively. It can be concluded that the water platform can be used to highly improve the sustainability of this process while the alcohol platform, due to the fact that using 1-decanol as solvent in the alcohol-platform contributes on its own more than the entire process on the other two platforms, is an unfavorable alternative.

Nevertheless, different fatty alcohols can be used in the alcohol platform, altering PC purity and energy consumption, both contributing to environmental impacts as calculated. The

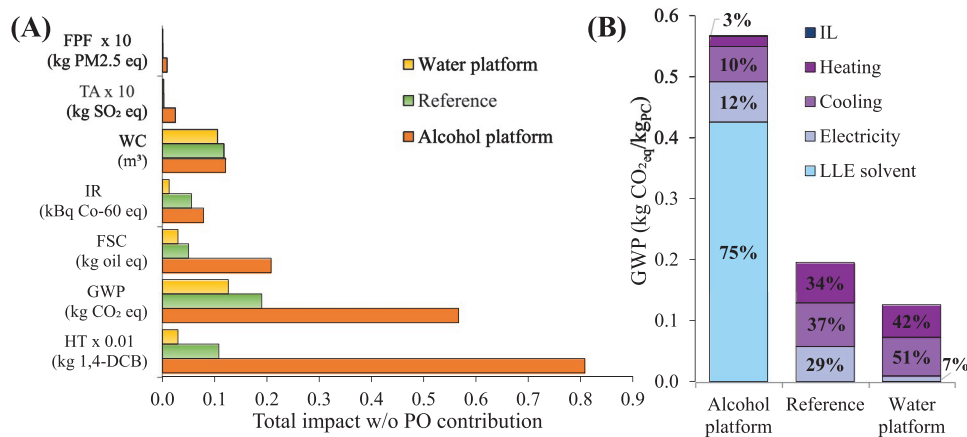


Figure 4. Main environmental impacts of the A) three CO₂ conversion processes and B) contribution of the different compounds and utilities to global warming potential to produce 1 kg of PC.

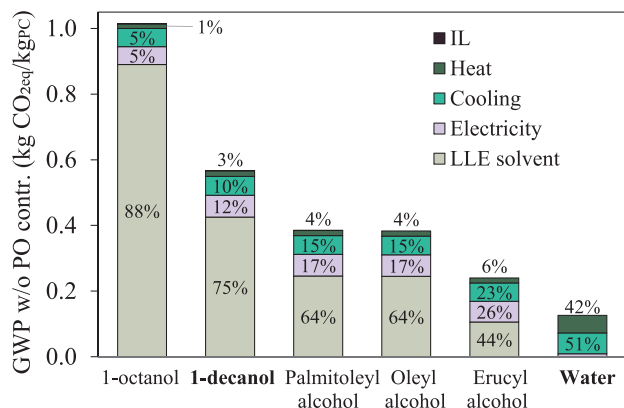


Figure 5. Influence of selecting different solvents in the LLE-based separation strategies in GWP to produce 1 kg of PC.

influence of employing different solvents on GWP can be examined in **Figure 5**. Once again, the use of water as extracting solvent is clearly favored due to presenting the lowest CO₂ equivalent emissions (0.13 kg CO₂ equiv. per kg_{PC}), while the alcohol platform moves between 0.24 and 1.01 kg CO₂ equiv. per kg_{PC}, depending on the selected alcohol. However, by choosing long-chain and saturated fatty alcohols, such as erucyl alcohol, the emissions can be reduced by 76% with respect to 1-octanol or by 58% with respect to 1-decanol. It is worth noticing that due to the lack of industrial production requirements for each specific fatty alcohol, the influence of the impacts of their individual syntheses has not been considered in this comparison and could alter the trend. Therefore, the differences in GWP with different alcohols are due to the different mass S/F ratio requirements to achieve a complete recovery of the IL, ranging from 0.16 for erucyl alcohol to 0.4 for 1-octanol.

2.3. Reaction Conversion and Temperature Influence on GWP

Figure 6A represents the influence in global warming potential of achieving different PO conversions in the reactor. As expected, a higher conversion implies lower CO₂ equivalent

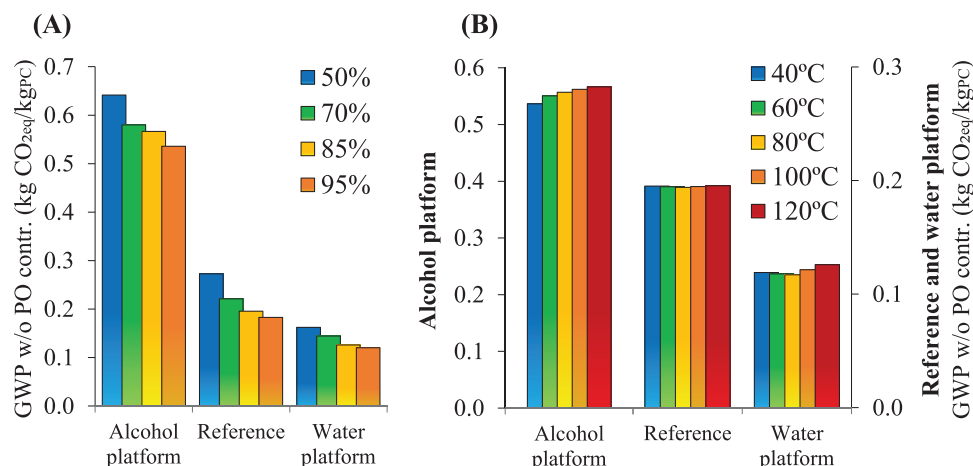


Figure 6. CO₂ equivalent emissions related to A) changing PO conversion or B) reactor temperature to produce 1 kg of PC with the three platforms.

emissions due to the conditioning lower energy demands resulting from lower recirculated reactants flow. Comparing the lowest and highest studied conversions (50% and 95%), a reduction in GWP of 0.11 kg CO₂equiv. per kg_{PC} can be obtained with the alcohol platform, 0.09 kg CO₂equiv. per kg_{PC} with reference process, and 0.04 kg CO₂equiv. per kg_{PC} with the water platform. Moving to **Figure 6B**, which collects the influence of changing the reaction temperature from 40 °C to 120 °C, lower effects than those obtained at different conversions can be observed. It is found that this variable affects the alcohol platform differently from the reference and water platform. As seen, lower temperatures benefit the alcohol platform, while in the case of the other two platforms, the most convenient temperature is 80 °C as both platforms present minimal emissions at that temperature. However, the influence of reaction temperature is more noticeable in the alcohol platform (with a decrease of 0.03 kg CO₂ equiv. per kg_{PC}) than in the water platform (−0.01 kg CO₂ equiv. per kg_{PC}) or the reference process (−0.001 kg CO₂ equiv. per kg_{PC}). It can be concluded that higher conversions, which can be reached by changing reactor residence time, are more desirable than low temperatures. This fact opposes the usual goals of catalyst design because working at low temperatures is generally pursued, but it seems that the influence of temperature at process level is relatively unimportant, and it may even be more advantageous to work at intermediate temperatures due to reconditioning after catalyst regeneration. Additional figures depicting the influence of conversion and temperature in other environmental categories can be found in **Figures S2 and S3**, Supporting Information. As seen, the rest of the environmental categories parameters generally follow a similar trend than that of GWP both for PO conversion and reactor temperature.

2.4. Liquid–Liquid Extraction Stages and Temperature

Figure 7 depicts the CO₂ equivalent emissions associated with carrying out the LLE at 25 °C or 50 °C and selecting different number of LLE stages, ranging from 1 to 9 in the alcohol platform and 2 to 9 in the water platform because for the latter, the IL cannot be completely recovered in only one stage. As seen,

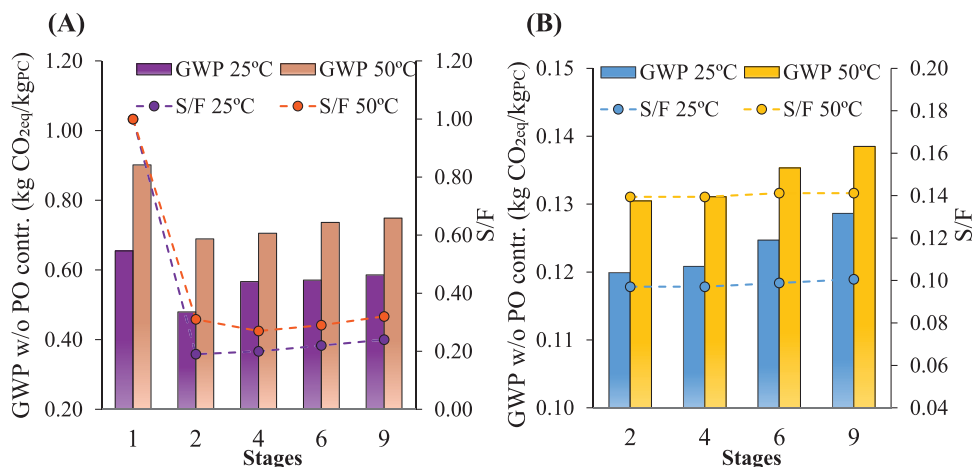


Figure 7. Influence of changing the LLE number of stages and temperature on global warming potential and mass S/F ratio, in the A) alcohol and B) water platforms.

carrying out the LLE at higher temperature in both platforms implies higher S/F requirements and higher CO₂ equivalent emissions; thus, it is not beneficial. On the other hand, generally a larger number of stages requires higher S/F ratios to achieve the IL recovery (except for the selection of a single stage on the alcohol platform for which the largest S/F would be required). Besides, water platform is less sensitive to changes in the number of stages than alcohol platform. Therefore, it is concluded that the optimum conditions for LLE on both platforms are 25 °C and two stages, reaching 0.69 and 0.12 kg CO₂ equiv. per kg_{PC} on the alcohol and water platforms, respectively.

2.5. Effect of Ionic Liquid

Last of all, it is important to study how the selection of different ILs, resulting from different syntheses, influences the environmental impacts of the process. For this purpose, based on the energy and chemicals consumption data presented in the literature for the synthesis of [bmim][Cl]^[28] and [P₆₆₆₁₄][Cl]^[29] two additional cases have been studied in which these requirements are doubled and quintupled to evaluate the uncertainty related to the IL manufacture impact. Table 1 collects these energy and chemical requirements for the conventional synthesis (Case 1^[28,29]) and the two additional syntheses (Cases 2 and 3).

Table 1. Cases of study for material and energy requirements in [bmim][Cl] and [P₆₆₆₁₄][Cl] syntheses. Case 1 requirements are extracted from references [28,29].

	[bmim][Cl]			[P ₆₆₆₁₄][Cl]		
	Case 1	Case 2	Case 3	Case 1	Case 2	Case 3
Heat [MJ kg ⁻¹ IL]	1.50	3.00	7.50	7.67	15.34	38.35
Electricity [MJ kg ⁻¹ IL]	0.21	0.42	1.05	0.61	1.22	3.05
1-methylimidazole [kg per kg[bmim][Cl]]	0.49	0.98	2.45	–	–	–
1-chlorobutane [kg per kg[bmim][Cl]]	0.61	1.22	3.05	–	–	–
Ethylacetate [kg per kg[bmim][Cl]]	0.04	0.08	0.20	–	–	–
1-chlorotetradecane [kg per kg[P ₆₆₆₁₄][Cl]]	–	–	–	0.50	1.00	2.50

By using the data in Table 1, the environmental impacts related to the syntheses of the ILs and the CO₂ conversion processes derived from these different synthesis cases have been obtained, as shown in Figure 8; Figure S4, Supporting Information. By looking at Figure 8, it is inferred that both ILs present similar impacts in the different categories, but their differences are accentuated in Cases 2 and 3. Nevertheless, moving to Figure S4, Supporting Information, these differences in the environmental loads disappear at process level because the reference process presents the same equivalent CO₂ emissions with both ILs. Moreover, the GWP is the same for Cases 1, 2, and 3 for the three platforms. This is due to the almost complete recovery of the IL, which imposes that the environmental costs associated with its synthesis become negligible because its consumption is insignificant. This means that IL recovery and reuse are more relevant than its nature or ability to catalyze near room temperature as said in the literature. In addition, it can be inferred that minor losses of IL or its catalytic activity would not significantly impair the sustainability of the system due to the low consumption of IL.

2.6. Techno-Economic Analysis

After having chosen the proper variables among those studied to obtain the best approach from an environmental point of view,

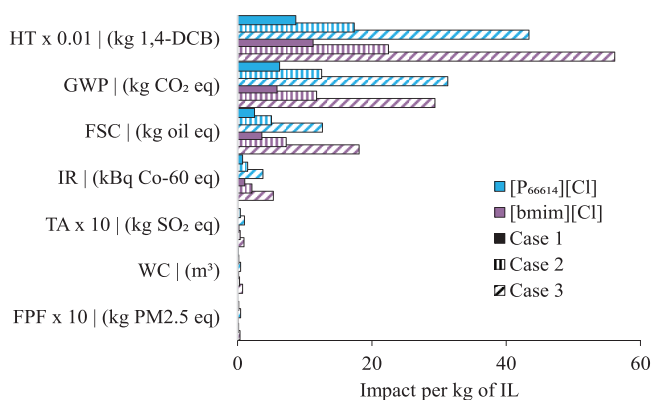


Figure 8. Environmental impacts related to the synthesis of 1 kg of [bmim][Cl] (lilac) or [P₆₆₆₁₄][Cl] (blue) for the three cases of study.

a preliminary economic analysis, based on estimates of utility and capital costs, has been conducted. A summary of the environmental and economic implications of the starting processes analyzed in Section 2.2 and of the environmentally optimized processes, based on the conclusions drawn from Sections 2.2-2.6 (whose specifications are shown in Table S3, Supporting Information), is shown in **Figure 9**. The detailed breakdown of the cost analysis of the environmentally optimized processes can be found in Table S4, Supporting Information.

As seen in Figure 9A, by following the inferences drawn throughout this work for a more sustainable design of CO₂ conversion processes, a reduction in CO₂ equivalent emissions is achieved for the three platforms, with the greatest reduction being obtained for the alcohol platform (−62%), compared to water platform (−5%) and reference (−3%). In addition, this process design strategy, based on environmental indicators, allows the improvement of economic parameters such as utility costs (Figure 9B) and capital costs (Figure 9C). The three platforms present utilities costs reduction between 23% (reference) and 35% (water platform). On the other hand, despite the fact that the reference platform has the highest operating costs due to the cost of alcohol, the alcohol platform would become the

most expensive in terms of operating costs, as can be seen in Figure S5, Supporting Information. In addition, while the water platform maintains the same process equipment-related costs, the reference process and the alcohol platform present slight reductions (1–3%). Thus, it is concluded that designing this CO₂ conversion process with the objective of improving their sustainability allows improving their financials at the same time. In summary, water platform appears to be the most suitable option for this type of process because it involves the lowest associated CO₂ emissions, implying a higher balance of CO₂ consumed than the other platforms, as well as the lowest operating costs. The alcohol platform, despite its advantageous low capital costs, implies higher operating costs than the reference process and higher GWP, making it less favorable than the reference process.

3. Conclusion

In this work, environmental and techno-economic assessments of CO₂ conversion processes to PC catalyzed by [bmim][Cl] and [P₆₆₆₁₄][Cl] ILs have been carried out. COSMO/Aspen methodology was employed to simulate the different processes and environmental impacts evaluated by applying life cycle assessment tools. Three different product/catalyst separation strategies were studied, in which distillation or liquid–liquid extraction were performed, the latter employing different extracting agents (water and fatty alcohols). An environmental response study was carried out in which reaction variables (conversion and temperature) and separation variables (solvent, LLE number of stages, S/F) were modified for the three process schemes. The processes were improved in terms of environmental benefits, and operational and capital costs were preliminarily calculated.

Regardless of the determinant environmental impact of PO reactant, the three strategies show opportunities for improvement in their environmental impacts. Furthermore, the catalyst's impacts by itself or its ability to catalyze near room temperature negligibly influence sustainability. By contrast,

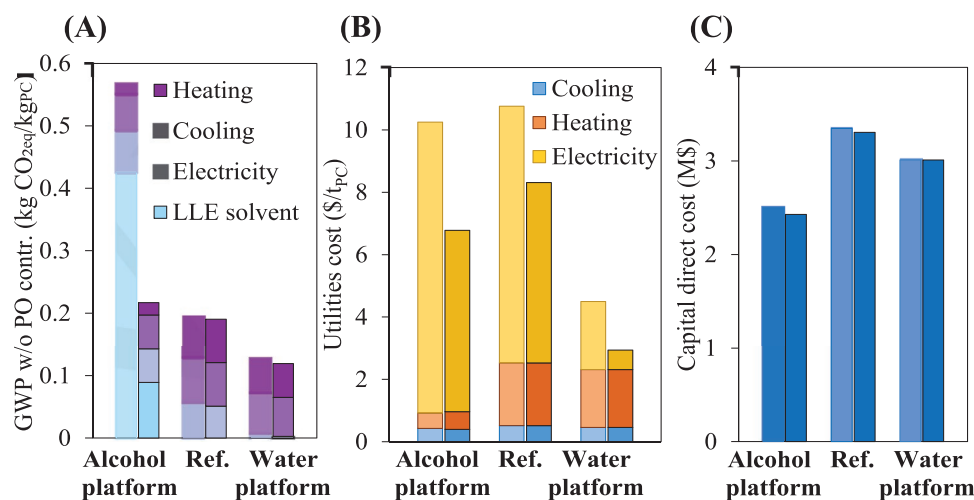


Figure 9. A) Global warming potential, B) utilities cost, and C) capital costs of the processes presented in Section 3.2 (left, soft colours) and environmentally optimized processes (right, dark colours).

conversion rate and S/F ratio allow improving both environmental impacts and energy consumption. Selecting LLE with fatty alcohols as extracting agents, which is completely controlled by the nature of the alcohol, presents the lowest energy consumption. However, due to alcohol high environmental burden and cost, plus process' high electricity requirements, it presents the highest CO₂ equivalent emissions (0.22 kg CO₂ equiv. per kg_{PC}) and the highest operational costs, becoming an unfavorable alternative even lowering capital expenditures (CAPEX). On the other hand, distillation-based separation presents both similar CO₂ equivalent emissions (0.19 kg CO₂ equiv. per kg_{PC}) and operational costs as alcohol platform, while the water-based separation stands out as the best alternative with the lowest operational costs and emissions (0.12 kg CO₂ equiv. per kg_{PC}), with intermediate CAPEX. The integration of COSMO/Aspen methodology with life cycle impact assessment tools such as SimaPro had been successfully used as an eco-design tool to reduce the environmental impacts and the cost of the assessed process. Thus, such methodology served to guide the improvement of the CCU processes' sustainability, being validated to perform further in-deep sustainability assessments of processes.

4. Computational Procedures

4.1. Component Definition and Property Method Specification in Aspen Plus

As ILs are not present in conventional Aspen Plus databases, a multiscale COSMO-based/Aspen Plus methodology previously employed in systems involving ILs was used.^[13b,16,30] In summary, the molecular structures of [bmim][Cl] and [P₆₆₆₁₄][Cl] were optimized by means quantum chemical structure calculations in Turbomole 7.3 software.^[31] Then, these structures were used to obtain the molecular weight, boiling point, σ -profiles, and COSMO volume of the IL by using COSMO-RS^[32] calculations in CosmoTherm v19. These data are required by the selected COSMO-SAC property method in Aspen Plus, to introduce the ILs as pseudocomponents.

4.2. Process Modeling

Aspen Plus v12 was used to simulate three different PC production processes, changing the catalyst/product separation, which are depicted in Figure 10 and based on literature.^[18] As

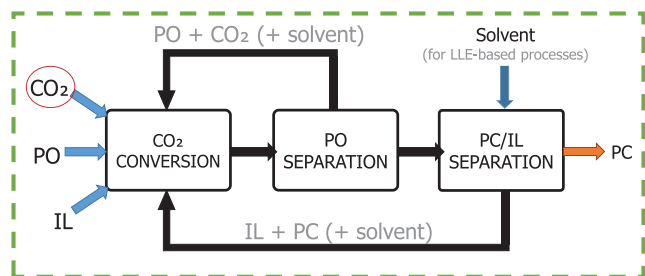


Figure 10. System boundaries of the three CO₂ conversion processes.

seen in Figure 10, the three processes present the same basic reaction and separation scheme, with essentially same system boundaries. In addition, Figure 11 shows the flow diagrams of the three processes, which share similar conditioning, reaction, and unconverted reactants–separation schemes. In detail, these similarities imply that the IL and PO streams are conditioned to the pressure (15 bar) and temperature (120 °C as starting condition) of the reactor (R-100; RStoic model with 85% conversion of PO as starting value) in P-100 and E-100, while the CO₂ stream is already at 15 bar and fed to the reactor. After R-100, the liquid stream is fed to a flash unit (V-100) working at 1 bar, and then, to a stripping column (D-100). D-100 is designed to maintain the reboiler temperature to 120 °C or lower, which is why, in the reference process and the alcohol process (Figure 11A,B) it works in vacuum conditions. D-100 allows a 99.5% recovery of PO in the distillate stream, which is mixed with the vapor streams leaving V-100 and R-100, conditioned to reaction conditions in C-100 and E-101 and fed back to the reactor. After D-100, each process carries out a different PC/IL separation. In the reference process (Figure 11A), the bottom stream exiting D-100 enters a vacuum distillation column (D-101) in which 99% PC is recovered in the distillate stream with a 99.9% mass purity which is conditioned to 1 bar and 25 °C in P-101 and E-104, while all the IL is recovered in the bottom stream and pressurized to 1 bar in P-102. In the alcohol platform, the bottom stream leaving D-100 is conditioned to 1 bar and 25 °C in P-101 and E-102 and undergoes a multistage liquid–liquid extraction

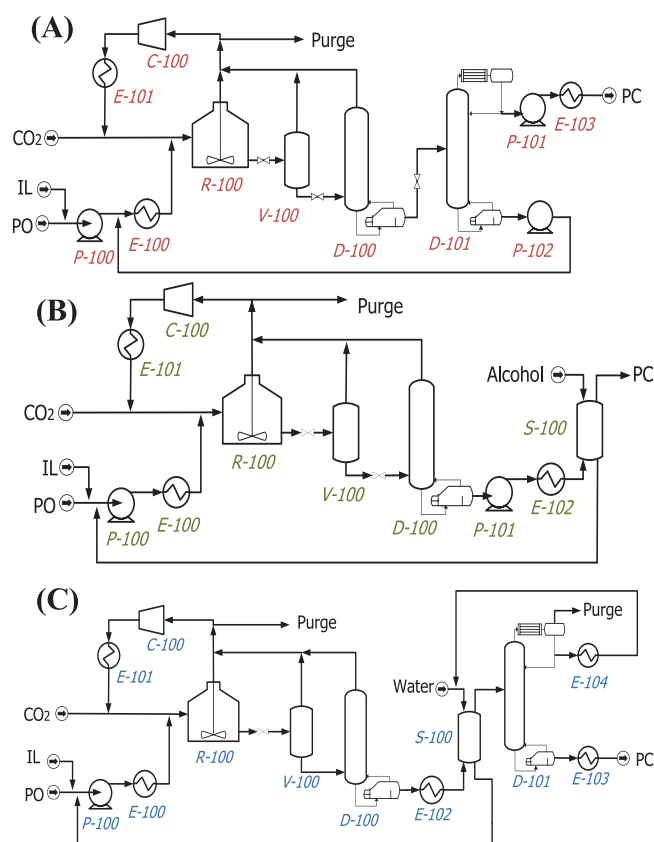


Figure 11. Process flow diagrams for red; A) the reference process green; B) the alcohol platform, and blue; C) the water platform.

Table 2. Process equipment specifications of CO₂ conversion processes to produce PC with the three strategies for the starting comparison.

Case	Distillation-based reference		Water platform			Alcohol platform	
	D-100	D-101	D-100	D-101	S-100	D-100	S-100
Column							
N stages	10	10	10	10	4	10	4
Feed Stage	1	5	1	5	S 1 / F 4	1	S 1 / F 4
Reflux	–	0.5	–	0.5	–	–	–
Maximum temperature [°C]	120	120	120	–	25	120	25
Solvent	–	–	–	–	Water	–	1-decanol
Variable	Distillate rate	Distillate rate	Distillate rate	Bottoms rate	S/F	Distillate rate	S/F
Specification	99.9% PO recovery	99.9% PC mass purity and recovery	99.9% PO recovery	99.9% PC mass purity and recovery	99.9% IL recovery and 1 atm in D-100	99.9% PO recovery	99.9% IL recovery

(S-100) in which alcohol is used as the extracting agent, fixing the solvent to feed (S/F) ratio needed for a 99.9% IL recovery. Then, a higher PC purity stream is obtained and a stream containing mainly alcohol and the recovered IL is fed back to the reactor after being mixed with pure PO and IL streams. In both water and alcohol platform, certain amount of solvent is recycled back to the reactor, but it has been proved that it does not decrease the yield of the reaction but instead enhances it.^[16,17] Last of all, in the water platform, the stream leaving the bottom of D-100 is conditioned to 25 °C in E-102 and enters a liquid–liquid extraction column (S-100) using water as extracting agent. A 99.9% recovery of IL is ensured by adjusting the S/F ratio and the IL-rich stream, which contains mainly water, and traces of PC are mixed with the fresh PO and IL streams while the PC-rich stream undergoes a distillation in D-101 in which 99% PC with a 99.9% mass purity is recovered in the bottom stream and is conditioned in E-103 to 25 °C, while the distillate stream contains mainly water and is conditioned to 25 °C in E-104 and fed back to S-100.

First, a comparison between the three separation strategies is made using specifications based on literature.^[18] Table 2 collects the main specifications of the process equipment for the starting comparison. Then, reaction conversion and temperature, LLE stages and temperature and alcohol solvent are changed and may result in necessary changes in other variables to maintain specifications. For all processes, 4000 kg h⁻¹ of CO₂ were used as the basis for calculation and the PO was fed ensuring a PO:CO₂ equimolar proportion in the reactor while it was ensured a 1:200 IL:PO molar proportion in the reactor. A pumping/compression efficiency of 70% and a driver efficiency of 95% were used for pumps and compressors.^[33]

4.3. Environmental Impact Parameters Calculation

The environmental performance of the simulated CO₂ conversion processes was evaluated by means of SimaPro 9.0.2 software and ReCiPe midpoint (E) methodology, with the aim of comparing their environmental burdens in different categories. The environmental impacts of these processes were calculated by using all inputs and outputs of materials and energy obtained from Aspen Plus simulations, as previously done in similar process simulation works.^[34] Ecoinvent 3.7 database was

used to calculate the impacts associated with the synthesis of the different materials as well as those associated with energy production. The datasets selected in Ecoinvent for the materials and sources of energy can be found in Table S1, Supporting Information. In addition, the impacts are calculated per kg of product, and the purges are not taken into account due to their negligible flow. As the alcohol platform renders a much lower PC mass purity (<96%) than the reference and the water platform (99.9%), its impacts are calculated per kg of propylene carbonate in the product stream.

4.4. Techno–Economic Assessment

A preliminary cost estimation of the different processes was carried out to compare them not only in environmental terms. To do so, the utility (LP or MP Steam, cooling water, and electricity) requirements and cost of the energy-consuming operations were calculated by corresponding Aspen Plus simulation blocks and assuming their default prices implemented in Aspen Plus v12 (1.90 · 10⁻⁶ \$ per kJ for LP steam, 2.2 · 10⁻⁶ \$ per kJ for MP Steam, 2.12 · 10⁻⁷ \$ per kJ for cooling water, and 775 · 10⁻² \$ per kWh for electricity). On the other hand, capital direct costs (CDC), including the purchase and installation of all the equipment, were calculated using Aspen Process Economic Analyzer (APEA), selecting the US_IP template. Last, to calculate the raw materials cost, a price of 1.68 \$ per kg was selected for PO and^[35] 6 · 10⁻⁶ \$ per kg for purified water,^[36] and, due to the lack of industrial prices for 1-decanol and erucyl alcohol, the price for oleyl alcohol (4.3 \$ per kg) was used.^[37]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

CO₂ conversion, ionic liquids, propylene carbonate, sustainable chemistry, techno-economic evaluation

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